AN APPLICATION OF CUMULANT TECHNIQUES
TO IRREVERSIBLE PROCESSES

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AN APPLICATION OF CUMULANT TECHNIQUES

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SUMMARY

In this work, we have developed a new approach to the problem of a simple system interacting with a quantum reservoir when the interaction can be described by $V = AB$, where A is an operator for the simple system, B is an operator for the reservoir. After defining a cumulant expansion of the reduced density operator $\rho_s(t)$ for the simple system, we show that the second cumulant is the only non-vanishing cumulant for a reservoir of non-interacting bosons. A scheme for obtaining successive approximations to the equations of motion for $\rho_s(t)$ is found in which the n^{th} approximation is obtained from the $(n-1)^{th}$ approximation by the addition of a term roughly proportional to the $(2n-1)^{th}$ power of the probability that the system makes a transition in a time interval of length t_c, the reservoir relaxation time. In these equations, reservoir variables occur only as correlation functions of bilinear combinations of reservoir operators in the interaction picture.

The first order approximation to the density operator equation of motion is applied to the case when the simple system is an harmonic oscillator. Two cases are treated, the damped harmonic oscillator and the oscillator with an external driving force. Comparison is made between these results and those obtained in other treatments.

There are two applications for which this formalism may be particularly suited. If we consider only binary collisions between the small system and reservoir, the second cumulant describes all the possible

scattering events a single particle could undergo while traversing a system of scatterers. Thus our technique may prove useful in multiple scattering theory. The other potential use is in the calculation of linewidths and lineshapes. These quantities are needed in fields such as quantum optics.

CHAPTER I

INTRODUCTION

In this work, we develop a new method for treating the time evolvement of a small system interacting with a larger, more complex system. By "small," we intend to describe a system which, when isolated from all external forces, may be treated in an exact way by the rules of quantum mechanics. That is, we can find the stationary solutions to the Schrodinger equation of the isolated small system. The complexity of the large system makes it impractical to attempt solving the Schrodinger equation of the combined system. We further restrict our attention to those cases where the interaction between the two systems has the form $V = A \cdot B$ where A and B are operator representations of dynamic variables belonging to the small system and the large system, respectively. For convenience, we refer to the small and large systems as the system and the reservoir, respectively.

The experimental situation we are trying to model is the typical one in which only part of a physical system is precisely prepared and the rest only partially controlled. As an example, one may think of an experiment performed on a volume of gas. By cooling the gas, one can insure that most of the molecules are in their electronic ground states. On the other hand, the gas interacts with the surrounding radiation field and the complete system must be considered to include both gas and radiation field. It is impossible to prepare the radiation field in a pure state and our knowledge of it is restricted to those average values appropriate to the temperature of the system. Further, all measurements taken in the course of the experiment are designed to test for changes in molecular states rather than in the radiation field. Thus, we would like to develop a method for calculating the expected value of these measurements in as exact a manner as possible and in which the reservoir variables enter as averaged quantities corresponding to our actual knowledge of its initial state. We should not forget to mention that our work actually applies to the example of the gas interacting with the radiation field since the interaction term of the total Hamiltonian for a system of charged particles and a radiation field in the Coulomb gauge is proportional to $\sum_i \vec{A}(\vec{r}_i)\cdot\vec{p}_i$ where $\vec{r}_i, \vec{p}_i$ are the position coordinate and momentum of the i^{th} particle and $\vec{A}$ is the vector potential of the radiation field. If we treat only radiation modes with wavelengths much longer than molecular dimensions, we may imagine $\vec{A}$ to be constant over a volume that on the average contains just one molecule and the interaction takes on the simple product form we require.

The mathematical framework we use in our investigation is that of the density operator developed by John von Neumann.[1] The main advantage of the density operator formalism lies in the efficient way it enables us to handle quantum systems about which we have less than complete information. The density operator and some of its properties are briefly discussed in Chapter II. Since knowledge of the full density operator, $\rho(t)$, at a time t enables us to calculate the expectation value of any operator at that same time, it still contains more information than we need. We are interested in the expectation values of systems operators rather than those of the reservoir. Thus, in Chapter III, the reduced density operator, $\rho_s(t)$, is defined as the trace of the full density operator over reservoir states.

To this point, we have followed a rather standard approach. The rest of this work is new although we make contact with standard results from time to time. Our stated purpose is to determine the dynamical history of the small system given its initial state and the initial statistical description of the reservoir. (We specify that the reservoir is distributed canonically over its energy states but this could easily be generalized.) Naturally, this is quite difficult and we finally resort to approximations but we are able to make approximations which seem to be much more appropriate to the problem than the standard perturbation theory treatments. Our final result will be a scheme for generating approximations to the equation of motion for $\rho_s(t)$ where the n^{th} approximation is obtained from the $(n-1)^{th}$ one by the addition of a term roughly proportional to the $(2n-1)^{th}$ power of the first order perturbation theory probability that the system will make a transition in a time interval of length t_c where t_c is the reservoir relaxation time. For systems that may be reasonably described as reservoirs, we expect t_c to be very short compared to the time required for the system to make a transition. Therefore, we expect the equation of motion finally derived in Chapter V to be an accurate description of a small system interacting with a larger one with many more degrees of freedom.

We now outline the steps that lead to these results. As mentioned above, we define $\rho_s(t)$ in Chapter III by taking the trace of $\rho(t)$ over reservoir states. One hopes that the act of taking the trace over reservoir states will lead to the replacement of reservoir operators by averaged quantities. How this is to be achieved is not obvious and different workers have employed different strategems. In some treatments, the full density operator is imagined to be factorizable into the form $\rho = \rho_r \rho_s$ at arbitrary times as it is at $t=0$.[2] Others have restricted their work to apply to times short on the system scale so as to be able to relate $\rho(t)$ to its exactly factorizable form at $t=0$ through low order perturbation theory.[3] In Chapter III, we take the unorthodox but exact step of introducing two disjoint system spaces. These spaces are labeled S_1 and S_2, respectively, and are spanned by eigenkets of the Hamiltonians H_{s_1} and H_{s_2}. H_{s_1} and H_{s_2} are identical in form to the unperturbed system Hamiltonian but since the spaces S_1 and S_2 are independent, all operators labeled with the index 1 commute with those labeled with 2. The advantage of this slightly complicated formalism is that, in the process, all reservoir operators are replaced by known averaged quantities. Our ability to calculate these averages stems from the fact that, in our development, the reservoir operators are first replaced in an exact way by their interaction picture representations. Since we know the initial distribution of reservoir states, we may in principle determine the average value of any interaction picture operators at an arbitrary time. This allows us to avoid making the almost universal assumption that the reservoir expectation values are unaffected by the interaction with the system.[2-5]

The steps discussed above result in equation (III-36) for the reduced density operator $\rho_s(t)$. The difficulty in dealing with operator quantities such as we obtain there arises for the most part from the non-commutivity of operators. In our treatment, the ordering of the various operators is dictated by the time ordering operators T and T_- of equation (III-36). By introducing the factorized form $T=T^A T^B$, we are able to treat system operators as c-numbers while taking reservoir averages. This turns out to be a great simplification which makes the rest of the work possible.

At the end of Chapter III, we have achieved our goal of obtaining an expression for the reduced density operator in which all reservoir operators have been replaced by averaged quantities. It must be admitted that these averages are not simple to compute and equation (III-37) is hardly more amenable to use than the original full density matrix. To proceed, we define an expansion for $\rho_s(t)$ in which these unwieldy terms will, in turn, be replaced by functions of system operators and bilinear averages of reservoir operators in the interaction picture at different times. These bilinear averages, $< B(t)B(t') >$, are called correlation functions in the literature[2,5] and contain important information about the statistical properties of the reservoir.

The motivation of the particular expansion we make is discussed in Chapter IV. We want an expansion that preserves the exponential character of the exact expression, equation (III-37), and the cumulant expansion of equation (IV-1) has that virtue. Later, we concentrate upon finding an equation of motion for $\rho_s(t)$ and it is common experience that exponential forms lead to simple differential equations.

The work of Chapter IV contains at least two original developments.

The first is that by factoring the time ordering operator, we may treat the system operators in equation (IV-1) as c-numbers for algebraic purposes. The second is that we discover that, for non-interacting boson reservoirs, only the second cumulant term is non-vanishing. For such reservoirs, there is no need to appeal to arguments about the weakness of the interaction strength.[6] For other reservoirs, one may use the second cumulant form in an analogy to the way that calculations based on small deviations from stable equilibrium are performed. In this chapter, we also establish that our expansion preserves probability and that $\rho_s(t)$ remains Hermitian.

At the end of Chapter IV (see equation (IV-19)), we obtain an apparently non-homogeneous equation of motion for $\rho_s(t)$. The seemingly non-homogeneous term $\hat{F}_1-\hat{F}_2$ is defined by equations (IV-17) and (IV-18). The bulk of the remaining work is devoted to finding an expansion for $\hat{F}_1-\hat{F}_2$ in terms of $\rho_s(t)$ so that we may obtain a local in time, linear in $\rho_s(t)$, first order equation of motion.

We pause in Chapter V to demonstrate that a first approximation of our results does reproduce the behavior of a harmonic oscillator in contact with a reservoir as found in other treatments. It turns out to be relatively easy to work out the shift in oscillator energy and the rate at which the oscillator reaches thermal equilibrium with the reservoir. In addition, there are two minor contributions from our approach that are missing from previous attempts. The first follows from the fact that we do not make the rotating wave approximation that is commonly invoked.[3,7,8] Thus, we obtain an oscillating factor multiplying the exponentially damped term in equation (V-69) for $< n(t) >_s$, the average occupation number for the operator. As this factor effects the spectral decomposition of $< n(t) >_s$, it may produce more accurate line width calculations based on the oscillator model. The second contribution is the rigorous addition of a classical driving force which results in equation (V-81). In perturbation theory treatments, the driving force term is simply added.[8] An example is worked out; the driving force is taken to be an impulse.

The work of Chapter V emphasizes a difficulty often overlooked in the oscillator problem when the reservoir is also taken to be a collection of oscillators. A standard method is to diagonalize the total Hamiltonian and to find the equilibrium condition in terms of the normal modes of the entire system.[8,9,10,11] The sticking point is that it is impossible to write out the transformation from bare states to normal modes in closed form. Hence, if the oscillator is initially in one of its bare states, the density matrix evaluated in this basis will describe the oscillators approach to equilibrium. But since the transformation that takes us from a basis in bare states to the normal mode representation is unknown, there is no way to show that these approaches give identical results.

In Chapter VI, we derive the method for generating the successive approximations to the equation of motion for $\rho_s(t)$. We explicitly write out the equation of motion for $\rho_s(t)$ correct to second order in our approximation. As discussed above, the second order form is obtained from the first order approximation by the addition of a term proportional to the third power of the probability that the system will undergo a transition in a time interval t_c as calculated by first order perturbation theory. Consequently, this last result should be applicable to cases where t_c approaches the lifetime of system states. We demonstrate in equation (VI-30) that we may recast the second order result in the form of the first order approximation by defining the effective reservoir correlation function $< B(t)B(t') >$. Thus, it seems possible to recover from our work the change in the reservoir due to the interaction with the system. Clearly, this would be an advantage over those treatments that assume that the reservoir correlation functions remain the same for all times.

CHAPTER II

THE DENSITY OPERATOR

Introduction

The concept of "state" is basic to any mathematical description of a physical system. When we say that a system is in a particular state, we mean that we have enough information to predict its behavior in future experiments. If we are able to specify the system's future behavior as completely as it is possible to do without violating the principles of quantum mechanics, we say that the system is in a pure state. In this case, we may represent the system uniquely by some vector in the Hilbert space spanned by the eigenvectors of a complete set of commuting observables appropriate to the system. In practice, however, we rarely have such complete information and we describe our system as being in a mixed state. A mixed state cannot be represented in a unique way by a particular vector in Hilbert space. Fortunately, another formalism exists that describes both pure and mixed states equally well; it is the density operator theory introduced by von Neumann.[1] In this chapter, we briefly discuss some of the more useful properties of the density operator.

In practice, the pure states of a system are the result of a somewhat artificial abstraction. One imagines that the system in question is isolated from the rest of the universe so that a manageable complete set of commuting system operators, $\{Q_i\}$, can be chosen and the simultaneous eigenstates of these operators, $\{|m>\}$, found to an acceptable order of accuracy. The index m represents the set of quantum numbers that differentiate between the eigenvectors of the $\{Q_i\}$. These eigenstates and their linear combinations constitute the pure states of the system. In the most general form, a pure state can be written as

$$|\psi^{(i)}\rangle = \sum_m c_m^{(i)} |m\rangle \qquad \text{II-1}$$

A central premise of Dirac's formulation of quantum mechanics is that the result of any measurement upon the system is represented by the mean value of some dynamic variable of the system. Consider the measurement that corresponds to the dynamic variable $\hat{A}$. If the system is in the pure state $|\psi^{(i)}\rangle$, the result of making the measurement is

$$\langle \hat{A} \rangle = \langle \psi^{(i)} | \hat{A} | \psi^{(i)} \rangle = \sum_{n,m} c_n^{(i)*} c_m^{(i)} A_{n,m} \qquad \text{II-2}$$

where

$$A_{n,m} = \langle n | A | m \rangle \qquad \text{II-3}$$

The Mixed State

The difficulty in transferring the results of the study of the pure states of a system to the laboratory lies in the impossibility in some cases of preparing the system in a state characterized by a unique set of $\{c_i\}$ in equation (II-1). Indeed, since the model of a system used in theoretical analysis never takes into account every contributing factor, it is not possible to specify an exactly complete set of system observables in non-trivial cases. This problem is commonly solved by averaging in an appropriate way over the pure states $|\psi^{(k)}>$ of the system so that one replaces equation (II-2) by

$$\langle \hat{A} \rangle = \sum_{n,m,k} w_k C_n^{(k)*} C_m^{(k)} A_{n,m} \qquad \text{II-4}$$

where w_k is the probability that the system is in the pure state represented by $|\psi^{(k)}>$. When equation (II-4) cannot be reduced uniquely to equation (II-2), we say that the system is in a mixed state.

The Density Matrix

As Roman[12] points out, the formalism that treats mixed states on a different footing than pure states is aesthetically lacking. The density matrix method removes this drawback.

If we define the density matrix by

$$\rho_{m,n} = \sum_{k} C_n^{(k)*} C_m^{(k)} \qquad \text{II-5}$$

equation (II-4) becomes

$$\langle \hat{A} \rangle = \sum_{n,m} A_{n,m} \rho_{m,n} \qquad \text{II-6}$$

As desired, we recover the simple form of equation (II-2) by setting $w_k = \delta_{ki}$. Then,

$$\rho_{m,n} = C_n^{(i)*} C_m^{(i)} \qquad \text{II-7}$$

Equation (II-6) may be rewritten as

$$\langle \hat{A} \rangle = \sum_n \Big(\sum_m A_{n,m} \rho_{m,n} \Big)$$

The quantity within parentheses has the form of the product of the matrix representations of two operators, A and ρ; therefore, we take equation (II-6) as the definition of the density operator, ρ, and write

$$\langle \hat{A} \rangle = \sum (A\rho)_{n,n} \qquad \text{II-6a}$$

$$= \mathrm{tr}\, A\rho$$

where tr denotes the trace. A useful representation of ρ is

$$\rho = \sum_{m,n,K} |m\rangle W_K C_n^{(K)*} C_m^{(K)} \langle n| \qquad \text{II-8}$$

where W_k is the probability that the system is in the state

$$|\psi_K\rangle = \sum_m C_m^{(K)} |m\rangle$$

At this point, one may do away with the distinction between pure and mixed states. Suppose that the system in question can possess N independent pure states. As shown by Roman,[12] ρ is completely determined by specifying the expectation values at some time of N^2-1 independent system variables $< A_i >$, by measurement or as an initial condition. This is possible because the $N \times N$ matrix (ρ_{nm}) has at most N^2-1 independent real parameters and the $< A_i >$ and equation (II-6) give us a system of N^2-1 independent equations by which they may be determined.[1,2,12]

The power of the density matrix formalism lies in its lack of ambiguity regardless of the completeness of our knowledge of the state of the system.

The General Properties of the Density Matrix

The following properties of the density matrix are demonstrated by von Neumann[1]:

(i) The density operator is Hermitian. That is

$$\rho = \rho^{\dagger} \qquad \text{II-9}$$

Hence

$$\rho_{m,n} = \rho^{*}_{n,m}$$

(ii) Since the unit operator must have expectation value 1,

$$\mathrm{tr}\,\rho = 1 \qquad \text{II-10}$$

(iii) The diagonal element, $\rho_{n,m}$, represents the probability that the system is in the pure state $|n>$.

(iv) The variations in time of the density operator depend upon the physical laws that govern the system; its value at any time may be obtained from its value at the reference time t=0 from

$$\rho(t) = e^{-i/\hbar Ht} \rho(0) \, e^{i/\hbar Ht} \qquad \text{II-11}$$

where H is the system Hamiltonian. From equation (II-11), it follows directly that the mean values of observables vary in time according to

$$\langle Q \rangle_t = tr\left\{ Q \, \rho(t) \right\} = tr\left\{ Q(t) \, \rho(0) \right\} \qquad \text{II-12}$$

This brief review of the density matrix contains all that we need for later use.

CHAPTER III

THE REDUCED DENSITY OPERATOR

Introduction

We consider the case of a small system interacting with a much larger one. By "small," we intend to describe a system which, when isolated from all external forces, may be treated in an exact way by the rules of quantum mechanics. The complexity of the large system makes it impractical to attempt to describe the combined system in terms of known stationary states. Our purpose is to set forth a procedure for determining the dynamical history of the small system in interaction with the large system (henceforth called the system and the reservoir, respectively) in which we represent the reservoir by the averaged values of suitable reservoir observables.

We begin by specifying the density operator of the entire system at the initial time. To obtain $\rho(t)$ at arbitrary times, we transform it from its value at t=0 by the time evolvement operator, $U(t) = e^{-iHt/\hbar}$, where H is the total system Hamiltonian. Since $\rho(t)$ contains more information than we need, we define the reduced density operator, $\rho_s(t)$, as the trace of $\rho(t)$ over reservoir states. By introducing a doubling of system space, we are able to replace reservoir operators in $\rho_s(t)$ by reservoir averages of operators in the interaction picture. Finally, by factoring the time ordering operator into parts that either act on system operators alone or on reservoir operators alone, we obtain a form in which we are able to treat system operators as ordinary functions.

The Combined System

We begin by introducing some necessary symbols. When isolated from one another, the two systems are represented by state vectors whose time evolvements are determined by

$$i\hbar \frac{\partial}{\partial t}|\Psi_r\rangle = H_r\,|\Psi_r\rangle \qquad \text{(reservoir),} \qquad \text{III-1}$$

and

$$i\hbar \frac{\partial}{\partial t}|\Psi_s\rangle = H_s\,|\Psi_s\rangle \qquad \text{(system).} \qquad \text{III-2}$$

We denote the stationary states of the isolated systems in the following way:

$$H_r|E_i\rangle = E_i\,|E_i\rangle \qquad \text{(reservoir),} \qquad \text{III-3}$$

and

$$H_s|S_i\rangle = \varepsilon_i\,|S_i\rangle \qquad \text{(system).} \qquad \text{III-4}$$

When the two systems are combined, the total Hamiltonian becomes

$$H = H_r + H_s + V \qquad \text{III-5}$$

where V describes the interaction between system and reservoir. For now, we take V to be time independent; later, we allow V to include a classical driving force that operates on the system alone.

In principle, all measurable quantities of the combined system can be calculated if only we know the density matrix operator, $\rho(t)$, for all times. If we have $\rho(t)$ at time t=0, we may obtain its value at all other times from the equation

$$\rho(t) = e^{-i(H_r+H_s+V)t/\hbar} \rho(0)\, e^{i(H_r+H_s+V)t/\hbar} \qquad \text{III-6}$$

At time t=0, the interaction has suddenly been "turned on" and we can write $\rho(0)$ as the product $\rho_s\rho_r$ where ρ_s is the appropriate density matrix operator for the isolated system at t=0 and ρ_r describes the initial state of the reservoir. Our ability to prepare the reservoir in a given initial configuration is limited and we make the modest assumption that it is in a canonical distribution of reservoir states consistent with a measured temperature, $T = \frac{1}{\theta k}$, where k is Boltzmann's constant. Thus,

$$\rho_r(t) = \sum_j |E_j\rangle Z^{-1} e^{-\theta E_j} \langle E_j| \qquad \text{III-7}$$

where Z is the reservoir partition function. The most general form for ρ_s (see equation (II-8)) is

$$\rho_s(t) = \sum_{i,j} |S_i\rangle P_{ij} |S_j\rangle \qquad \text{III-8}$$

where

$$\sum_j P_{jj} = 1 \qquad \text{III-9}$$

For our purposes, we imagine that initially the system was in the i^{th} eigenstate of H_s so that

$$\rho_s = |S_i\rangle\langle S_i| \qquad \text{III-10}$$

This assumption is for convenience only and all subsequent results can be immediately generalized.

Substituting $\rho(0) = \rho_s\rho_r$, we obtain from equation (III-6)

$$\rho(t) = \sum_j e^{-i(H_r+H_s+V)t/\hbar} |S_i\rangle|E_j\rangle \frac{e^{-\theta E_j}}{Z} \langle E_j|\langle S_i| e^{i(H_r+H_s+V)t/\hbar} \qquad \text{III-11}$$

The motivation for the next step is provided by the practical notion that the most interesting quantities are those that describe the system at later times with reservoir effects averaged over all possible reservoir states. Such a quantity is usually the expectation value of some observable whose operator representation is a function of system coordinates alone. Consider just such an observable, $\hat{O}_s$. At time t, its expectation value is given by

$$\langle \hat{O}_s(t)\rangle = tr_{r,s}\,[\hat{O}_s\,\rho(t)] \qquad \text{III-12}$$

$$= \sum_{K,j} \langle S_j|\langle E_K|\hat{O}_s\,\rho(t)\,|E_K\rangle|S_j\rangle$$

$$= \sum_j \langle S_j|\,\hat{O}_s \sum_K \langle E_K|\,\rho(t)\,|E_K\rangle|S_j\rangle$$

where we have used the fact that $\hat{O}_s$ operates on system states only. We are then led to define the reduced density operator[2]

$$\rho_s(t) = \sum_K \langle E_K | \rho(t) | E_K \rangle \qquad \text{III-13}$$

which enables us to write equation (III-12) in the formally simpler way

$$\langle \hat{O}_s(t) \rangle = \sum_j \langle S_j | \hat{O}_s \rho_s(t) | S_j \rangle \qquad \text{III-14}$$

$$= tr_s [\hat{O}_s \, \rho_s(t)]$$

Using the definition of the reduced density operator and equation (III-11), we have

$$\rho_s(t) = \sum_{j,K} \langle E_K | e^{-i(H_r+H_s+V)t/\hbar} | S_i \rangle | E_j \rangle \qquad \text{III-15}$$

$$\times Z e^{-\theta E_j} \langle E_j | \langle S_i | e^{i(H_r+H_s+V)t/\hbar} | E_K \rangle$$

At this point, we digress to establish an equivalent way of expressing the operator

$$\hat{O} = \langle E_K | F(\hat{q}_s, \hat{Q}_r) | S_i \rangle | E_j \rangle \; \langle E_j | \langle S_i | F^{+}(\hat{q}_s, \hat{Q}_r) | E_K \rangle \qquad \text{III-16}$$

where F is an arbitrary function of system operators $\hat{q}_s$ and reservoir operators $\hat{Q}_r$. Since the reservoir operators are replaced by matrix elements, we call $\hat{O}$ a system operator. The matrix elements of the system operator are given by

$$\hat{O}_{m,n} = \langle S_m| \langle E_k| F(\hat{q}_s, \hat{Q}_r)|E_j\rangle|S_i\rangle \qquad \text{III-17}$$

$$\times \langle S_i| \langle E_j| F^{+}(\hat{q}_s, \hat{Q}_r)|E_k\rangle|S_n\rangle$$

Thus, $\hat{O}_{m,n}$ is the product of the two commuting complex numbers

$$c_m = \langle S_m| \langle E_k| F(\hat{q}_s, \hat{Q}_r)|E_j\rangle|S_i\rangle$$

and

$$c_n = \langle S_i| \langle E_j| F^{+}(\hat{q}_s, \hat{Q}_r)|E_k\rangle|S_n\rangle$$

Hence,

$$\hat{O}_{m,n} = c_m c_n = c_n c_m .$$

Now for the crucial step: We imagine that the subspaces spanned by the system states of c_m and c_n (S_2 and S_1, respectively) are disjoint.[14] Consequently, we introduce subscripts to distinguish between the two independent subspaces S_1 and S_2. Then

$$c_n = \langle S_{i_1}| \langle E_j| F^{+}(\hat{q}_{s_1}, \hat{Q}_r)|E_k\rangle|S_{n_1}\rangle \qquad \text{III-18}$$

and

$$c_m = \langle S_{m_2}| \langle E_k| F(\hat{q}_{s_2}, \hat{Q}_r|E_j\rangle|S_{i_2}\rangle \qquad \text{III-19}$$

Clearly, this procedure does not affect the numerical values of c_n and c_m. But now that the subspaces spanned by the $|S_{m_1}\rangle$ and the $|S_{m_2}\rangle$ are disjoint, we can say that the operators $\hat{q}_{s_1}$ commute with the operators $\hat{q}_{s_2}$. Hence, we can write

$$\hat{O}_{m,n} = C_n C_m \qquad \text{III-20}$$

$$= \langle S_{i_1}| \langle E_j | F^{+}(\hat{q}_{s_1}, \hat{Q}_r) | E_k \rangle | S_{n_1} \rangle$$

$$\times \langle S_{m_2}| \langle E_k | F(\hat{q}_{s_2}, \hat{Q}_r) | E_j \rangle | S_{i_2} \rangle$$

$$= \langle S_{m_2}| \langle S_{i_1}| \langle E_j | F^{+}(\hat{q}_{s_1}, \hat{Q}_r) | E_k \rangle \langle E_k | F(\hat{q}_{s_2}, \hat{Q}_r) | E_j \rangle | S_{i_2} \rangle | S_{n_1} \rangle$$

We have used the independence of the S_1 space from the S_2 space to move the ket $|S_{n_1}>$ past $F(\hat{q}_{s_2}, \hat{Q}_r)$ and the bra $< S_{m_2}|$ $F(\hat{q}_{s_1}, \hat{Q}_r)$.

A definition of $\hat{O}$ equivalent to equation (III-16) is

$$\hat{O} = \langle S_{i_1}| \langle E_j | F^{+}(\hat{q}_{s_1}, \hat{Q}_r) | E_k \rangle \langle E_k | F(\hat{q}_{s_2}, Q_r) | E_j \rangle | S_{i_2} \rangle \qquad \text{III-21}$$

Equation (III-21) makes sense only if we use it in the following way. Suppose we are to find $\hat{O}|S_n>$. Then we label $|S_n>$ as a vector in S_1 space and proceed with S_1 vectors and operators regarded as being independent of S_2 vectors and operators. If we are to find $< S_m|\hat{O}$, we label $< S_m|$ as a vector in S_2 space and proceed as before.

Returning to equation (III-15), we see that the quantity being summed over,

$$Z^{-1} e^{-\theta E_j} \langle E_k | e^{-i(H_r+H_s+V)t/\hbar} | S_i \rangle | E_j \rangle \langle E_j | \langle S_i | e^{i(H_r+H_s+V)t/\hbar} | E_k \rangle$$

has the same form as the reduced operator $\hat{O}$ in equation (III-12) with

$$F(\hat{q}_s, \hat{Q}_r) = e^{-i(H_r + H_s + V)t/\hbar}$$

and

$$F^{+}(\hat{q}_s, \hat{Q}_r) = e^{i(H_r + H_s + V)t/\hbar}$$

Thus, we can write equation (III-15) in the equivalent form

$$\rho_s(t) = \sum_{j,k} Z^{-1} e^{-\theta E_j} \langle S_{i_1}| \langle E_j| e^{i(H_r + H_{s_1} + V_1)t/\hbar} \qquad \text{III-22}$$

$$\times |E_k\rangle\langle E_k| e^{-i(H_r + H_{s_2} + V_2)t/\hbar} |E_j\rangle |S_{i_2}\rangle$$

where, as before, the system operators in H_{s_1} and V_1 only act on states labeled with the subscript 1 and a corresponding relation exists between H_{s_2}, V_2 and states labeled with the subscript 2.

Now the strategy becomes apparent; we can perform the sum over the complete set $|E_k\rangle$ (complete in the space of the reservoir) and obtain for equation (III-22),

$$\rho_s(t) = \sum_j Z^{-1} e^{-\theta E_j} \langle S_{i_1}| \langle E_j| e^{i(H_r + H_{s_1} + V_1)t/\hbar} \qquad \text{III-23}$$

$$\times e^{-i(H_r + H_{s_2} + V_2)t/\hbar} |E_j\rangle |S_{i_2}\rangle$$

$$= \langle S_{i_1}| \sum_j \frac{e^{-\theta E_j}}{Z} \langle E_j| e^{i(H_r + H_{s_1} + V_1)t/\hbar} e^{-i(H_r + H_{s_2} + V_2)t/\hbar} |E_j\rangle |S_{i_2}\rangle$$

Our desire to represent the reservoir by averaged quantities has apparently been satisfied. Still, equation (III-23) is only a formal restatement of equation (III-15) and is no more amenable to use in calculations. To make progress, we must manipulate equation (III-23) a little more.

We employ the identities[15]:

$$e^{i(H_r+H_{s_1}+V_1)t/\hbar} = \left(T_- \, e^{i/\hbar\int_0^t V_{I_1}(t')dt'}\right) e^{i(H_{s_1}+H_r)t/\hbar} \qquad \text{III-24}$$

and

$$e^{-i(H_r+H_{s_2}+V_2)t/\hbar} = e^{-i(H_r+H_{s_2})t/\hbar}\left(T \, e^{-i/\hbar\int_0^t V_{I_2}(t')dt'}\right) \qquad \text{III-25}$$

where

$$V_{I_1}(t') = e^{i(H_{s_1}+H_r)t/\hbar}\, V_1 \, e^{-i(H_{s_1}+H_r)t/\hbar} \qquad \text{III-26}$$

and

$$V_{I_2}(t') = e^{i(H_{s_2}+H_r)t/\hbar}\, V_2 \, e^{-i(H_{s_2}+H_r)t/\hbar} \qquad \text{III-27}$$

The operator T_- orders the product $V_{I_1}(t_1)V_{I_1}(t_2) \ldots V_{I_1}(t_n)$ in the n^{th} term of the expansion of T_- $\exp\left[\frac{i}{\hbar}\int_0^t dt' \, V_{I_1}(t')\right]$ so that operators at earlier times are always to the left of operators at later times. Similarly, the operator T orders the product $V_{I_2}(t_1)V_{I_2}(t_2) \ldots V_{I_2}(t_n)$ in the expansion of T $\exp\left[-\frac{i}{\hbar}\int_0^t dt' V_{I_2}(t')\right]$ so that operators at later times are always to the left of operators at earlier times. Equations (III-24) and (III-25) are certainly true at t=0 since both sides of either equation reduce to unity then. It is fairly easy to show that, if we assume the equations are true at arbitrary times, then the first derivatives with respect to time of both sides of either equation (III-24) or (III-25) are equal. When two quantities are equal at some time and both satisfy the same linear, first order, differential equation at arbitrary times, then they are equal at all times.

Since both H_{s_1} and H_{s_2} commute with H_r, we may write

$$e^{i(H_{s_1}+H_r)t/\hbar} = e^{iH_{s_1}t/\hbar}\, e^{iH_r t/\hbar} \qquad \text{III-28}$$

and

$$e^{-i(H_{s_2}+H_r)t/\hbar} = e^{-iH_r t/\hbar}\, e^{-iH_{s_2}t/\hbar} \qquad \text{III-29}$$

Substituting equations (III-24), (III-25), (III-28), and (III-29) into equation (III-23) and using the identify

$$e^{iH_r t/\hbar}\, e^{-iH_r t/\hbar} = 1$$

we find

$$\rho_s(t) = \langle S_{i_1}| \sum_j Z^{-1} e^{-\theta E_j} \langle E_j| \left(T_- e^{i/\hbar \int_0^t dt_1 V_{I_1}(t_1) dt_1}\right) e^{iH_{s_1}t/\hbar} \qquad \text{III-30}$$

$$\times\, e^{-iH_{s_2}t/\hbar} \left(T\, e^{-i/\hbar \int_0^t dt_2 V_{I_2}(t_2) dt_2}\right) |E_j\rangle |S_{i_2}\rangle$$

The next step is to move the operators $\exp(iH_{s_1}t/\hbar)$ and $\exp(-iH_{s_2}t/\hbar)$ to the extreme right and left, respectively. We recall that this is possible because the space S_1 is independent of the S_2 space and, therefore, H_{s_1} commutes with everything labeled with a 2 and H_{s_2} likewise commutes with everything labeled with a 1. Hence,

$$\rho_s(t) = e^{-iH_{s_2}t/\hbar} \langle S_{i_1}| \sum_j Z^{-1} e^{-\theta E_j} \langle E_j| \left(T_- e^{i/\hbar \int_0^t dt' V_{I_1}(t')}\right) \qquad \text{III-31}$$

$$\times \left(T\, e^{i/\hbar \int_0^t dt' V_{I_2}(t')}\right) |E_j\rangle |S_{i_2}\rangle\, e^{iH_{s_1}t/\hbar}$$

If at this point, we were to content ourselves with expanding the various exponentials, we would merely recover perturbation theory. We wish to do more than that of course but in order to do so, we must sacrifice some of the general nature of the discussion. Therefore, we specify that the interaction between the system and reservoir to be described by[16]

$$V = \sum_{i=1}^{n} A_i(\hat{q}_s)\, B_i(\hat{Q}_r) = A \cdot B \qquad \text{III-32}$$

where the quantities A_i are functions of the system variables alone; the quantities B_i are likewise functions of reservoir variables alone. Since by hypothesis V is time independent, we extend that restriction to the terms A_iB_i. Further, we suppose that the operator expressions A_iB_i are Hermitian.

We obtain the interaction picture form of V

$$V_I = e^{i(H_s+H_r)t'/\hbar}\, V\, e^{-i(H_s+H_r)t'/\hbar}$$

by substituting

$$\hat{q}_s(t') = e^{iH_s t'/\hbar}\, \hat{q}_s\, e^{-iH_s t'/\hbar} \qquad \text{III-33}$$

and

$$\hat{Q}_r(t') = e^{iH_r t'/\hbar}\, \hat{Q}_r\, e^{-iH_r t'/\hbar} \qquad \text{III-34}$$

for $\hat{q}_s$ and $\hat{Q}_r$ in equation (III-32). Since H_s and H_r are Hermitian, V_I remains Hermitian at all times. For convenience, we introduce the short-hand notation

$$V_I(t') = A_I(\hat{q}_s(t'))\, B_I(\hat{Q}_r(t')) \qquad \text{III-35}$$

$$\equiv A(t')\, B(t')$$

Substituting equation (III-35) into equation (III-31), we obtain

$$\rho_s(t) = e^{-iH_{s_2}t/\hbar} \langle s_{i_1}| \qquad \text{III-36}$$

$$\times \sum_j \frac{e^{-\theta E_j}}{Z} \langle E_j| \left(T_- e^{i/\hbar \int_0^t dt_1 A_1(t_1) B(t_1)}\right) \left(T e^{-i/\hbar \int_0^t dt_2 A_2(t_2) B(t_2)}\right) |E_j\rangle$$

$$\times |s_{i_2}\rangle e^{iH_{s_1}t/\hbar}$$

We note that the time ordering of the B operators may be carried out independently of the ordering of the A operators since the spaces involved are disjoint. Hence we are justified in decomposing T and T_- into $T^{A_2}T^B$ and $T_-^{A_1}T_-^B$, respectively, where, for example, T^{A_2} orders the $A_2(t')$ operators alone and T^B orders the $B(t')$ operators.[17] Then, we again appeal to the commutivity of S_1 operators with respect to S_2 operators to draw $T_-^{A_1}T^{A_2}$ to the left of the bra $\langle E_j|$. That is,

$$\rho_s(t) = e^{-iH_{s_2}t/\hbar} \langle s_{i_1}| T_-^{A_1} T^{A_2} \qquad \text{III-37}$$

$$\times \sum_j \frac{e^{-\theta E_j}}{Z} \langle E_j| \left(T_-^B e^{i/\hbar \int_0^t dt_1 A_1(t_1) B(t_1)}\right) \left(T^B e^{-i/\hbar \int_0^t dt_2 A_2(t_2) B(t_2)}\right) |E_j\rangle$$

$$\times |s_{i_2}\rangle e^{iH_{s_1}t/\hbar}$$

$$= e^{-iH_{s_2}t/\hbar} \langle s_{i_1}| T_-^{A_1} T^{A_2} \hat{\phi}(t) |s_{i_2}\rangle e^{iH_{s_1}t/\hbar}$$

where

$$\hat{\phi}(t) = \sum_j Z^{-1} e^{-\beta E_j} \times \langle E_j | \left(T_-^B e^{\frac{i}{\hbar}\int_0^t dt' A_1(t') B(t')} \right) \left(T^B e^{-\frac{i}{\hbar}\int_0^t dt' A_2(t') B(t')} \right) | E_j \rangle \qquad \text{III-38}$$

We stress that the quantity on the left hand side of equation (III-37) is not a scalar product. The notation requires that we expand $\hat{\phi}(t)$ into a sum of products of various numbers of A_1 and A_2 operators at different times, operate upon $|S_{i_2}>$ and $< S_{i_1}|$ by the A_2 and A_1 operators, respectively, to obtain $|\psi_2>$ and $< \psi_1'|$ ($|\psi_2>$ is the result of operating upon $|S_{i_2}>$ by the A_2 operators and $< \psi_1'|$ is the result of operating upon $< S_{i_1}|$ by the A_1 operators), and finally forming the operator $|\psi_2> < \psi_1'|$.

This last step is important in the development of the method. Since the order of an A product is ultimately determined by the $T_-^{A_1} T^{A_2}$ operator, we can perform any intermediate algebraic manipulation of $\hat{\phi}(t)$ as if $A_1(t')$ and $A_2(t')$ were merely functions and not operators.[18]

Summary

By doubling the system Hilbert space and introducing the factored form of the time ordering operator, we arrive at equations (III-37) and (III-38). These equations involve of necessity only averages of reservoir operators but these averages are still far too complicated to calculate. Since we are now free to treat the A operators in the expression for $\hat{\phi}(t)$ as c-numbers, we look for an expansion of $\hat{\phi}(t)$ that will convert the average over reservoir states of an exponential into another exponential form in which the averaged quantities appear in the exponent.

CHAPTER IV

THE CUMULANT EXPANSION

Introduction

A cumulant expansion of $\hat{\emptyset}(t)$ is defined. The explicit expressions for the first two cumulants are written in equations (IV-2) and (IV-4). By truncating the expansion at the second cumulant, we arrive at an approximation (exact in the case of a reservoir of free bosons) for $\rho_s(t)$, given by equation (IV-7), in which reservoir variables appear only as correlation functions. We demonstrate that this approximation to $\rho_s(t)$ is Hermitian and conserves probability. Finally, we derive an equation of motion for $\rho_s(t)$ which forms the basis of all subsequent work.

The Cumulant Expansion

If the interaction between the system and reservoir is correctly described by equation (III-35), then $\rho_s(t)$ is given exactly by equation (III-37). How do we best utilize this expression? In most non-trivial cases, one resorts to some sort of an expansion and the success of such a procedure depends upon the suitability of the expansion chosen. Taking note of the exponential character of the operator quantities in equation (III-38) and realizing that we can treat the A operators as functions since $T_-^{A_1} T^{A_2}$ will not be applied until we substitute equation (III-38) back into equation (III-37), we try an expansion of the cumulant type[14]:

$$\hat{\phi}_\lambda(t) = \sum_j Z^{-1} e^{-\theta E_j} \langle E_j | \left(T_-^B e^{\frac{i}{\hbar}\lambda\int_0^t dt' A_1(t') B(t')} \right) \qquad \text{IV-1}$$

$$\times \left(T^B e^{-\frac{i}{\hbar}\lambda\int_0^t dt' A_2(t') B(t')} \right) | E_j \rangle$$

$$= e^{\sum_n \lambda^n W_n}$$

The parameter λ has been inserted for calculational convenience and will be set to unity in due time. The expansion defined in equation (IV-1) has the chief virtue of retaining the exponential character of the exact form of $\hat{\phi}(t)$.

One obtains expressions for the W_n's by taking an appropriate number of derivatives with respect to λ on both sides of equation (IV-1) and then setting λ equal to zero. In particular, by taking the first derivative and setting λ to zero, we find:

$$W_1 = \frac{i}{\hbar} Z^{-1} \sum_j e^{-\theta E_j} \left[\langle E_j | \int_0^t dt' A_1(t') B(t') - \int_0^t dt' A_2(t') B(t') | E_j \rangle \right] \qquad \text{IV-2}$$

$$= \frac{i}{\hbar} \int_0^t dt' \left[A_1(t') - A_2(t') \right] \langle B \rangle$$

where

$$\langle B \rangle = Z^{-1} \sum_j e^{-\theta E_j} \langle E_j | B(t') | E_j \rangle \qquad \text{IV-3}$$

$$= Z^{-1} \sum_j e^{-\theta E_j} \langle E_j | e^{i H_r t/\hbar} B e^{-i H_r t/\hbar} | E_j \rangle$$

(continued)

$$= Z^{-1} \sum_j e^{-\theta E_j} \langle E_j | e^{iE_j t/\hbar} B \; e^{-iE_j t/\hbar} | E_j \rangle$$

$$= Z^{-1} \sum_j e^{-\theta E_j} \langle E_j | B | E_j \rangle$$

We have used equations (III-3), (III-26), and (III-34) in obtaining equation (IV-3). In the same way, taking the second derivative of both sides of equation (IV-1) results in the expression:

$$2W_2 + W_1^2 = -\frac{1}{\hbar^2} Z^{-1} \sum_j e^{-\theta E_j} \Big[\langle E_j | T_-^B \int_0^t dt' \int_0^t dt'' A_1(t') B(t') A_1(t'') B(t'')$$

$$+ T^B \int_0^t dt' \int_0^t dt'' A_2(t') B(t') A_2(t'') B(t'')$$

$$- 2 \int_0^t dt' \int_0^t dt'' A_1(t') B(t') A_2(t'') B(t'') | E_j \rangle \Big]$$

Hence,

$$W_2 = -\frac{1}{2\hbar^2} \Bigg[\int_0^t dt' \int_0^t dt'' \Big\{ A_1(t') A_1(t'') \left(\langle T_-^B B(t') B(t'') \rangle - \langle B \rangle^2 \right) \qquad \text{IV-4}$$

$$+ A_2(t') A_2(t'') \left(\langle T^B B(t') B(t'') \rangle - \langle B \rangle^2 \right)$$

$$- 2 A_1(t') A_2(t'') \left(\langle B(t') B(t'') \rangle - \langle B \rangle^2 \right) \Big\} \Bigg]$$

where

$$\langle B(t') B(t'') \rangle = \sum_j Z^{-1} e^{-\theta E_j} \langle E_j | B(t') B(t'') | E_j \rangle \qquad \text{IV-5}$$

In the work that follows, we retain only W_1 and W_2 in the cumulant expansion of $\phi_\lambda(t)$. Then setting $\lambda=1$,

$$\hat{\phi}(t) = e^{W_1 + W_2} \tag{IV-6}$$

In Appendix A, we show that if the reservoir is composed of free bosons, and if B(t) is a linear combination of reservoir creation and destruction operators, all cumulants except ω_2 vanish. Thus, if our reservoir is a radiation field, a system of non-interacting oscillators or a phonon bath, the truncation is exact. No approximation at all has been introduced.

Equations (III-37) and (IV-6) combine to give us

$$\rho_s(t) = e^{-iH_{s_2}t/\hbar} \langle S_{i_1}| T_-^{A_1} T^{A_2} \, e^{W_1 + W_2} \, |S_{i_2}\rangle \, e^{iH_{s_1}t/\hbar} \tag{IV-7}$$

At this point, it is probably wise to inquire whether the trace of $\rho_s(t)$ over system states is unity as it should be. At $t=0$, equation (IV-7) becomes

$$\rho_s(0) = \langle S_{i_1}| 1 | S_{i_2}\rangle$$

Then,

$$\begin{aligned} tr_s \, \rho_s(0) &= \sum_j \langle S_{j_2}| \langle S_{i_1}| 1 | S_{i_2}\rangle |S_{j_1}\rangle \\ &= \sum_j \langle S_{j_2}| S_{i_2}\rangle \langle S_{i_1}| S_{j_1}\rangle \\ &= \sum_j \delta_{ij} = 1. \end{aligned}$$

as required. Note that in evaluating the trace, we followed our rather unorthodox prescription for obtaining matrix elements. It is also worth pointing out for later use that

$$\langle S_{i_1} | \mathbb{1} | S_{i_2} \rangle = | S_{i_2} \rangle \langle S_{i_1} |$$

$$= | S_i \rangle \langle S_i |$$

Thus, once a vector or operator has been positioned so that its function is no longer ambiguous without the subscripts, the subscripts may be dropped.

Now differentiate both sides of equation (IV-7) with respect to time

$$\frac{d\rho_s(t)}{dt} = -\frac{i}{\hbar} H_s \rho_s(t) + \frac{i}{\hbar} \rho_s(t) H_s \qquad \text{IV-8}$$

$$+ e^{-iH_{s_2}t/\hbar} \langle S_{i_1} | T_-^{A_1} T^{A_2} \left(\frac{d}{dt}(W_1 + W_2) e^{W_1+W_2} \right) | S_{i_2} \rangle e^{iH_{s_1}t/\hbar}$$

We have dropped the subscripts of H_s in the first two terms on the right hand side since, as we have just discussed, there is no ambiguity as to what H_s operates upon. Using equations (IV-2) and (IV-4),

$$\frac{d}{dt} W_1 = \frac{i}{\hbar} \left(A_1(t) - A_2(t) \right) \langle B \rangle \qquad \text{IV-9}$$

and

$$\frac{d}{dt} W_2 = -\frac{1}{\hbar^2}\int_0^t dt'' A_1(t'')\, A_1(t)\, \beta_{t'',t} - \frac{1}{\hbar^2}\int_0^t dt'' A_2(t) A_2(t'') \beta_{t,t''} + \frac{1}{\hbar^2}\int_0^t dt'' A_2(t)\, A_1(t'')\, \beta_{t'',t} + \frac{1}{\hbar^2}\int_0^t dt'' A_2(t'') A_1(t) \beta_{t,t''} \qquad \text{IV-10}$$

where

$$\beta_{t'',t} = \langle B(t'') B(t) \rangle - \langle B \rangle^2 \qquad \text{IV-11}$$

and

$$\beta_{t,t''} = \langle B(t)\, B(t'') \rangle - \langle B \rangle^2 \qquad \text{IV-12}$$

Together, equations (IV-8), (IV-9), and (IV-10) lead us to write

$$\begin{aligned}
\frac{d}{dt}\rho_s(t) = &-\frac{i}{\hbar}\left[H_s, \rho_s(t)\right] \\
&+ \frac{i}{\hbar}\, e^{-iH_{s_2}t/\hbar} \langle S_{i_1}| T_-^{A_1} T^{A_2}\left\{(A_1(t) - A_2(t)) \langle B \rangle\, e^{W_1+W_2}\right\} |S_{i_2}\rangle\, e^{iH_{s_1}t/\hbar} \\
&- \frac{1}{\hbar^2}\, e^{-iH_{s_2}t/\hbar} \langle S_{i_1}| T_-^{A_1} T^{A_2}\left\{\int_0^t dt'' A_1(t'') A_1(t)\, \beta_{t'',t}\, e^{W_1+W_2}\right\} |S_{i_2}\rangle\, e^{iH_{s_1}t/\hbar} \\
&- \frac{1}{\hbar^2}\, e^{-iH_{s_2}t/\hbar} \langle S_{i_1}| T_-^{A_1} T^{A_2}\left\{\int_0^t dt'' A_2(t) A_2(t'')\, \beta_{t,t''}\, e^{W_1+W_2}\right\} |S_{i_2}\rangle\, e^{iH_{s_1}t/\hbar} \\
&+ \frac{1}{\hbar^2}\, e^{-iH_{s_2}t/\hbar} \langle S_{i_1}| T_-^{A_1} T^{A_2}\left\{\int_0^t dt'' A_2(t) A_1(t'')\, \beta_{t'',t}\, e^{W_1+W_2}\right\} |S_{i_2}\rangle\, e^{iH_{s_1}t/\hbar} \\
&+ \frac{1}{\hbar^2}\, e^{-iH_{s_2}t/\hbar} \langle S_{i_1}| T_-^{A_1} T^{A_2}\left\{\int_0^t dt'' A_2(t'') A_1(t)\, \beta_{t,t''}\, e^{W_1+W_2}\right\} |S_{i_2}\rangle\, e^{iH_{s_1}t/\hbar}
\end{aligned}$$

This last expression may be somewhat simplified. The A_2 operators with time argument t can be placed to the extreme left by operating with T^{A_2} and using $e^{-iH_s t/\hbar} A_2(t) = A_2\, e^{-iH_s t/\hbar}$ where A_2 is in the Schrodinger picture. Similarly, the A_1 operator can be moved to the extreme right and put into the Schrodinger picture. Then,

$$
\begin{aligned}
\frac{d}{dt}\rho_s(t) = &-\frac{i}{\hbar}[H_s, \rho_s(t)] - \frac{i}{\hbar}[A, \rho_s(t)] \qquad \text{IV-13} \\
&-\frac{1}{\hbar^2} e^{-iH_s t/\hbar} \langle S_{i_1}| T_-^{A_1} T^{A_2} \left\{ \int_0^t dt''\, A_1(t'')\, \beta_{t'',t}\, e^{W_1+W_2} \right\} |S_{i_2}\rangle e^{iH_s t/\hbar} A_1 \\
&+\frac{1}{\hbar^2} e^{-iH_s t/\hbar} \langle S_{i_1}| T_-^{A_1} T^{A_2} \left\{ \int_0^t dt''\, A_2(t'')\, \beta_{t,t''}\, e^{W_1+W_2} \right\} |S_{i_2}\rangle e^{iH_s t/\hbar} A_1 \\
&-\frac{1}{\hbar^2} A_2\, e^{-iH_s t/\hbar} \langle S_{i_1}| T_-^{A_1} T^{A_2} \left\{ \int_0^t dt''\, A_2(t'')\, \beta_{t,t''}\, e^{W_1+W_2} \right\} |S_{i_2}\rangle e^{iH_s t/\hbar} \\
&+\frac{1}{\hbar^2} A_2\, e^{-iH_s t/\hbar} \langle S_{i_1}| T_-^{A_1} T^{A_2} \left\{ \int_0^t dt''\, A_1(t'')\, \beta_{t'',t}\, e^{W_1+W_2} \right\} |S_{i_2}\rangle e^{iH_s t/\hbar}
\end{aligned}
$$

We now take the trace of both sides of equation (IV-13). Since the trace is invariant under cyclic permutations,

$$
tr_s[H_s, \rho_s(t)] = tr_s[A, \rho_s(t)] = 0
$$

and

$$\frac{d}{dt}\,\mathrm{tr}_s\,\rho_s(t) = -\frac{1}{\hbar^2}\sum_j \langle S_{j_2}|\, e^{-iH_{s_2}t/\hbar} \qquad \text{IV-14}$$

$$\times\Big[\langle S_{i_1}|\,T_-^{A_1}T^{A_2}\Big\{\int_0^t dt''\,A_1(t'')\,\beta_{t'',t}\,e^{W_1+W_2}\Big\}|S_{i_2}\rangle$$

$$-\langle S_{i_1}|\,T_-^{A_1}T^{A_2}\Big\{\int_0^t dt''\,A_2(t'')\,\beta_{t,t''}\,e^{W_1+W_2}\Big\}|S_{i_2}\rangle\Big]\,e^{iH_{s_1}t/\hbar}A_1|S_{j_1}\rangle$$

$$-\frac{1}{\hbar^2}\sum_j \langle S_{j_2}|\,A_2\,e^{-iH_{s_2}t/\hbar}$$

$$\times\Big[\langle S_{i_1}|\,T_-^{A_1}T^{A_2}\Big\{\int_0^t dt''\,A_2(t'')\,\beta_{t,t''}\,e^{W_1+W_2}\Big\}|S_{i_2}\rangle$$

$$-\langle S_{i_1}|\,T_-^{A_1}T^{A_2}\Big\{\int_0^t dt''\,A_1(t'')\,\beta_{t'',t}\,e^{W_1+W_2}\Big\}|S_{i_2}\rangle\Big]\,e^{iH_{s_1}t/\hbar}|S_{j_1}\rangle$$

By inserting a complete set of S_1 states, the first term on the right hand side of equation (IV-14) can be written

$$-\frac{1}{\hbar^2}\sum_{j,k}\langle S_{j_2}|\,e^{-iH_{s_2}t/\hbar}\langle S_{i_1}|\,T_-^{A_1}T^{A_2}\Big\{\int_0^t A_1(t'')\beta_{t'',t}\,e^{W_1+W_2}\Big\}|S_{i_2}\rangle$$

$$\times\, e^{iH_{s_1}t/\hbar}\,|S_{k_1}\rangle\langle S_{k_1}|\,A_1|S_{j_1}\rangle$$

But

$$\langle S_{k_1}|\,A_1|\,S_{j_1}\rangle = \langle S_{k_2}|\,A_2|\,S_{j_2}\rangle$$

and since $< S_{k_2}|A_2|S_{j_2} >$ is merely a c-number, we can rearrange the first term to read

$$-\frac{1}{\hbar^2}\sum_{j,k}\langle S_{k_2}|A_2|S_{j_2}\rangle$$

$$\times\langle S_{j_2}|e^{-iH_{S_2}t/\hbar}\langle S_{i_1}|T_-^{A_1}T^{A_2}\left\{\int_0^t dt''A_1(t'')\beta_{t'';t}e^{W_1+W_2}\right\}|S_{i_1}\rangle e^{iH_{S_1}t/\hbar}|S_{k_1}\rangle$$

$$=-\frac{1}{\hbar^2}\sum_{k}\langle S_{k_2}|A_2\,e^{-iH_{S_2}t/\hbar}$$

$$\times\langle S_{i_1}|T_-^{A_1}T^{A_2}\left\{\int_0^t dt''A_1(t'')\beta_{t'';t}e^{W_1+W_2}\right\}|S_{i_1}\rangle e^{iH_{S_1}t/\hbar}|S_{k_1}\rangle$$

Thus, the first term on the right hand side of equation (IV-14) exactly cancels the third term of the right hand side. Similarly, the second term cancels the fourth. Hence,

$$\frac{d}{dt}\,\mathrm{tr}_S\,\rho_S(t)=0$$

and this combined with the initial condition

$$\mathrm{tr}_S\,\rho_S(0)=1 \qquad \text{IV-15}$$

insures that

$$\mathrm{tr}_S\,\rho_S(t)=1 \qquad \text{IV-16}$$

holds at arbitrary times.

Returning to equation (IV-13), we introduce the operators $\hat{F}_1$ and $\hat{F}_2$ where

$$\hat{F}_1 = e^{-iH_{s_2}t/\hbar}\langle S_{i_1}|T_-^{A_1}T^{A_2}\left\{\int_0^t dt''\,\beta_{t'',t}\,A_1(t'')\,e^{W_1+W_2}\right\}|S_{i_2}\rangle e^{iH_{s_1}t/\hbar} \qquad \text{IV-17}$$

and

$$\hat{F}_2 = e^{-iH_{s_1}t/\hbar}\langle S_{i_1}|T_-^{A_1}T^{A_2}\left\{\int_0^t dt''\,\beta_{t,t''}\,A_2(t'')\,e^{W_1+W_2}\right\}|S_{i_2}\rangle e^{iH_{s_2}t/\hbar} \qquad \text{IV-18}$$

We can then express equation (IV-13) in the compact form

$$\frac{d}{dt}\rho_s(t) = -\frac{i}{\hbar}[H_s,\rho_s(t)] - \frac{i}{\hbar}\langle B\rangle[A,\rho_s(t)] \qquad \text{IV-19}$$

$$-\frac{1}{\hbar^2}\hat{F}_1A_1 - \frac{1}{\hbar^2}A_2\hat{F}_2 + \frac{1}{\hbar^2}A_2\hat{F}_1 + \frac{1}{\hbar^2}\hat{F}_2A_1$$

$$= -\frac{i}{\hbar}[H_s,\rho_s(t)] - \frac{i}{\hbar}\langle B\rangle[A,\rho_s(t)] + \frac{1}{\hbar^2}[A,\hat{F}_1-\hat{F}_2]$$

where we have again dropped subscripts on the Schrödinger operator A.

Equation (IV-19) is as far as we can go in the exact treatment. The operator quantity $\hat{F}_1$-$\hat{F}_2$ is extremely complicated and we examine it with more care farther on (see Chapter VI). For now, we argue as follows: As before, we suppose that $B_{t,t''}$ represents a reservoir whose relaxation time, t_c, is much shorter than the inverse of any natural frequency of the system. We then assume that A(t") changes so little from its value at t in the interval $t \geqq t'' \geqq t-t_c$ that, with negligible error, we can make the approximations[20]

$$\hat{F}_1 \cong e^{-iH_{s_2}t/\hbar} \langle S_{i_1} | T_-^{A_1} T^{A_2} e^{W_1+W_2} | S_{i_2} \rangle e^{iH_{s_1}t/\hbar} \times \int_0^t dt'' \beta_{t'',t} A(t''-t) \qquad \text{IV-20}$$

$$\cong \rho_s(t) \int_0^t dt'' \beta_{t'',t} A(t''-t)$$

and

$$\hat{F}_2 \cong \int_0^t dt'' \beta_{t,t''} A(t''-t) \rho_s(t) \qquad \text{IV-21}$$

In this approximation, the equation of motion for $\rho_s(t)$ becomes

$$\frac{d}{dt}\rho_s(t) = -\frac{i}{\hbar}[H_s, \rho_s(t)] - \frac{i}{\hbar}\langle B \rangle [A, \rho_s(t)] + \frac{1}{\hbar^2}\left[A, \rho_s(t)\int_0^t dt'' \beta_{t'',t} A(t''-t)\right] - \frac{1}{\hbar^2}\left[A, \int_0^t dt'' \beta_{t,t''} A(t''-t) \rho_s(t)\right] \qquad \text{IV-22}$$

Summary

In this chapter, we have introduced a cumulant expansion for $\rho_s(t)$. The equation of motion, equation (IV-19), is still exact if the reservoir is made of non-interacting bosons. Equation (IV-22) is our first attempt to make an approximation based on the shortness of the reservoir relaxation time. This procedure is to be investigated more fully in Chapter VI but first we shall apply this first approximation to an example, an harmonic oscillator interacting with a reservoir. This problem has been approached by many others and we would like to see if our method produces sensible results.

CHAPTER V

APPLICATIONS

Introduction

As a demonstration of the usefulness of the theory developed in the preceding chapters, we investigate the case of a quantum harmonic oscillator interacting with another system designated as the reservoir. We then treat the slightly more complicated case of an oscillator interacting with a reservoir while being subjected to a classical driving force.

The Damped Harmonic Oscillator

We apply the results of Chapter IV to the case of a quantum harmonic oscillator interacting with an unspecified reservoir. The interaction term of the Hamiltonian is taken to have the form

$$V = q\cdot B$$

where q is the position coordinate of the oscillator and B is some function of reservoir variables.

For convenience, we begin by summarizing some of the known properties of the free oscillator.[21] The evolution of the free oscillator is determined by the system Hamiltonian

$$H_s = \frac{1}{2m} P^2 + \frac{m\omega_o^2}{2} q^2 \qquad \text{V-1}$$

$$= \hbar\omega_o \left(a^+ a + \tfrac{1}{2}\right)$$

where the operators p and q correspond to the oscillator's momentum and position, respectively. The oscillator's mass and frequency are denoted by m and ω_o. The non-hermitian operators a and a^+ are related to q and p by

$$a = \left(\frac{m\omega_o}{2\hbar}\right)^{1/2} \left(q + \frac{i}{m\omega_o} p\right) \qquad \text{V-2}$$

and

$$a^+ = \left(\frac{m\omega_o}{2\hbar}\right)^{1/2} \left(q - \frac{i}{m\omega_o} p\right) \qquad \text{V-3}$$

The commutation rule

$$-\frac{i}{\hbar}[q, p] = 1 \qquad \text{V-4}$$

and equations (V-2) and (V-3) lead directly to

$$[a, a^+] = 1 \qquad \text{V-5}$$

By taking the product a^+a, we form the useful hermitian operator known as the number operator. We denote the eigenvectors of a^+a as $|n>$ where

$$a^+a|n\rangle = n|n\rangle, \quad n = 0, 1, \cdots \qquad \text{V-6}$$

$$\langle n|n'\rangle = \delta_{n,n'} \qquad \text{V-7}$$

and

$$\sum_{n=0}^{\infty} |n\rangle\langle n| = 1 \qquad \text{V-8}$$

Equations (V-1), (V-5), (V-6), and (V-7) are all that one needs to demonstrate the following:

$$H_s|n\rangle = \hbar\omega_0 (n + \tfrac{1}{2}) |n\rangle \qquad \text{V-9}$$

$$a^+|n\rangle = (n+1)^{1/2} |n+1\rangle \qquad \text{V-10}$$

and

$$a|n\rangle = (n)^{1/2} |n-1\rangle \qquad \text{V-11}$$

How do we characterize the dynamical history of the oscillator in contact with a reservoir? There are various ways of course, but the expectation values at time t of the operators $\hat{n} = a^+a$ and q, denoted by $< n(t) >_s$ and $< q(t) >_s$, respectively, seem particularly revealing. In the process of finding solutions to the equations of motion for these quantities, we will discover the equilibrium distribution of oscillator energy eigenstates, the shift in the frequency of the free oscillator due to the reservoir and the rate at which the system approaches equilibrium.

As a preliminary to the above program, let us use the perturbation theory and our intuition to obtain an idea of the correct oscillator behavior.

Suppose $P_n(t)$ is the probability that, at time t, the oscillator is in the nth unperturbed oscillator state and that $W_{n,n'}^{E_k,E_j}$ is the rate at which the oscillator makes a transition from the n'th oscillator state to the nth state while, simultaneously, the reservoir makes a transition from a state with energy E_j to a state with energy E_k. We assume that $P_n(t)$ obeys the Pauli master equation,[4]

$$\frac{d P_n(t)}{dt} = - P_n(t) Z^{-1} \sum_{n'} \int dE_k \int dE_j \, e^{-\theta E_j} g(E_k) g(E_j) W_{n',n}^{E_k,E_j} \qquad \text{V-12}$$

$$+ Z^{-1} \sum_{n'} \int dE_k \int dE_j \, e^{-\theta E_j} g(E_k) g(E_j) W_{n,n'}^{E_k,E_j} P_{n'}(t)$$

where $g(E_j)$ is the reservoir density of states function. That is, $dE_j g(E_j)$ is the number of reservoir states with energy between E_j and E_j+dE_j. We have averaged over initial reservoir states and summed over final reservoir states because we are only interested in the change in occupation of system states. The reservoir is assumed to be distributed over its energy states according to the weighting function $Z^{-1} e^{-\theta E_j}$ where Z is the reservoir partition function and $\theta = \frac{1}{kT}$, and T is the temperature. Despite its complicated form, equation (V-12) has a reasonable interpretation. $P_n(t)$ decreases due to transitions out of the nth oscillation state to any other oscillator state. If the nth oscillator state is certainly occupied, the rate at which transitions are made from the nth to, say, the n'th state is given by

$$Z^{-1} \int dE_k \int dE_j \, e^{-\theta E_j} g(E_k) g(E_j) W_{n',n}^{E_k,E_j}$$

As mentioned above, we are not interested in the final reservoir state, hence we integrate over E_k. We average over initial reservoir states. The rate at which transitions are made to any oscillator state is obtained by summing over n'. But this is the rate of transitions out of the n^{th} state when it is certainly occupied; to obtain the general result we multiply by $P_n(t)$ and obtain the first term of equation (V-12); the rate at which $P_n(t)$ decreases. The second term, the rate at which $P_n(t)$ increases is found by a similar argument.

We approximate $W_{n,n'}^{E_k,E_j}$ by Fermi's golden rule,[22]

$$W_{n,n'}^{E_k,E_j} = \frac{2\pi}{\hbar}\,\delta(E_j - E_k + \hbar\omega_0(n'-n))\,|\langle n|\langle E_k|q\cdot B|E_j\rangle|n'\rangle|^2$$

$$= \frac{2\pi}{\hbar}\,\delta(E_j - E_k + \hbar\omega_0(n'-n))\,|\langle n|q|n'\rangle|^2\,|\langle E_k|B|E_j\rangle|^2$$

By using equations (V-2), (V-3), (V-7), (V-10), and (V-11), it is easy to verify that

$$|\langle n|q|n'\rangle|^2 = \left(\frac{\hbar}{2m\omega_0}\right)\left[(n'+1)\,\delta_{n,n'+1} + n'\,\delta_{n,n'-1}\right]$$

Thus

$$W_{n,n'}^{E_k,E_j} = \frac{\pi}{\hbar}\left(\frac{\hbar}{m\omega_0}\right)\left[(n'+1)\,\delta_{n,n'+1} + n'\,\delta_{n,n'-1}\right] \qquad \text{V-13}$$

$$\times\,\delta(E_j - E_k + \hbar\omega_0(n'-n))\,|\langle E_k|B|E_j\rangle|^2$$

Substituting equation (V-13) into (V-12), summing over n' and integrating over E_k, we find

$$\frac{dP_n(t)}{dt} = -\frac{\pi}{\hbar}\left(\frac{\hbar}{m\omega_0}\right) P_n(t) \int dE_j \Big\{ Z^{-1} e^{-\theta E_j} g(E_j) \tag{V-14}$$

$$\times \left[g(E_j - \hbar\omega_0)(n+1) |\langle E_j - \hbar\omega_0 | B | E_j \rangle|^2 + g(E_j + \hbar\omega_0) n |\langle E_j + \hbar\omega_0 | B | E_j \rangle|^2 \right] \Big\}$$

$$+ \frac{\pi}{\hbar}\left(\frac{\hbar}{m\omega_0}\right) P_{n+1}(t) \int dE_j\, Z^{-1} e^{-\theta E_j} g(E_j)$$

$$\times \left[g(E_j + \hbar\omega_0)(n+1) |\langle E_j + \hbar\omega_0 | B | E_j \rangle|^2 \right]$$

$$+ \frac{\pi}{\hbar}\left(\frac{\hbar}{m\omega_0}\right) P_{n-1}(t) \int dE_j\, Z^{-1} e^{-\theta E_j} g(E_j)$$

$$\times \left[g(E_j - \hbar\omega_0)\, n\, |\langle E_j - \hbar\omega_0 | B | E_j \rangle|^2 \right]$$

We obtain an equation for $\frac{d < n(t) >_s}{dt}$ by multiplying both sides of equation (V-14) by, and then summing over, n:

$$\frac{d\langle n(t)\rangle_s}{dt} = -\frac{\pi}{\hbar}\left(\frac{\hbar}{m\omega_0}\right) Z^{-1} \int dE_j\, e^{-\theta E_j} g(E_j) \tag{V-15}$$

$$\times \left[g(E_j + \hbar\omega_0) |\langle E_j + \hbar\omega_0 | B | E_j \rangle|^2 \right.$$

$$\left. - g(E_j - \hbar\omega_0) |\langle E_j - \hbar\omega_0 | B | E_j \rangle|^2 \right] \langle n(t)\rangle_s$$

(continued)

$$+\frac{\pi}{\hbar}\left(\frac{\hbar}{m\omega_0}\right) Z^{-1}\int dE_j\, e^{-\theta E_j} g(E_j)$$

$$\times\left[g(E_j-\hbar\omega_0)\,|\langle E_j-\hbar\omega_0|B|E_j\rangle|^2\right]$$

By making the change of variable $E_j \to E_j - \frac{\hbar\omega_o}{2}$, we can write

$$\frac{\pi}{\hbar} Z^{-1}\int dE_j\, e^{-\theta E_j} g(E_j) g(E_j+\hbar\omega_0)\,|\langle E_j+\hbar\omega_0|B|E_j\rangle|^2 \qquad \text{V-16}$$

$$= e^{\frac{\theta\hbar\omega_0}{2}}\, I(\omega_0)$$

where

$$I(\omega_0) = \frac{\pi}{\hbar} Z^{-1}\int dE_j\, e^{-\theta E_j} g\left(E_j+\frac{\hbar\omega_0}{2}\right) g\left(E_j-\frac{\hbar\omega_0}{2}\right) \qquad \text{V-17}$$

$$\times\left|\left\langle E_j+\frac{\hbar\omega_0}{2}\right|B\left|E_j-\frac{\hbar\omega_0}{2}\right\rangle\right|^2$$

(Note that $I(\omega_o)$ is an even function of ω_o.) In the same way, letting $E_j \to E_j + \frac{\hbar\omega_o}{2}$,

$$\frac{\pi}{\hbar} Z^{-1}\int dE_j\, e^{-\theta E_j} g(E_j) g(E_j-\hbar\omega_0)\,|\langle E_j-\hbar\omega_0|B|E_j\rangle|^2 \qquad \text{V-18}$$

$$= e^{-\frac{\theta\hbar\omega_0}{2}}\, I(\omega_0)$$

Using equations (V-17) and (V-18) in equation (V-15), we obtain

$$\frac{d\langle n(t)\rangle}{dt} = -2\left(\frac{\hbar}{m\omega_0}\right) I(\omega_0) \sinh\frac{\theta\hbar\omega_0}{2} \langle n(t)\rangle_s + \frac{\hbar}{m\omega_0} I(\omega_0)\, e^{-\frac{\theta\hbar\omega_0}{2}} \qquad \text{V-19}$$

We have found that first order perturbation theory and the Pauli master equation lead us to expect that $< n(t) >_s$ exponentially decays from its initial value at t=0 and asymptotically converges to the equilibrium value

$$\lim_{t\to\infty} \langle n(t)\rangle_s = \frac{1}{2}\frac{e^{-\frac{\theta\hbar\omega_0}{2}}}{\sinh\frac{\theta\hbar\omega_0}{2}} = \frac{1}{e^{\theta\hbar\omega_0}-1} \qquad \text{V-20}$$

at a rate determined by $\frac{2\hbar}{m\omega_0} I(\omega_0) \sinh\frac{\theta\hbar\omega_0}{2}$.

We also expect that the frequency of the oscillator will be shifted from its unperturbed value by the interaction. In that case, the oscillator will experience a restoring force proportional to $-\omega^2 q$ where

$$\omega = \omega_0 + \delta\omega \qquad \text{V-21}$$

and $\delta\omega$ is the shift in frequency. Then, keeping only terms linear in $\delta\omega$,

$$\omega^2 = \omega_0^2 + 2\omega_0\delta\omega \qquad \text{V-22}$$

For a free oscillator, $\hbar\omega_0$ is the separation of adjacent energy levels, $\epsilon_n - \epsilon_{n-1}$ or $\epsilon_{n+1} - \epsilon_n$. We will estimate $\delta\omega$ by calculating the second order shifts (first order corrections vanish) in the differences $\varepsilon_n - \varepsilon_{n-1}$ and $\varepsilon_{n+1} - \varepsilon_n$, averaging them, and then dividing by $\hbar$. That is,

$$\delta\omega_n = \frac{1}{2\hbar}\left(\delta\varepsilon_{n+1}^{(2)} - \delta\varepsilon_n^{(2)} + \delta\varepsilon_n^{(2)} - \delta\varepsilon_{n-1}^{(2)}\right) \qquad \text{V-23}$$

$$= \frac{1}{2\hbar}\left(\delta\varepsilon_{n+1}^{(2)} - \delta\varepsilon_{n-1}^{(2)}\right)$$

where from perturbation theory,[22]

$$\delta\varepsilon_{n'}^{(2)} = \mathcal{P}\sum_{n''}\int dE_i \int dE_j\, Z^{-1} e^{-\theta E_i} g(E_i) g(E_j) \times \frac{|\langle E_i|B|E_j\rangle|^2\, |\langle n'|q|n''\rangle|^2}{(n'-n'')\hbar\omega_0 + E_i - E_j}$$

Once again, we have averaged over reservoir states E_i since we are calculating the shift in the n'^{th} oscillator state while the reservoir is distributed canonically. The symbol $\mathcal{P}$ denotes that the principal value of the integrals is to be taken.

As before,

$$|\langle n'|q|n''\rangle|^2 = \left(\frac{\hbar}{2m\omega_0}\right)\left((n'+1)\,\delta_{n'+1,n''} + n'\,\delta_{n'-1,n''}\right) \qquad \text{V-24}$$

Consequently,

$$\delta\varepsilon_{n'}^{(2)} = \left(\frac{\hbar}{2m\omega_0}\right)\mathcal{P}\int dE_i\int dE_j\, Z^{-1} e^{-\theta E_i} g(E_i) g(E_j) \qquad \text{V-25}$$

$$\times\left[\frac{(n'+1)\,|\langle E_i|B|E_j\rangle|^2}{E_i - E_j - \hbar\omega_0} + \frac{n'\,|\langle E_i|B|E_j\rangle|^2}{E_i - E_j + \hbar\omega_0}\right]$$

Equations (V-23) and (V-25), lead us to

$$\delta\omega_n = \frac{1}{2\hbar}\left(\delta\mathcal{E}^{(2)}_{n+1} - \delta\mathcal{E}^{(2)}_{n-1}\right) \qquad \text{V-26}$$

$$= \left(\frac{\hbar}{2m\omega_0}\right) \mathcal{P}\int dE_i \int dE_j\, e^{-\theta E_i} g(E_i) g(E_j) Z^{-1}$$

$$\times\left[\frac{|\langle E_i|B|E_j\rangle|^2}{E_i - E_j - \hbar\omega_0} + \frac{|\langle E_i|B|E_j\rangle|^2}{E_i - E_j + \hbar\omega_0}\right]$$

Then by equations (V-22) and (V-26), the harmonic restoring force to second order is proportional to

$$-\left(\omega_0^2 + \frac{1}{m}\mathcal{P}\int dE_i dE_j\, Z^{-1} e^{-\theta E_i} g(E_i) g(E_j)\right. \qquad \text{V-27}$$

$$\left.\times\left[\frac{|\langle E_i|B|E_j\rangle|^2}{E_i - E_j - \hbar\omega_0} + \frac{|\langle E_i|B|E_j\rangle|^2}{E_i - E_j + \hbar\omega_0}\right]\right)$$

Equations (V-19) and (V-27) must be approximately correct; therefore, the results of our more careful treatment should reduce to them in the proper limit.

With these results in mind, we turn our attention back to equation (IV-22)

$$\frac{d}{dt}\rho_s(t) = -\frac{i}{\hbar}\left[H_s, \rho_s(t)\right] - \frac{i}{\hbar}\langle B\rangle\left[q, \rho_s(t)\right] \qquad \text{V-28}$$

$$+\frac{1}{\hbar^2}\left[q, \rho_s(t)\int_0^t dt''\, \beta_{t'',t}\, q(t''-t)\right]$$

$$-\frac{1}{\hbar^2}\left[q, \int_0^t dt''\, \beta_{t,t''}\, q(t''-t)\, \rho_s(t)\right]$$

where q has been substituted for A. With no loss of generality, we can assume that $< B > = 0$ since, in any case, we may write the interaction part of the Hamiltonian as $q\cdot(B - < B >)$; the total Hamiltonian would remain the same if the system Hamiltonian is redefined as $H_s + < B >_q$. The effect of all this is merely to shift the origin of the oscillator coordinates in phase space.

By defining the operators

$$Q_1(t) = \int_0^t dt'' \beta_{t'',t}\, q(t''-t) \qquad \text{V-29}$$

and

$$Q_2(t) = \int_0^t dt'' \beta_{t,t''}\, q(t''-t) \qquad \text{V-30}$$

equation (V-28) reduces to

$$\frac{d}{dt}\rho_s(t) = -\frac{i}{\hbar}[H_s, \rho_s(t)] + \frac{1}{\hbar^2}[q, \rho_s(t) Q_1(t)] - \frac{1}{\hbar^2}[q, Q_2(t)\rho_s(t)] \qquad \text{V-31}$$

We now demonstrate that, as a consequence of our assumption, the reservoir relaxation time, t_c, is very much less than ω_o^{-1}, the quantities Q_1 and Q_2 are time independent for t very much greater than ω_o^{-1}. Actually, since

$$Q_2 = Q_1^+ \qquad \text{V-32}$$

it is sufficient to treat Q_1 alone.

We recall that the operator q(t"-t) appearing in equation (V-29) is in the interaction picture. Hence, by equations (V-2) and (V-3),

$$q(t''-t) = \left(\frac{\hbar}{2m\omega_0}\right)^{1/2} \left(a(t''-t) + a^+(t''-t) \right) \qquad \text{V-33}$$

$$= \left(\frac{\hbar}{2m\omega_0}\right)^{1/2} \left(a\, e^{-i\omega_0(t''-t)} + a^+ e^{i\omega_0(t''-t)} \right)$$

where a and a^+ are now in the Schrödinger picture.

The other quantity in the integrand of equation (V-29), $B_{t'',t}$, is defined by equations (IV-5), (IV-11), and (IV-12) with < B > set to zero. Hence,

$$\beta_{t'',t} = \langle B(t'')\, B(t) \rangle \qquad \text{V-34}$$

$$= Z^{-1} \int dE_j\, e^{-\theta E_j}\, g(E_j) \langle E_j | B(t'') B(t) | E_j \rangle$$

By inserting a factor of unity in the form

$$\int dE_k\, g(E_k)\, |E_k\rangle\langle E_k| = 1$$

and using the relations

$$B(t) = e^{iH_r t/\hbar}\, B\, e^{-iH_r t/\hbar}$$

and

$$e^{-iH_r t/\hbar}|E_K\rangle = e^{iE_K t/\hbar}|E_K\rangle$$

we can write

$$\beta_{t'',t} = Z^{-1}\int dE_j \int dE_K\, e^{-\theta E_j} g(E_j)\, g(E_K) \qquad \text{V-35}$$
$$\times |\langle E_j|B|E_K\rangle|^2\, e^{i(E_j - E_K)(t''-t)/\hbar}$$

We define the Fourier transform of $\beta_{t'',t}$ by

$$\beta_{t'',t} = \frac{1}{2\pi}\int_{-\infty}^{\infty} d\omega\, e^{-i\omega(t''-t)}\beta(\omega) \qquad \text{V-36}$$

Then

$$\beta(\omega) = \int_{-\infty}^{\infty} d(t''-t)\, e^{i\omega(t''-t)}\beta_{t'',t} \qquad \text{V-37}$$

Equations (V-35) and (V-37) combine to produce the result

$$\beta(\omega) = 2\pi\, Z^{-1}\int dE_j\, e^{-\theta E_j} g(E_j) g(E_j+\hbar\omega)|\langle E_j|B|E_j+\hbar\omega\rangle|^2 \qquad \text{V-38}$$
$$= 2\, e^{\frac{\theta\hbar\omega}{2}}\, I(\omega)$$

where equations (V-16) and (V-17) and the identity

$$2\pi\delta(E_j - E_K + \hbar\omega) = \int_{-\infty}^{\infty} d(t''-t)\; e^{i(E_j - E_K + \hbar\omega)(t''-t)/\hbar}$$

have been used.

Inserting the Fourier expansion of $\beta_{t'',t}$ into the expression for $Q_1(t)$, we have

$$Q_1(t) = \frac{1}{2\hbar}\left(\frac{\hbar}{2m\omega_0}\right)^{1/2} \times \int_0^t dt'' \int_{-\infty}^{\infty} d\omega\; e^{-i\omega(t''-t)}\beta(\omega)\left(a e^{-i\omega_0(t''-t)} + a^{+} e^{i\omega_0(t''-t)}\right) \qquad \text{V-39}$$

Interchanging the order of integration,

$$Q_1(t) = \frac{1}{2\hbar}\left(\frac{\hbar}{2m\omega_0}\right)^{1/2} \int_{-\infty}^{\infty} d\omega\, \beta(\omega)\left[a \int_0^t e^{i(\omega+\omega_0)t'} dt' + a^{+} \int_0^t e^{-i(\omega-\omega_0)t'} dt'\right] \qquad \text{V-40}$$

where we have substituted t' for t-t". The time integration is elementary,

$$Q_1(t) = \frac{1}{2\pi}\left(\frac{\hbar}{2m\omega_0}\right)^{1/2} \int_{-\infty}^{\infty} d\omega\, \beta(\omega)\left[a \frac{e^{i(\omega+\omega_0)t} - 1}{i(\omega+\omega_0)} + a^{+} \frac{e^{i(\omega-\omega_0)t} - 1}{i(\omega-\omega_0)}\right] \qquad \text{V-41}$$

If the reservoir relaxation time is t_c, it is well known that the transform, $\beta(\omega)$, of the correlation function, $\beta_{t'',t}$, has a bandwidth, Δ_ω, proportional to t_c^{-1}.[23] Since $t_c^{-1} \gg \omega_o$ by hypothesis, then $\Delta_\omega \gg \omega_o$. Consider the integral

$$M = -\int_{-\infty}^{\infty} d\omega\, \beta(\omega)\, \frac{1 - e^{i(\omega-\omega_o)t}}{i(\omega-\omega_o)}$$

$$= \int_{-\infty}^{\infty} d\omega\, \beta(\omega)\, \frac{\sin(\omega-\omega_o)t}{\omega-\omega_o} + i \int_{-\infty}^{\infty} d\omega\, \beta(\omega)\, \frac{1-\cos(\omega-\omega_o)t}{\omega-\omega_o}$$

On the right, let $\omega' = \omega - \omega_o$. Then,

$$M = \int_{-\infty}^{\infty} d\omega'\, \beta(\omega'+\omega_o)\, \frac{\sin\omega' t}{\omega'} + i \int_{-\infty}^{\infty} d\omega'\, \beta(\omega'+\omega_o)\, \frac{1-\cos\omega' t}{\omega'} \qquad \text{V-42}$$

$$= \int_{-\infty}^{-\xi} d\omega'\, \frac{\beta(\omega'+\omega_o)}{\omega'} \sin\omega' t + i \int_{-\infty}^{-\xi} d\omega'\, \frac{\beta(\omega'+\omega_o)}{\omega'} (1-\cos\omega' t)$$

$$+ \int_{-\xi}^{\xi} d\omega'\, \frac{\beta(\omega'+\omega_o)}{\omega'} \sin\omega' t + i \int_{-\xi}^{\xi} d\omega'\, \frac{\beta(\omega'+\omega_o)}{\omega'} (1-\cos\omega' t)$$

$$+ \int_{\xi}^{\infty} d\omega'\, \frac{\beta(\omega'+\omega_o)}{\omega'} \sin\omega' t + i \int_{\xi}^{\infty} d\omega'\, \frac{\beta(\omega'+\omega_o)}{\omega'} (1-\cos\omega' t)$$

This last expression is correct for arbitrary ξ, of course, but we choose ξ such that $\beta(\omega'+\omega_o)$ does not change appreciably (that is, $\beta(\omega'+\omega_o)$ does not differ from $\beta(\omega_o)$ by more than a predetermined fraction of $\beta(\omega_o)$) in the interval $-\xi \leq \omega' \leq \xi$. ξ may be as large as ω_o since our discussion of the reservoir bandwidth guarantees that ω_o is well within that frequency interval. In any case, we may approximate M as follows:

$$M \cong \int_{-\infty}^{-\xi} d\omega' \frac{\beta(\omega'+\omega_0)}{\omega'} \sin\omega' t + i \int_{-\infty}^{-\xi} d\omega' \frac{\beta(\omega'+\omega_0)}{\omega'} (1-\cos\omega' t) \qquad \text{V-43}$$

$$+ \beta(\omega_0)\left[\int_{-\xi}^{\xi} d\omega' \frac{\sin\omega' t}{\omega'} + i \int_{-\xi}^{\xi} d\omega' \frac{1-\cos\omega' t}{\omega'} \right]$$

$$+ \int_{\xi}^{\infty} d\omega' \frac{\beta(\omega'+\omega_0)}{\omega'} \sin\omega' t + i \int_{\xi}^{\infty} d\omega' \frac{\beta(\omega'+\omega_0)}{\omega'} (1-\cos\omega' t)$$

Riemann's theorem from advanced calculus states[24]: If $F(x)$ is sectionally continuous in (α,β), then

$$\lim_{t\to\infty} \int_{\alpha}^{\beta} dx\, F(x) \begin{Bmatrix} \sin tx \\ \cos tx \end{Bmatrix} = 0$$

If we assume that $\beta'(\omega'+\omega_0)$ is sectionally continuous in the intervals $(-\infty,-\xi)$ and (ξ,∞), it is reasonable to apply the theorem to the first and third lines on the right hand side of equation (V-43) if we require that $t \gg \frac{2\pi}{\xi}$. Further,

$$\int_{-\xi}^{\xi} d\omega' \frac{(1-\cos\omega' t)}{\omega'} = 0$$

since the integrand is an odd function of ω'. Hence,

$$M \cong \beta(\omega_0) \int_{-\xi}^{\xi} d\omega' \frac{\sin\omega' t}{\omega'} + i \left[\int_{-\infty}^{-\xi} d\omega' \frac{\beta(\omega'+\omega_0)}{\omega'} + \int_{\xi}^{\infty} d\omega' \frac{\beta(\omega'+\omega_0)}{\omega'} \right]$$

By assumption $\xi t >> 2\pi$, so with small error we can replace

$$\int_{-\xi}^{\xi} d\omega' \frac{\sin \omega' t}{\omega'} = \int_{-\xi t}^{\xi t} dx \frac{\sin x}{x}$$

by

$$\int_{-\infty}^{\infty} dx \frac{\sin x}{x} = \pi$$

If we take the limit $\xi \to 0$ (keeping the product $\xi t >> 2\pi$), the quantity in brackets is identical to the principal value of the integral.[25] Therefore

$$M \cong \pi \beta(\omega_0) + i \mathcal{P}\int_{-\infty}^{\infty} d\omega \frac{\beta(\omega_0 + \omega)}{\omega} \qquad \text{V-44}$$

This result could have been obtained directly from equation (V-40) by using the sumbolic identity[26]

$$\lim_{t \to \infty} \int_0^t dt' \, e^{i(\omega - \omega_0)t'} = \pi \delta(\omega - \omega_0) + i \mathcal{P} \frac{1}{\omega - \omega_0} \qquad \text{V-45}$$

Instead of repeating the steps leading to equation (V-44), we therefore write

$$\lim_{t \to \infty} \int_0^t dt' \, e^{i(\omega + \omega_0)t'} = \pi \delta(\omega + \omega_0) + i \mathcal{P} \frac{1}{\omega + \omega_0} \qquad \text{V-46}$$

and it follows from equations (V-45) and (V-46) that

$$Q_1 = \frac{1}{2\pi}\left(\frac{\hbar}{2m\omega_0}\right)^{1/2}\left[a\left(\pi\beta(-\omega_0) + i\,P\int_{-\infty}^{\infty} d\omega' \frac{\beta(\omega'-\omega_0)}{\omega'}\right) + a^{+}\left(\pi\beta(\omega_0) + i\,P\int_{-\infty}^{\infty} d\omega' \frac{\beta(\omega'+\omega_0)}{\omega'}\right)\right] \qquad \text{V-47}$$

Then by equation (V-32),

$$Q_2 = \frac{1}{2\pi}\left(\frac{\hbar}{2m\omega_0}\right)^{1/2}\left[a\left(\pi\beta(\omega_0) - i\,P\int_{-\infty}^{\infty} d\omega' \frac{\beta(\omega'+\omega_0)}{\omega'}\right) + a^{+}\left(\pi\beta(-\omega_0) - i\,P\int_{-\infty}^{\infty} d\omega' \frac{\beta(\omega'-\omega_0)}{\omega'}\right)\right] \qquad \text{V-48}$$

If we use equation (V-38) to replace $\beta(\omega)$ by $2e^{\frac{\theta\hbar\omega}{2}} I(\omega)$, we can show that

$$\pi\beta(-\omega_0) + i\,P\int_{-\infty}^{\infty} d\omega' \frac{\beta(\omega'-\omega_0)}{\omega'} = 2\pi\, e^{-\frac{\theta\hbar\omega_0}{2}}\left[I(\omega_0) + \frac{i}{\pi} P\int_{-\infty}^{\infty} d\omega' \frac{e^{\frac{\theta\hbar\omega'}{2}} I(\omega'-\omega_0)}{\omega'}\right]$$

where we have used the fact that $I(\omega)$ is an even function of ω. In the same way,

$$\pi\beta(\omega_0) + i\,P\int_{-\infty}^{\infty} d\omega' \frac{\beta(\omega'+\omega_0)}{\omega'} = 2\pi\, e^{\frac{\theta\hbar\omega_0}{2}}\left[I(\omega_0) + \frac{i}{\pi} P\int_{-\infty}^{\infty} d\omega' \frac{e^{\frac{\theta\hbar\omega'}{2}} I(\omega'+\omega_0)}{\omega'}\right]$$

Hence

$$Q_1 = \left(\frac{\hbar}{2m\omega_0}\right)^{1/2} \left[a\, e^{-\frac{\theta\hbar\omega_0}{2}} \left(I(\omega_0) + \frac{i}{\pi} P \int_{-\infty}^{\infty} d\omega' \frac{e^{\frac{\theta\hbar\omega'}{2}} I(\omega_0 - \omega')}{\omega'} \right) \right. \qquad \text{V-49}$$

$$\left. + a^{+} e^{\frac{\theta\hbar\omega_0}{2}} \left(I(\omega_0) + \frac{i}{\pi} P \int_{-\infty}^{\infty} d\omega' \frac{e^{\frac{\theta\hbar\omega'}{2}} I(\omega_0 + \omega')}{\omega'} \right) \right]$$

and

$$Q_2 = \left(\frac{\hbar}{2m\omega_0}\right)^{1/2} \left[a\, e^{\frac{\theta\hbar\omega_0}{2}} \left(I(\omega_0) - \frac{i}{\pi} P \int_{-\infty}^{\infty} d\omega' \frac{e^{\frac{\theta\hbar\omega'}{2}} I(\omega_0 + \omega')}{\omega'} \right) \right. \qquad \text{V-50}$$

$$\left. + a^{+} e^{-\frac{\theta\hbar\omega_0}{2}} \left(I(\omega_0) - \frac{i}{\pi} P \int_{-\infty}^{\infty} d\omega' \frac{e^{\frac{\theta\hbar\omega'}{2}} I(\omega_0 - \omega')}{\omega'} \right) \right]$$

Equations (V-31), (V-49), and (V-50) are all we need to calculate $< n(t) >_s$ and $< q(t) >_s$. The expectation value at time t of any function of oscillator operators is given by

$$\langle O_s(t) \rangle = tr_s\left(O_s\, \rho_s(t) \right) \qquad \text{V-51}$$

where O_s is in the Schrödinger picture. Then,

$$\frac{d}{dt} \langle O_s(t) \rangle = tr_s\left(O_s \frac{d\rho_s(t)}{dt} \right)$$

Using equation (V-3) for $\frac{d\rho_s(t)}{dt}$,

$$\frac{d\langle O_s(t)\rangle}{dt} = -\,tr_s\left(O_s\,[H_s, \rho_s(t)]\right) \qquad \text{V-52}$$

$$-\,tr_s\left(O_s\,[q, \{Q_1\,\rho_s(t) - \rho_s(t)\,Q_2\}]\right)$$

By using the identity

$$tr\ AB = tr\ BA,$$

it is easy to demonstrate that

$$tr(\hat{O}[A,B]) = tr([\hat{O},A]B). \qquad \text{V-53}$$

Hence,

$$\frac{d\langle O_s(t)\rangle}{dt} = -\frac{i}{\hbar}\,tr_s\left([O_s, H_s]\,\rho_s(t)\right) \qquad \text{V-54}$$

$$-\frac{1}{\hbar^2}\,tr_s\left([O_s, q]\{Q_1\rho_s(t) - \rho_s(t)Q_2\}\right)$$

We will now use this formula to obtain the equation of motion for $< q(t) >_s$, the average position coordinate of the oscillator. Putting q in place of O_s in equation (V-54) and using

$$[q, H_s] = \frac{i\hbar}{m}\,p$$

and

$$[q, q] = 0$$

we obtain

$$\frac{d\langle q(t)\rangle}{dt} = \frac{1}{m}\,tr_s\left(p\rho_s(t)\right) = \frac{1}{m}\langle p(t)\rangle \qquad \text{V-55}$$

Repeating this operation with p substituted for O_s in equation (V-54), we find

$$\frac{d\langle P(t)\rangle}{dt} = -m\omega_o^2 \, tr_s(q_b\rho_s(t)) + \frac{i}{\hbar} tr_s((Q_1-Q_2)\rho_s(t)) \qquad \text{V-56}$$

It follows from equations (V-49) and (V-50) that

$$Q_1 - Q_2 = \left(\frac{\hbar}{2m\omega_o}\right)^{1/2} I(\omega_o)\left(e^{\frac{\theta\hbar\omega_o}{2}} - e^{-\frac{\theta\hbar\omega_o}{2}}\right)(a-a^+) \qquad \text{V-57}$$

$$+ \frac{i}{\pi}\left(\frac{\hbar}{2m\omega_o}\right)^{1/2}\left[P\int_{-\infty}^{\infty} d\omega' \frac{e^{\frac{\theta\hbar}{2}(\omega_o+\omega')} I(\omega_o+\omega')}{\omega'} + P\int_{-\infty}^{\infty} d\omega' \frac{e^{-\frac{\theta\hbar}{2}(\omega_o-\omega')} I(\omega_o-\omega')}{\omega'}\right]$$

Equation (V-57) can be simplified by combining the two principal part integrals. To this end, we make the change of variables $\omega_o+\omega' = \omega$ in the first integral and $\omega_o-\omega' = \omega$ in the second. Then,

$$P\int_{-\infty}^{\infty} d\omega' \frac{e^{\frac{\theta\hbar}{2}(\omega_o+\omega')} I(\omega_o+\omega')}{\omega'} + P\int_{-\infty}^{\infty} d\omega' \frac{e^{-\frac{\theta\hbar}{2}(\omega_o-\omega')} I(\omega_o-\omega')}{\omega'}$$

$$= P\int_{-\infty}^{\infty} d\omega \frac{\left(e^{\frac{\theta\hbar\omega}{2}} - e^{-\frac{\theta\hbar\omega}{2}}\right) I(\omega)}{\omega-\omega_o}$$

Then substituting $2\mathrm{Sinh}\,\frac{\theta\hbar\omega}{2} = e^{\frac{\theta\hbar\omega}{2}} - e^{\frac{-\theta\hbar\omega}{2}}$, we find

$$Q_1 - Q_2 = 2\left(\frac{\hbar}{2m\omega_0}\right)^{1/2} I(\omega_0)\,\mathrm{Sinh}\,\frac{\theta\hbar\omega_0}{2}\,(a - a^+) \qquad \text{V-58}$$

$$+\ \frac{2i}{\pi}\left(\frac{\hbar}{2m\omega_0}\right)^{1/2} P\int_{-\infty}^{\infty} d\omega\ \frac{I(\omega)\,\mathrm{Sinh}\,\frac{\theta\hbar\omega}{2}}{\omega - \omega_0}\,(a + a^+)$$

But since

$$\left(\frac{\hbar}{2m\omega_0}\right)^{1/2}(a + a^+) = q$$

and

$$\left(\frac{\hbar}{2m\omega_0}\right)^{1/2}(a - a^+) = \frac{i}{m\omega_0}\,p$$

it follows that

$$Q_1 - Q_2 = i\,\frac{2\,I(\omega_0)}{m\omega_0}\,\mathrm{Sinh}\,\frac{\theta\hbar\omega_0}{2}\ \ p \qquad \text{V-59}$$

$$+\ \frac{2i}{\pi}\,P\int_{-\infty}^{\infty} d\omega\ \frac{I(\omega)\,\mathrm{Sinh}\,\frac{\theta\hbar\omega_0}{2}}{\omega - \omega_0}\ q$$

Then,

$$\frac{d\langle p(t)\rangle}{dt} = -m\omega_0^2\,\langle q(t)\rangle - \frac{2\,I(\omega_0)}{m\hbar\omega_0}\,\mathrm{Sinh}\,\frac{\theta\hbar\omega_0}{2}\,\langle p(t)\rangle \qquad \text{V-60}$$

$$-\ \frac{2}{\pi\hbar}\,P\int_{-\infty}^{\infty} d\omega\ \frac{I(\omega)\,\mathrm{Sinh}\,\frac{\theta\hbar\omega}{2}}{\omega - \omega_0}\ \langle q(t)\rangle$$

(continued)

$$= -\frac{2I(\omega_0)}{m\hbar\omega_0} \sinh\frac{\theta\hbar\omega_0}{2} \langle p(t)\rangle$$

$$-\left[m\omega_0^2 + \frac{2}{\pi\hbar} P\int_{-\infty}^{\infty} d\omega \frac{I(\omega)\sinh\frac{\theta\hbar\omega}{2}}{\omega-\omega_0}\right]\langle q(t)\rangle$$

Equations (V-55) and (V-60) combine to produce the desired equation of motion,

$$\frac{d^2\langle q(t)\rangle}{dt} = -\frac{2}{m\hbar\omega_0} I(\omega_0)\sinh\frac{\theta\hbar\omega_0}{2} \frac{d\langle q(t)\rangle}{dt}$$

$$-\left[\omega_0^2 + \frac{2}{\pi m\hbar} P\int_{-\infty}^{\infty} d\omega \frac{I(\omega)\sinh\frac{\theta\hbar\omega}{2}}{\omega-\omega_0}\right]\langle q(t)\rangle \qquad \text{V-61}$$

Equation (V-61) shows that the interaction between the oscillator and reservoir produces a change in the restoring force of the oscillator as well as a velocity dependent damping force. The change in oscillator frequency required to give the second term on the right of equation (V-61) is precisely that predicted by the perturbation method of equation (V-27).

The damping term in equation (V-61) will eventually lead to a condition of equilibrium between the oscillator and reservoir. To determine its properties, we calculate

$$\langle n(t)\rangle = tr_s\left(a^+a\ \rho_s(t)\right) \qquad \text{V-62}$$

Now, the Schrödinger operator a^+a has as eigenstates the unperturbed energy states of the free oscillator Hamiltonian. We expect any shift in the oscillator frequency to complicate matters since any equilibrium distribution of states will involve the renormalized states. Equation (V-61) tells us that it is the principal part contributions to Q_1 and Q_2 that produces this frequency shift. So that our results may be more easily interpreted, we will ignore the principal parts and write instead:

$$Q_1 \cong \left(\frac{\hbar}{2m\omega_0}\right)^{1/2} I(\omega_0)\left(a e^{-\frac{\theta\hbar\omega_0}{2}} + a^+ e^{\frac{\theta\hbar\omega_0}{2}}\right) \qquad \text{V-63}$$

and

$$Q_2 \cong \left(\frac{\hbar}{2m\omega_0}\right)^{1/2} I(\omega_0)\left(a e^{\frac{\theta\hbar\omega_0}{2}} + a^+ e^{-\frac{\theta\hbar\omega_0}{2}}\right) \qquad \text{V-64}$$

With these approximations, we substitute a^+a for $\hat{O}_s$ in equation (V-54) to obtain

$$\begin{aligned}\frac{d\langle n(t)\rangle}{dt} = &-\frac{i}{\hbar}\, tr_s\left([a^+a, H_s]\,\rho_s(t)\right) + \frac{1}{\hbar^2}\left(\frac{\hbar}{2m\omega_0}\right)^{1/2} \\ &\times I(\omega_0)\, tr_s\left\{\left(a e^{-\frac{\theta\hbar\omega_0}{2}} + a^+ e^{\frac{\theta\hbar\omega_0}{2}}\right)[a^+a, q]\,\rho_s(t)\right\} \\ &-\frac{1}{\hbar^2}\left(\frac{\hbar}{2m\omega_0}\right)^{1/2} \\ &\times I(\omega_0)\, tr_s\left\{[a^+a, q]\left(a e^{\frac{\theta\hbar\omega_0}{2}} + a^+ e^{-\frac{\theta\hbar\omega_0}{2}}\right)\rho_s(t)\right\}\end{aligned}$$

It is a simple matter to verify that

$$[a^+a, H_s] = 0$$

and

$$[a^+a, q] = \left(\frac{\hbar}{2m\omega_o}\right)^{1/2}(a - a^+)$$

Thus,

$$\frac{d\langle n(t)\rangle}{dt} = -\frac{2}{m\hbar\omega_o} I(\omega_o) \sinh\frac{\theta\hbar\omega_o}{2} \langle n(t)\rangle \qquad \text{V-65}$$

$$+ \frac{1}{m\hbar\omega_o} I(\omega_o) \sinh\frac{\theta\hbar\omega_o}{2} \langle a^2(t) + a^{+2}(t)\rangle$$

$$+ \frac{1}{m\hbar\omega_o} I(\omega_o)\, e^{-\frac{\theta\hbar\omega_o}{2}}$$

where we have used

$$tr_s\left([a^{+2} + a^2]\,\rho_s(t)\right) = \langle a^2(t) + a^{+2}(t)\rangle$$

and

$$tr_s\, \rho_s(t) = 1$$

We can now calculate $\frac{d}{dr} < a^2(t)+a^{+2}(t) >_s$ by returning to equation (V-54) and substituting a^2+a^{+2} for $\hat{0}_s$. Using the same approximation for Q_1 and Q_2, we obtain

$$\frac{d\langle a^2(t)+a^{+2}(t)\rangle}{dt} = \frac{4}{\hbar m\omega_o} I(\omega_o) \operatorname{Sinh}\frac{\theta\hbar\omega_o}{2} \langle n(t)\rangle$$ V-66

$$- \frac{2}{\hbar m\omega_o} I(\omega_o) \operatorname{Sinh}\frac{\theta\hbar\omega_o}{2} \langle a^2(t)+a^{+2}(t)\rangle$$

$$- 2\omega_o i \langle a^2(t) - a^{+2}(t)\rangle - \frac{2}{\hbar m\omega_o} I(\omega_o) e^{-\frac{\theta\hbar\omega_o}{2}}$$

The same procedure applied once again provides the needed rate equation for $i < a^2(t) - a^{+2}(t) >$:

$$i\,\frac{d\langle a^2(t)-a^{+2}(t)\rangle}{dt} = 2\omega_o \langle a^2(t) + a^{+2}(t)\rangle$$ V-67

$$- \frac{2}{\hbar m\omega_o} I(\omega_o) \operatorname{Sinh}\frac{\theta\hbar\omega_o}{2} i\langle a^2(t) - a^{+2}(t)\rangle$$

Equations (V-65), (V-66), and (V-67) form a system of coupled, linear, first order differential equations in the variables $< n(t) >$, $< a^2(t)+ a^{+2}(t) >$, and $i < a^2(t)-a^{+2}(t) >$. One needs only to specify the initial values of these variables to uniquely determine their values at all times. Since the oscillator is initially in a pure state of the unperturbed oscillator Hamiltonian, we have the initial values:

$$\langle n(t)\rangle\Big|_{t=0} = n_i$$ V-68

$$\langle a^2(t)+a^{+2}(t)\rangle\Big|_{t=0} = 0$$

and

$$i\langle a^2(t) - a^{+2}(t)\rangle\Big|_{t=0} = 0$$

The solutions of the differential equations that satisfy the initial conditions are:

$$\langle n(t)\rangle = n_\theta + \frac{n_i - n_\theta}{\tilde{\omega}^2} e^{-2K_1 t}\left[\omega_o^2 - (\omega_o^2 - \tilde{\omega}^2)\cos 2\tilde{\omega} t\right] \qquad \text{V-69}$$

$$\langle a^2(t) + a^{+2}(t)\rangle = \frac{2K_1}{\tilde{\omega}}(n_i - n_\theta) e^{-2K_1 t} \sin 2\tilde{\omega} t \qquad \text{V-70}$$

and

$$i\langle a^2(t) - a^{+2}(t)\rangle = \frac{2K_1\omega_o}{\tilde{\omega}^2}(n_i - n_\theta) e^{-2K_1 t}(1 - \cos 2\tilde{\omega} t) \qquad \text{V-71}$$

where

M_i = the initial occupation number of the oscillator;

$M_\theta = \frac{1}{e^{\theta\hbar\omega_o} - 1}$, the average occupation number for an oscillator distributed among its free states at temperature $T = \frac{1}{k\theta}$; V-72

$$\tilde{\omega} = \sqrt{(\omega_o^2 - K_1^2)} \qquad \text{V-73}$$

and

$$K_1 = \frac{1}{m\hbar\omega_o} I(\omega_o) \sinh \frac{\theta\hbar\omega_o}{2} . \qquad \text{V-74}$$

We demonstrate the method used to find these solutions in the next section.

Equation (V-69) shows that, in the infinite time limit, the average occupation number approaches the expected constant value appropriate for an oscillator in equilibrium at the temperature of the reservoir. From the same equation, we see that the rate of approach to equilibrium is determined by $K_1 = \frac{1}{m\hbar\omega_o} I(\omega_o) \sinh \frac{\theta\hbar\omega_o}{2}$.

Comparing these results to those obtained by perturbation theory (c.f. equations (V-19) and (V-20)), we see that this more careful treatment differs only in the inclusion of a damped oscillatory factor in the time evolvement of $< n(t) >$.[27] The oscillatory factor is a result of not having made the "rotating wave" approximation[3,7,8] and presumably could be obtained via perturbation theory as well. In our formalism, dropping the $< a^2(t)+a^{+2}(t) >$ term of equation (V-65) would be equivalent to making the rotating wave approximation.

The Driven Oscillator

We add to the interaction term of the full Hamiltonian a term representing a classical driving force. That is,

$$V(t) = q \cdot B + q \cdot v(t) = q \cdot B_T(t) \qquad \text{V-75}$$

where v(t) is an ordinary time dependent function and, as before, B is a time independent function of reservoir coordinates. The fact that the full Hamiltonian, $H_r + H_s + V(t)$ is now time dependent requires that we change equation (III-7) to read

$$\rho(t) = T\, e^{-i(H_r + H_s)\frac{t}{\hbar} - \frac{i}{\hbar}\int_0^t V(t')dt'} \rho(0) \times T_- e^{i(H_r+H_s)\frac{t}{\hbar} + \frac{i}{\hbar}\int_0^t V(t')dt'} \qquad \text{V-76}$$

The equation for the reduced density matrix operator is changed slightly from equation (III-11) so that

$$\rho_s(t) = \langle S_{i_1}| \sum_j \Big\{ Z^{-1} e^{-\theta E_j} \langle E_j | T_- \, e^{i/\hbar[(H_r+H_{s_1})t + \int_0^t dt' V_1(t')]} \times T e^{-i/\hbar[(H_r+H_{s_2})t + \int_0^t dt' V_2(t')]} |E_j\rangle \Big\} |S_{i_2}\rangle \qquad \text{V-77}$$

We need the following theorems[28]:

$$T_- \exp\Big[\frac{i}{\hbar} Ht + \frac{i}{\hbar}\int_0^t dt' V(t')\Big] = T_- \exp\Big[\frac{i}{\hbar}\int_0^t V_I(t')dt'\Big] \exp \frac{i}{\hbar} Ht \qquad \text{V-78}$$

and

$$T \exp\Big[-\frac{i}{\hbar} Ht - \frac{i}{\hbar}\int_0^t dt' V(t')\Big] = \exp -\frac{i}{\hbar} Ht \; T\exp\Big[-\frac{i}{\hbar}\int_0^t dt' V_I(t')\Big] \qquad \text{V-79}$$

where $V_I(t') = e^{i/\hbar Ht'} \, V(t') \, e^{-i/\hbar Ht'}$.

Hence

$$\rho_s(t) = e^{-i/\hbar H_{s_2} t} \langle S_{i_1}| \sum_j \Big\{ Z^{-1} e^{-\theta E_j} \langle E_j | T_- e^{i/\hbar \int_0^t dt' V_{I_1}(t')} \times T e^{-i/\hbar \int_0^t dt' V_{I_2}(t')} |E_j\rangle \Big\} |S_{i_2}\rangle e^{i/\hbar H_{s_1} t} \qquad \text{V-80}$$

Equation (V-80) is exactly of the same form as equation (III-31). We may then define a cumulant expansion just as before. The classical forcing function, v(t), will appear in the resulting expression for W_1 but not in the equation for W_2. This is easily seen from equation (IV-4). The integrands on the right hand side of that equation contain factors of the type

$$\langle B_T(t') B_T(t'') \rangle - \langle B_T(t') \rangle \langle B_T(t'') \rangle$$

$$= \langle B(t') B(t'') \rangle - \langle B(t') \rangle \langle B(t'') \rangle + \langle B(t') v(t'') \rangle$$

$$+ v(t') \langle B(t'') \rangle + v(t') v(t'') - \langle B(t') \rangle v(t'')$$

$$- v(t') \langle B(t'') \rangle - v(t') v(t'')$$

$$= \langle B(t') B(t'') \rangle - \langle B(t') \rangle \langle B(t'') \rangle$$

where we have used equation (V-75) and the fact that v(t) is an ordinary function of time. Hence, the contributions due to v(t) in W_2 exactly cancel.

Retracing the work of Chapter IV and assuming that $< B > = 0$, we would arrive at the equation of motion for $\rho_s(t)$:

$$\frac{d\rho_s(t)}{dt} = -\frac{i}{\hbar}[H_s, \rho_s(t)] - \frac{i}{\hbar}[q, \rho_s(t)]\, v(t) \qquad \text{V-81}$$

$$+ \frac{1}{\hbar^2}[q, Q_1 \rho_s(t)]$$

$$- \frac{1}{\hbar^2}[q, \rho_s(t) Q_2]$$

and for any oscillator variable

$$\frac{d\langle O_s(t)\rangle}{dt} = -\frac{i}{\hbar}\, tr_s\left([O_s, H_s]\,\rho_s(t)\right) - \frac{i}{\hbar}\, v(t)\, tr_s\left([O_s, H_s]\,\rho_s(t)\right) \qquad \text{V-82}$$

$$+\frac{1}{\hbar^2}\, tr_s\left([O_s, q]\left\{Q_1\rho_s(t) - \rho_s(t)\,Q_2\right\}\right)$$

Repeating the calculations of the first section of this chapter, we easily obtain equations of motions for $< q(t) >$, $< p(t) >$, $< n(t) >$, $< a^2(t)+a^{+2}(t) >$, and $i < a^2(t)-a^{+2}(t) >$. Ignoring principal part contributions, they are:

$$\frac{d^2\langle q(t)\rangle}{dt} = -2K_1\frac{d\langle q(t)\rangle}{dt} - \omega_0^2\langle q(t)\rangle - v(t) \qquad \text{V-83}$$

$$\langle p(t)\rangle = m\,\frac{d\langle q(t)\rangle}{dt} \qquad \text{V-84}$$

$$\frac{d\langle n(t)\rangle}{dt} = -2K_1\langle n(t)\rangle + K_1\langle a^2(t) + a^{+2}(t)\rangle \qquad \text{V-85}$$

$$+\frac{1}{m\hbar\omega_0}\, I(\omega_0)\, e^{-\frac{\theta\hbar\omega_0}{2}} - \frac{1}{m\hbar\omega_0}\, v(t)\langle p(t)\rangle$$

$$\frac{d\langle a^2(t)+a^{+2}(t)\rangle}{dt} = 4K_1\langle n(t)\rangle - 2K_1\langle a^2(t) + a^{+2}(t)\rangle \qquad \text{V-86}$$

$$-2\omega_0\, i\langle a^2(t) - a^{+2}(t)\rangle - \frac{2}{m\hbar\omega_0}\, I(\omega_0)\, e^{-\frac{\theta\hbar\omega_0}{2}} + \frac{2}{m\hbar\omega_0}\, v(t)\langle p(t)\rangle$$

and

$$\frac{i\,d\langle a^2(t)-a^{+2}(t)\rangle}{dt} = 2\omega_0\langle a^2(t) + a^{+2}(t)\rangle \qquad \text{V-87}$$

$$-2K_1\, i\langle a^2(t) - a^{+2}(t)\rangle + \frac{2}{\hbar}\, v(t)\langle q(t)\rangle$$

where

$$K_1 = \frac{1}{m\hbar\omega_0} I(\omega_0) \sinh \frac{\theta\hbar\omega_0}{2} \qquad \text{V-88}$$

and

$$I(\omega_0) = \pi Z^{-1} \int dE_j\, g(E_j + \tfrac{\hbar\omega_0}{2})\, g(E_j - \tfrac{\hbar\omega_0}{2})\, |\langle E_j + \tfrac{\hbar\omega_0}{2} | B | E_j - \tfrac{\hbar\omega_0}{2} \rangle|^2 \qquad \text{V-89}$$

The solution to equation (V-83) is well known from elementary mechanics.[29] In the most general form, it is

$$\langle q(t) \rangle = \langle q(t) \rangle_f - \frac{1}{\tilde{\omega} m} \int_0^t dt'\, e^{-K_1 (t-t')} \sin \tilde{\omega}(t-t')\, v(t') \qquad \text{V-90}$$

where $< q(t) >_f$ is the solution in the absence of the driving force.

Equations (V-85) through (V-87) can be written in the form

$$\frac{d}{dt} X_i(t) = \sum_j A_{ij} X_j(t) + D_i(t) \qquad \text{V-91}$$

where

$$X = \begin{pmatrix} \langle n(t) \rangle \\ \langle a^2(t) + a^{+2}(t) \rangle \\ i\langle a^2(t) - a^{+2}(t) \rangle \end{pmatrix} \qquad \text{V-92}$$

$$A = \begin{pmatrix} -2K_1 & K_1 & 0 \\ 4K_1 & -2K_1 & -2\omega_0 \\ 0 & 2\omega_0 & -2K_1 \end{pmatrix} \qquad \text{V-93}$$

and

$$D = \begin{pmatrix} -\frac{1}{m\hbar\omega_0} v(t)\langle p(t)\rangle + \frac{1}{m\hbar\omega_0} I(\omega_0)\, e^{-\frac{\theta h\omega_0}{2}} \\ \frac{2}{m\hbar\omega_0} v(t)\langle p(t)\rangle - \frac{2}{m\hbar\omega_0} I(\omega_0)\, e^{-\frac{\theta\hbar\omega_0}{2}} \\ \frac{2}{\hbar} v(t)\,\langle q(t)\rangle \end{pmatrix} \qquad \text{V-94}$$

One may decouple the equations (V-91) by finding the matrix S that diagonalizes A. Multiplying (V-91) by S_{ki} and summing over i, we obtain

$$\frac{d}{dt}\sum_i S_{ki} X_i(t) = \sum_j \sum_i S_{ki} A_{ij} X_j(t) + \sum_i S_{ki} D_i(t) \qquad \text{V-95}$$

We may insert unity in the form

$$1 = \sum_\ell S^{-1}_{j\ell} S_{\ell j}$$

into equation (V-95) so that

$$\frac{d}{dt}\left(\sum_i S_{ki} X_i(t)\right) = \sum_\ell \sum_j \left(\sum_i S_{ki} A_{ij} S^{-1}_{j\ell}\right) \times S_{\ell j} X_j(t) + \sum_i S_{ki} D_i(t) \qquad \text{V-96}$$

Then by hypothesis,

$$\sum_i S_{ki} A_{ij} S^{-1}_{j\ell} = \lambda_k \delta_{k\ell}$$

where λ_k is the k^{th} eigenvalue of the matrix A. Therefore,

$$\frac{d}{dt}\left(\sum_i S_{ki} X_i(t)\right) = \lambda_k \left(\sum_j S_{kj} X_j(t)\right) + \sum_i S_{ki} D_i(t) \qquad \text{V-97}$$

Defining the functions

$$U_k(t) = \sum_i S_{ki} X_i(t) \qquad \text{V-98}$$

equation (V-97) becomes

$$\frac{d}{dt} U_k(t) = \lambda_k U_k(t) + \sum_i S_{ki} D_i(t) \qquad \text{V-99}$$

This equation is an elementary type[30] and has solution

$$U_k(t) = e^{\lambda_k t} U_k(0) + \sum_i S_{ki} \int_0^t dt' \, e^{-\lambda_k (t'-t)} D_i(t') \qquad \text{V-100}$$

Then from equation (V-98),

$$X_j(t) = \sum_k S^{-1}_{jk} U_k(t) \qquad \text{V-101}$$

$$= \sum_k S^{-1}_{jk} \left[e^{\lambda_k t} U_k(0) + \sum_i S_{ki} \int_0^t dt' \, e^{-\lambda_k (t'-t)} D_i(t') \right.$$

It is a matter of some algebra to show that

$$\lambda_1 = -2K_1 \qquad \text{V-102}$$

$$\lambda_2 = -2K_1 + i2\tilde{\omega}$$

$$\lambda_3 = -2K_1 - i2\tilde{\omega}$$

$$S = \begin{pmatrix} \omega_0^2 & 0 & -\frac{1}{2}\omega_0 K_1 \\ K_1^2 & \frac{i}{2}\tilde{\omega} K_1 & -\frac{1}{2}\omega_0 K_1 \\ K_1^2 & -\frac{i}{2}\tilde{\omega} K_1 & -\frac{1}{2}\omega_0 K_1 \end{pmatrix} \qquad \text{V-103}$$

and

$$S^{-1} = \begin{pmatrix} \frac{1}{\tilde{\omega}^2} & -\frac{1}{2\tilde{\omega}^2} & -\frac{1}{2\tilde{\omega}^2} \\ 0 & -\frac{i}{K_1\tilde{\omega}} & \frac{i}{K_1\tilde{\omega}} \\ \frac{2K_1}{\omega_0\tilde{\omega}^2} & -\frac{\omega_0}{K_1\tilde{\omega}^2} & -\frac{\omega_0}{K_1\tilde{\omega}^2} \end{pmatrix} \qquad \text{V-104}$$

where

$$\tilde{\omega}^2 = \omega_0^2 - K_1^2 \qquad \text{V-105}$$

By imposing the boundary conditions,

$$\langle n(t) \rangle \Big|_{t=0} = n_i$$

and

$$\langle a^2(t)+a^{+2}(t)\rangle\Big|_{t=0} = i\,\langle a^2(t)-a^{+2}(t)\rangle\Big|_{t=0} = 0 \qquad \text{V-106}$$

we find

$$\langle n(t)\rangle = \langle n(t)\rangle^f - \frac{1}{m\tilde{\omega}^2\hbar\omega_0}\int_0^t dt'\, e^{2K_1(t'-t)} \qquad \text{V-107}$$

$$\times\left\{\omega_0^2 - K_1^2 \cos 2\tilde{\omega}(t'-t) + \tilde{\omega} K_1 \sin 2\tilde{\omega}(t'-t)\right\} v(t')\langle p(t')\rangle$$

$$-\frac{\omega_0 K_1}{2\hbar\tilde{\omega}^2}\int_0^t dt'\, e^{2K_1(t'-t)}\left(1-\cos 2\tilde{\omega}(t'-t)\right) v(t')\langle q(t')\rangle$$

where $< n(t) >^f$ is the solution when $v(t) = 0$.

As an example, suppose the combined system is subjected to a pulse at time t_c. Then,

$$v(t) = A\,\delta(t_c - t) \qquad \text{V-108}$$

$$\langle q(t)\rangle = -\frac{A}{\tilde{\omega} m}\begin{cases} e^{-K_1(t-t_c)}\sin\tilde{\omega}(t-t_c), & t > t_c \\ 0, & t \le t_c \end{cases} \qquad \text{V-109}$$

$$\langle p(t)\rangle = -\frac{A}{\tilde{\omega}}\begin{cases} e^{-K_1(t-t_c)}\left(K_1\sin\tilde{\omega}(t-t_c) + \tilde{\omega}\cos\tilde{\omega}(t-t_c)\right), & t > t_c \\ 0, & t \le t_c \end{cases} \qquad \text{V-110}$$

and

$$\langle n(t)\rangle = \langle n(t)\rangle^{f} + \frac{A^2}{m\tilde{\omega}^2\hbar\omega_o}\begin{cases} e^{-2K_1(t-t_c)}\left(\omega_o^2 - K_1^2\cos 2\tilde{\omega}(t-t_c)\right. \\ \qquad \left. - \tilde{\omega}K_1\sin 2\tilde{\omega}(t-t_c)\right), & t>t_c \\ 0, & t\leq t_c \end{cases} \quad \text{V-111}$$

Summary

We have shown that by using the approximate equation of motion (IV-22), our method produces results that agree with less rigorous treatments based on perturbation theory. We have not used the rotating wave approximation as is commonly done and the damping terms of equations (V-69) and (V-111) are multiplied by oscillating factors absent from other treatments.

In the next chapter, we investigate the significance of the approximation used here. It turns out that equation (IV-22) is the result of truncating an expansion of the exact equation of motion for $\rho(t)$ in which the n^{th} term is proportional to $t_c^{(2n-1)}$ where t_c is the reservoir relaxation time. Thus, the results of this chapter and those of perturbation theory are valid only for reservoirs which relax quickly. Just how one decides whether a given relaxation time is short enough for a given approximation is also discussed in the next chapter.

CHAPTER VI

FURTHER DEVELOPMENTS

Introduction

The work of Chapter IV produced an equation of motion for the reduced density operator,

$$\frac{d\rho_s(t)}{dt} = -\frac{i}{\hbar}\left[H_s, \rho_s(t)\right] + \frac{1}{\hbar^2}\left[A, \hat{F}_1 - \hat{F}_2\right] \qquad \text{VI-1}$$

where

$$\hat{F}_1 = e^{-iH_{s_2}t/\hbar} \langle S_{i_1}| T_-^{A_1} T^{A_2} \left\{ \int_0^t dt'' \langle B(t'')B(t)\rangle A_1(t'') e^{W(t)} \right\} |S_{i_2}\rangle e^{iH_{s_1}t/\hbar}$$

We have again made the assumption that $\langle B \rangle = 0$. By comparing equations (IV-17) and (IV-18), it can be demonstrated that $\hat{F}_2$ is obtained by taking the Hermitian adjoint of $\hat{F}_1$ and interchanging the subscripts 1 and 2. W(t) is the second cumulant defined in equation (IV-4).

By making the approximations contained in equations (IV-20) and (IV-21), $\hat{F}_1$-$\hat{F}_2$ was replaced by an operator quantity whose asymptotic value is time independent. The results obtained in Chapter V by this approximation are almost identical to those obtained by others using first order perturbation theory together with the assumption that the reservoir remains at all times in a canonical distribution of states at the initial temperature. Our approach is less dependent upon intricate comparisons of the various time scales involved than some other treatments but, up to this point, we share with these workers the concept referred to in the literature as the Markoff approximation.[31] In our case, this simply means that the change in the density matrix at time t does not depend upon its value at any other time but t. It was this notion that led us to equations (IV-20) and (IV-21). In this chapter, we treat our problem with more care in the hope of discovering a more precise criterion for imposing the Markoff approximation than the vague statement about the shortness of t_c in comparison to the inverse of the system's natural frequencies.

The Earlier-Later Expansion

By defining

$$\mathcal{U}(t,t'') = T_-^{A_1} T^{A_2} A_1(t'')\, e^{W(t)} \qquad \text{VI-2}$$

where

$$W(t) = \frac{-1}{2\hbar^2} \int_0^t dt_1 \int_0^t dt_2 \Big\{ A_1(t_1) A_1(t_2) \langle T_-^B B(t_1) B(t_2) \rangle + A_2(t_1) A_2(t_2) \langle T^B B(t_1) B(t_2) \rangle - 2 A_1(t_1) A_2(t_2) \langle B(t_1) B(t_2) \rangle \Big\} \qquad \text{VI-3}$$

we may write

$$\hat{F}_1 = e^{-iH_{s_2} t/\hbar} \langle S_{i_1} | \int_0^t dt'' \langle B(t'') B(t) \rangle\, \mathcal{U}(t,t'') | S_{i_2} \rangle\, e^{iH_{s_1} t/\hbar} \qquad \text{VI-4}$$

Our method of attack is to develop an expansion for $U(t,t'')$ in which the

k^{th} term is smaller than the $(k-1)^{th}$ term by a factor proportional to the reservoir relaxation time. To this end, we make the decomposition

$$W(t) = W(t'') + W_{e,\ell}(t,t'') + W_{\ell}(t,t'') \qquad \text{VI-5}$$

where

$$W(t'') = -\frac{1}{2\hbar^2}\int_0^{t''}dt_1\int_0^{t''}dt_2\Big\{A_1(t_1)A_1(t_2)\langle T_-^B B(t_1)B(t_2)\rangle$$
$$+A_2(t_1)A_2(t_2)\langle T^B B(t_1)B(t_2)\rangle - 2A_1(t_1)A_2(t_2)\langle B(t_1)B(t_2)\rangle\Big\} \qquad \text{VI-6}$$

$$W_{e,\ell}(t,t'') = -\frac{1}{\hbar^2}\int_{t''}^{t}dt_1\int_0^{t''}dt_2\Big\{A_1(t_1)A_1(t_2)\langle B(t_1)B(t_2)\rangle + A_2(t_1)A_2(t_2)\langle B(t_1)B(t_2)\rangle$$
$$- A_1(t_1)A_2(t_2)\langle B(t_1)B(t_2)\rangle - A_1(t_2)A_2(t_1)\langle B(t_2)B(t_1)\rangle\Big\} \qquad \text{VI-7}$$

and

$$W_{\ell}(t,t'') = -\frac{1}{2\hbar^2}\int_{t''}^{t}dt_1\int_{t''}^{t}dt_2\Big\{A_1(t_1)A_1(t_2)\langle T_-^B B(t_1)B(t_2)\rangle$$
$$+A_2(t_1)A_2(t_2)\langle T^B B(t_1)B(t_2)\rangle - 2A_1(t_1)A_2(t_2)\langle B(t_1)B(t_2)\rangle\Big\} \qquad \text{VI-8}$$

To obtain equation (VI-7), we have carried out the ordering on the B operators since the integrals over t_1 and t_2 do not overlap. Also, there has been a change of variables to obtain a simpler result.

Substituting equation (VI-5) into equation (VI-2) we find

$$U(t,t'') = T_-^{A_1} T^{A_2}\left(A_1(t'') e^{w(t'')} \; e^{w_{e,\ell}(t,t'') + w_\ell(t,t'')}\right)$$

We may factor $e^{w+w_{e,\ell}+w_\ell}$ since we may treat $w_{e,\ell}$ and w_ℓ as ordinary functions until we apply the operators $T_-^{A_1}$ and $T_-^{A_2}$. In the same vein, we may expand $e^{w_{e,\ell}+w_\ell}$ to obtain

$$U(t,t'') = \sum_K \frac{1}{K!} T_-^{A_1} T^{A_2}\left\{(w_{e,\ell} + w_\ell)^K A_1(t'') e^{w(t'')}\right\} \qquad \text{VI-9}$$

This last form is the desired expansion if we can show that the series converges. We have no rigorous proof that it does in fact converge but a qualitative investigation of the oscillator problem of Chapter V leads one to be optimistic (see Appendix B). The result of that investigation implies that the condition for convergence of the series in equation (VI-9) is that

$$\frac{\hbar}{2m\omega_0} \frac{B^2 t_c^2}{\hbar^2} \ll 1 \qquad \text{VI-10}$$

That is, the combination of the shortness of the reservoir relaxation time and the weakness of the interaction strength must be such that the probability that the system will make a transition in a time interval comparable to t_c is small.

Under the assumption that the above comment actually applies in our case, we return to equation (VI-9) and write

$$U(t,t'') \cong T_-^{A_1} T^{A_2} \left(A_1(t'') e^{W(t'')} \right) \qquad \text{VI-11}$$

$$+ T_-^{A_1} T^{A_2} \left(A_1(t'') W_\ell e^{W(t'')} \right) + T_-^{A_1} T^{A_2} \left(A_1(t'') W_{e,\ell} e^{W(t'')} \right)$$

Since t'' is the latest time in $e^{w(t'')}$, the first term is simply equivalent to

$$\left(T_-^{A_1} T^{A_2} e^{W(t'')} \right) A_1(t'') \qquad \text{VI-12}$$

The second is more complicated. Substituting for W_ℓ from its definition, equation (VI-8), we obtain

$$T_-^{A_1} T^{A_2} \left(A_1(t'') W_\ell e^{W(t'')} \right) \qquad \text{VI-13}$$

$$= -\frac{1}{2\hbar^2} \int_{t''}^{t} dt_1 \int_{t''}^{t} dt_2 \Big\{ \langle T_-^{B} B(t_1) B(t_2) \rangle \, T_-^{A_1} T^{A_2} \left(A_1(t'') A_1(t_1) A_1(t_2) e^{W(t'')} \right)$$

$$+ \langle T^{B} B(t_1) B(t_2) \rangle \, T_-^{A_1} T^{A_2} \left(A_1(t'') A_2(t_1) A_2(t_2) e^{W(t'')} \right)$$

$$-2 \langle B(t_1) B(t_2) \rangle \, T_-^{A_1} T^{A_2} \left(A_1(t'') A_1(t_1) A_2(t_2) e^{W(t'')} \right) \Big\}$$

In this case $t_1, t_2 > t''$; therefore,

$$T_-^{A_1} T^{A_2} \left(A_1(t'') A_1(t_1) A_1(t_2) e^{W(t'')} \right) \qquad \text{VI-14}$$

$$= \left(T_-^{A_1} T^{A_2} e^{W(t'')} \right) A_1(t'') \, T_-^{A_1} \left(A_1(t_1) A(t_2) \right)$$

But

$$A_1(t'')\, T_-^{A_1}(A_1(t_1)A_1(t_2)) = A_1(t'')\, A_1(t_1)\, A_1(t_2)\, \Theta(t_2-t_1) \qquad \text{VI-15}$$

$$+ A_1(t'')\, A_1(t_2)\, A_1(t_1)\, \Theta(t_1-t_2)$$

$$= [A_1(t''), A_1(t_1)]\, \Theta(t_2-t_1)\, A_1(t_2)$$

$$+ A_1(t_1)\, [A_1(t''), A_1(t_2)]\, \Theta(t_2-t_1)$$

$$+ [A_1(t''), A_1(t_2)]\, \Theta(t_1-t_2)\, A_1(t_1)$$

$$+ A_1(t_2)\, [A_1(t''), A_1(t_1)]\, \Theta(t_1-t_2)$$

$$+ T_-^{A_1}(A_1(t_1)\, A_1(t_2))\, A(t'')$$

where

$$\Theta(t_1-t_2) = \begin{cases} 1, & t_1 > t_2 \\ 0, & t_1 < t_2 \end{cases}$$

Then,

$$T_-^{A_1} T^{A_2} (A_1(t'')\, A_1(t_1)\, A_1(t_2)\, e^{W(t'')}) \qquad \text{VI-16}$$

$$= (T_-^{A_1} T^{A_2} e^{W(t'')}) \Big\{ [A_1(t''), A_1(t_1)]\, \Theta(t_2-t_1)\, A_1(t_2)$$

(continued)

$$+ A_1(t_1)[A_1(t''), A_1(t_2)]\,\Theta(t_2-t_1) + [A_1(t''), A_1(t_2)]\,\Theta(t_1-t_2)\,A_1(t_1)$$

$$+ A_1(t_2)[A_1(t''), A_1(t_1)]\,\Theta(t_1-t_2)\Big\} + \left(T_-^{A_1} T^{A_2} A_1(t_1) A_1(t_2)\, e^{W(t'')}\right) A_1(t'')$$

Since $[A_1(t), A_2(t')] = 0$,

$$T_-^{A_1} T^{A_2}\left(A_1(t'') A_2(t_1)\, A_2(t_2)\, e^{W(t'')}\right) \qquad \text{VI-17}$$

$$= T_-^{A_1} T^{A_2}\left(A_2(t_1) A_2(t_2)\, e^{W(t'')}\right) A_1(t'')$$

In a similar way,

$$T_-^{A_1} T^{A_2}\left(A_1(t'') A_1(t_1)\, A_2(t_2)\, e^{W(t'')}\right) \qquad \text{VI-18}$$

$$= T_-^{A_1} T^{A_2}\left(A_1(t_1) A_2(t_2)\, e^{W(t'')}\right) A_1(t'')$$

$$+ T_-^{A_1} T^{A_2}\left(A_2(t_2)\, e^{W(t'')}\right)[A_1(t''), A_1(t_1)]$$

Substituting equations (VI-16), (VI-17), and (VI-18) into equation (VI-13), we obtain

$$T_-^{A_1} T^{A_2}\left(A_1(t'')\, W_2\, e^{W(t'')}\right) \qquad \text{VI-19}$$

$$= T_-^{A_1} T^{A_2}\left(W_2\, e^{W(t'')}\right) A_1(t'')$$

(continued)

$$-\frac{1}{\hbar^2}\int_{t''}^{t} dt_1 \int_{t''}^{t} dt_2 \, \langle B(t_2)B(t_1)\rangle \Big\{ \theta(t_1-t_2)\big(T_-^{A_1}T^{A_2}\, e^{W(t'')}\big)$$

$$\times\big([A_1(t''), A_1(t_2)]A_1(t_1) + A_1(t_2)[A_1(t''), A_1(t_1)]\big)\Big\}$$

$$+\frac{1}{\hbar^2}\int_{t''}^{t} dt_1 \int_{t''}^{t} dt_2 \langle B(t_1)B(t_2)\rangle\, T_-^{A_1}T^{A_2}\big(A_2(t_2)e^{W(t'')}\big)[A_1(t''), A_1(t_1)]$$

Repeating this procedure, we find that

$$T_-^{A_1}T^{A_2}\big(A_1(t'')\, W_{e,\ell}\, e^{W(t'')}\big) \qquad \text{VI-20}$$

$$= T_-^{A_1}T^{A_2}\big(W_{e,\ell}\, e^{W(t'')}\big)$$

$$-\frac{1}{\hbar^2}\int_{t''}^{t} dt_1 \int_{0}^{t''} dt_2 \langle B(t_2)B(t_1)\rangle\, T_-^{A_1}T^{A_2}\big(A_1(t_2)e^{W(t'')}\big)[A_1(t''), A_1(t_1)]$$

$$+\frac{1}{\hbar^2}\int_{t''}^{t} dt_1 \int_{0}^{t''} dt_2 \langle B(t_1)B(t_2)\rangle\, T_-^{A_1}T^{A_2}\big(A_2(t_2)\, e^{W(t'')}\big)\, [A_1(t''), A_1(t_1)]$$

Using these results in the equation for $U(t,t'')$ and after a sequence of straightforward manipulations,

$$U(t,t'') \qquad \text{VI-21}$$

$$= T_-^{A_1}T^{A_2}\big[(1 + W_{e,\ell} + W_\ell)\, e^{W(t'')}\big]\, A_1(t'')$$

$$-\frac{1}{\hbar^2}\int_{t''}^{t} dt_1 \int_{0}^{t} dt_2 \, \langle T_-^{B} B(t_1)B(t_2)\rangle\big(T_-^{A_1}T^{A_2}A_1(t_2)\, e^{W(t'')}\big)\, [A_1(t''), A_1(t_1)]$$

(continued)

$$+\frac{1}{\hbar^2}\int_{t''}^{t}dt_1\int_{0}^{t}dt_2\,\langle B(t_1)B(t_2)\rangle\left(T_-^{A_1}T^{A_2}A_2(t_2)\,e^{W(t'')}\right)[A_1(t''),A_1(t_1)]$$

$$+\frac{1}{\hbar^2}\int_{t''}^{t}dt_1\int_{t''}^{t}dt_2\,\langle B(t_2)B(t_1)\rangle\,\Theta(t_1-t_2)\left(T_-^{A_1}T^{A_2}e^{W(t'')}\right)[A_1(t_1),[A_1(t''),A_1(t_2)]]$$

Consistent with the approximations already made, we are justified in replacing $T_-^{A_1}T^{A_2}[(1+w_e+w_{e\ell})\ e^{w(t'')}]$ by $T_-^{A_1}T^{A_2}e^{w(t)}$. Also, equation (VI-2) shows that

$$T_-^{A_1}T^{A_2}A_1(t_2)\,e^{W(t'')}=\mathcal{U}(t'',t_2)$$

and

$$T_-^{A_1}T^{A_2}A_2(t_2)\,e^{W(t'')}=\mathcal{U}^{\dagger}(t'',t_2)$$

But these quantities appear in terms already considered small and we may write

$$T_-^{A_1}T^{A_2}A_1(t_2)\,e^{W(t'')}=\left(T_-^{A_1}T^{A_2}e^{W(t'')}\right)A_1(t_2)$$

and

$$T_-^{A_1}T^{A_2}A_1(t_2)\,e^{W(t'')}=A_2(t_2)\left(T_-^{A_1}T^{A_2}e^{W(t'')}\right)$$

Therefore,

$$\mathcal{U}(t,t'') \tag{VI-22}$$

$$= \left(T_-^{A_1} T^{A_2} e^{W(t)}\right) A_1(t'')$$

$$- \frac{1}{\hbar^2} \int_0^t dt_1 \int_0^t dt_2 \langle T_-^B B(t_1) B(t_2) \rangle \left(T_-^{A_1} T^{A_2} e^{W(t'')}\right) A_1(t_2) \Theta(t_1 - t'') [A_1(t''), A_1(t_1)]$$

$$+ \frac{1}{\hbar^2} \int_0^t dt_1 \int_0^t dt_2 \langle B(t_1) B(t_2) \rangle A_2(t_2) \left(T_-^{A_1} T^{A_2} e^{W(t'')}\right) \Theta(t_1 - t'') [A_1(t''), A_1(t_1)]$$

$$+ \frac{1}{\hbar^2} \int_0^t dt_1 \int_0^t dt_2 \langle B(t_2) B(t_1) \rangle \left(T_-^{A_1} T^{A_2} e^{W(t'')}\right) \Theta(t_1 - t_2) \Theta(t_2 - t'') [A_1(t_1), [A_1(t''), A_1(t_2)]]$$

We use this expression for U(t,t") in equation (VI-4) to obtain

$$\hat{F}_1 = \int_0^t dt'' \langle B(t'') B(t) \rangle \rho_s(t) A(t'' - t) \tag{VI-23}$$

$$- \frac{1}{\hbar^2} \int_0^t dt'' \int_0^t dt_1 \int_0^t dt_2 \Big\{ \langle B(t'') B(t) \rangle \langle T_-^B B(t_1) B(t_2) \rangle$$

$$\times e^{-iH_s(t-t'')/\hbar} \rho_s(t'') e^{iH_s(t-t'')/\hbar} A(t_2 - t) \Theta(t_1 - t'') [A(t'' - t), A(t_1 - t)] \Big\}$$

$$+ \frac{1}{\hbar^2} \int_0^t dt'' \int_0^t dt_1 \int_0^t dt_2 \Big\{ \langle B(t'') B(t) \rangle \langle B(t_1) B(t_2) \rangle$$

$$\times A(t_2 - t) e^{-iH_s(t-t'')/\hbar} \rho_s(t'') e^{iH_s(t-t'')/\hbar} \Theta(t_1 - t'') [A(t'' - t), A(t_1 - t)] \Big\}$$

$$+ \frac{1}{\hbar^2} \int_0^t dt'' \int_0^t dt_1 \int_0^t dt_2 \Big\{ \langle B(t'') B(t) \rangle \langle B(t_2) B(t_1) \rangle$$

$$\times e^{-iH_s(t-t'')/\hbar} \rho_s(t) e^{iH_s(t-t'')/\hbar} \Theta(t_1 - t_2) \Theta(t_2 - t'') [A(t_1 - t), [A(t'' - t), A(t_2 - t)]] \Big\}$$

Since the positions of the A operators are now fixed, the subscripts have been dropped. Again there has been much tedious rearrangement to arrive at this result, but the essential feature is the commutivity of A_1 and A_2 operators. Equation (IV-7) has been used to obtain the density operators that occur. Since we suppose that reservoir correlation function is zero for $|t-t''| > t_c$, we may obtain a local-in-time equation by setting $e^{-iH_s(t-t'')/\hbar} \rho_s(t'') e^{iH_s(t-t'')/\hbar} = \rho_s(t)$. This is consistent with our previous approximations and clearly points out that we imagine that t_c is so short that the system hasn't time to interact with the reservoir and propagates freely during the interval. Thus,

$$\begin{aligned}\hat{F}_1 = &\int_0^t dt'' \langle B(t'')B(t)\rangle \rho_s(t) A(t''-t) - \frac{1}{\hbar^2}\int_0^t dt'' \int_0^t dt_1 \int_0^t dt_2 \Big\{ \langle B(t'')B(t)\rangle \qquad \text{VI-24}\\ &\times \langle T_-^B B(t_1)B(t_2)\rangle \rho_s(t) A(t_2-t)\,\Theta(t_1-t'')\,[A(t''-t),A(t_1-t)]\Big\}\\ &+ \frac{1}{\hbar^2}\int_0^t dt'' \int_0^t dt_1 \int_0^t dt_2 \Big\{ \langle B(t'')B(t)\rangle \langle B(t_1)B(t_2)\rangle\\ &\times A(t_2-t)\,\rho_s(t)\,\Theta(t_1-t'')\,[A(t''-t),A(t_1-t)]\Big\}\\ &+ \frac{1}{\hbar^2}\int_0^t dt'' \int_0^t dt_1 \int_0^t dt_2 \Big\{ \langle B(t'')B(t)\rangle \langle B(t_2)B(t_1)\rangle\\ &\times \Theta(t_1-t_2)\,\Theta(t_2-t'')\,\rho_s(t)\,[A(t_1-t),[A(t''-t),A(t_2-t)]]\Big\}\end{aligned}$$

It cannot have escaped the reader that the derivation of equation (VI-24) is a tortuous sequence of rearrangements. Sometimes this is a clear signal that there is a better way to arrive at the same result. In this case, H. A. Gersch has found an integral equation for $U(t,t'')$ which can be solved by an iterative process. The only additional assumption is that $[A(t),A(t')]$ is a c-number. Besides its ease of application, it has the advantage of producing at all orders a local-in-time equation for $\rho_s(t)$. The awkward approach contained here is presented in order to include the case when $[A(t),A(t')]$ is an operator.

For the rest of the discussion, we suppose that the commutator of the operators is a c-number. Then the last term of equation (VI-24) vanishes. We then find $\hat{F}_2$ by taking the adjoint of $\hat{F}_1$. Thus,

$$\hat{F}_1-\hat{F}_2 = \rho_s(t)\Bigg[\int_0^t dt''\Big\{\langle B(t'')B(t)\rangle A(t''-t) \tag{VI-25}$$

$$-\frac{1}{\hbar^2}\int_0^t dt_1\int_0^t dt_2 \langle B(t'')B(t)\rangle\langle T_-^B B(t_1)B(t_2)\rangle\,\theta(t_1-t'')[A(t''),A(t_1)]\,A(t_2-t)$$

$$+\frac{1}{\hbar^2}\int_0^t dt_1\int_0^t dt_2\langle B(t)B(t'')\rangle\langle B(t_2)B(t_1)\rangle\;\theta(t_1-t'')\,[A(t''),A(t_1)]A(t_2-t)\Big\}\Bigg]$$

$$-\Bigg[\int_0^t dt''\Big\{\langle B(t)B(t'')\rangle A(t''-t)$$

$$-\frac{1}{\hbar^2}\int_0^t dt_1\int_0^t dt_2\langle B(t)B(t'')\rangle\langle T^B B(t_1)B(t_2)\rangle\theta(t_1-t'')[A(t''),A(t_1)]A(t_2-t)$$

$$+\frac{1}{\hbar^2}\int_0^t dt_1\int_0^t dt_2\langle B(t'')B(t)\rangle\langle B(t_2)B(t_1)\rangle\,\theta(t_1-t'')\,[A(t''),A(t_1)]\,A(t_2-t)\Big\}\Bigg]$$

$$\times\,\rho_s(t)$$

We can recast this last expression in a more suggestive form by appropriately relabeling integration variables; we find

$$\hat{F}_1 - \hat{F}_2 \qquad \text{VI-26}$$

$$= \rho_s(t)\Big[\int_0^t dt''\, A(t''-t)\Big\{\langle B(t'')B(t)\rangle$$

$$-\frac{1}{\hbar^2}\int_0^t dt_1\int_0^t dt_2\,\langle B(t_2)B(t)\rangle\langle T_-^B B(t_1)B(t'')\rangle\theta(t_1-t_2)\,[A(t_2),A(t_1)]$$

$$+\frac{1}{\hbar^2}\int_0^t dt_1\int_0^t dt_2\,\langle B(t)B(t_2)\rangle\langle B(t'')B(t_1)\rangle\,\theta(t_1-t_2)[A(t_2),A(t_1)]\Big\}\Big]$$

$$-\Big[\int_0^t dt''\, A(t''-t)\Big\{\langle B(t)B(t'')\rangle$$

$$+\frac{1}{\hbar^2}\int_0^t dt_1\int_0^t dt_2\,\langle B(t)B(t_2)\rangle\langle T_-^B B(t_1)B(t_2)\rangle\,\theta(t_1-t_2)[A(t_2),A(t_1)]$$

$$-\frac{1}{\hbar^2}\int_0^t dt_1\int_0^t dt_2\langle B(t_2)B(t)\rangle\langle B(t'')B(t_1)\rangle\theta(t_1-t_2)[A(t_2),A(t_1)]\Big\}\Big]\,\rho_s(t)$$

By defining

$$\langle B(t)B(t'')\rangle_d = \langle B(t)B(t'')\rangle + \frac{1}{\hbar^2}\int_0^t dt_1\int_0^t dt_2\Big\{\langle B(t)B(t_2)\rangle \qquad \text{VI-27}$$

$$\times\langle T^B B(t_1)B(t'')\rangle\,\theta(t_1-t_2)[A(t_2),A(t_1)]\Big\} - \frac{1}{\hbar^2}\int_0^t dt_1\int_0^t dt_2\Big\{\langle B(t_2)B(t)\rangle$$

$$\times\langle B(t'')B(t_1)\rangle\,\theta(t_1-t_2)\,[A(t_2),A(t_1)]\Big\}$$

and

$$\langle B(t'')B(t)\rangle_d = \langle B(t)B(t'')\rangle_d^* \qquad \text{VI-28}$$

we recover the simple forms of the Markoff approximation:

$$\hat{F}_1 - \hat{F}_2 = \rho_s(t)\int_0^t dt''\, A(t''-t)\,\langle B(t'')B(t)\rangle_d - \int_0^t dt''\, A(t''-t)\langle B(t)B(t'')\rangle_d\, \rho_s(t) \qquad \text{VI-29}$$

In this case, the integrals will exhibit, in general, a time dependence even in the asymptotic limit. The most obvious interpretation of equation (VI-27) is that it describes the effect of the system upon the dynamical behavior of the reservoir.

Using equation (VI-29) for $\hat{F}_1$-$\hat{F}_2$, equation (VI-1) becomes

$$\frac{d\rho_s(t)}{dt} = -\frac{i}{\hbar}[H_s, \rho_s(t)] + \frac{1}{\hbar^2}\Big[A, \rho_s(t)\int_0^t dt''\, A(t''-t)\langle B(t'')B(t)\rangle_d - \int_0^t dt''\, A(t''-t)\langle B(t)B(t'')\rangle_d\, \rho_s(t)\Big] \qquad \text{VI-30}$$

With this result, we are prepared to begin an analysis similar to the work done in Chapter V but, now the reservoir is allowed to have memory. The effect on the reservoir due to its interaction with the system is not so quickly distributed over the reservoir degrees of freedom and, as a result, the system experiences an interaction which is modified by its recent history. Investigation of these memory effects represents a program for future investigation.

CHAPTER VII

CONCLUSIONS AND RECOMMENDATIONS

Our work has shown that the cumulant technique provides an efficient and accurate way to determine the dynamic history of a simple system as it interacts with a reservoir. The customary delicate discussion of an hierarchy of time scales has been replaced by considerations of a more physical nature. We choose the proper approximation to the equation of motion of the reduced density matrix by estimating the change in the system during a time interval equal to the reservoir relaxation time. If this change is small, we will obtain good results by considering only the lower order approximations to the equation of motion. The equation of motion itself has been cast in a relatively simple form. The reduced density operator appears in a linear way, evaluated at the same time throughout.

There are a number of ways that these results could be used in future investigations. The effective correlation functions defined at the end of Chapter V need to be interpreted more precisely. It may be that a diagrammatic method could be developed so as to describe the higher order approximations to the equation of motion in terms of physical processes similar to the interpretation given to the diagrams of standard perturbation theory. The density matrix formalism is extensively used in laser theory and since our work is more accurate than the usual perturbation treatment, our results could lead to a better understanding of the various processes. Finally, since the cumulant is a resummation of the perturbation theory, each cumulant represents many interactions. Thus, it would seem natural to apply our technique to multiple scattering problems.

Another aspect of our work should be mentioned; the cumulant approach has pedagogical value. The formalism is particularly suited to discussions of reservoir memory. The effect of the reservoir's relaxation time on the system's approach to equilibrium is clear and the relaxation time is, in turn, shown through the correlation functions to depend on the number of reservoir degrees of freedom.

APPENDIX A

PROOF OF VANISHING OF FOURTH CUMULANT FOR FREE BOSON RESERVOIRS

In this appendix, we demonstrate the condition for which the fourth cumulant W_4 of the expansion of equation (III-1) vanishes. As it turns out, all cumulants, W_n for $n > 2$, vanish under the same condition.[32]

As discussed in Chapter V in regard to W_1, we assume that all cumulants $W_{2n+1} = 0$ for $n = 0,1, \ldots$. Thus, according to the prescription given in Chapter III for calculating a given cumulant,

$$W_4 + \frac{1}{2} W_2^2 = \frac{1}{4!\hbar^4} \int_0^t dt_1 \int_0^t dt_2 \int_0^t dt_3 \int_0^t dt_4 \Big\{ A_1(t_1)A_1(t_2)A_1(t_3)A_1(t_4) \qquad \text{A-1}$$

$$\times \langle T_-^B B(t_1) B(t_2) B(t_3) B(t_4) \rangle$$

$$+ A_2(t_1) A_2(t_2) A_2(t_3) A_2(t_4) \langle T^B B(t_1) B(t_2) B(t_3) B(t_4) \rangle$$

$$+ 6 A_1(t_1) A_1(t_2) A_2(t_3) A_2(t_4) \langle T^B_{-1,2} B(t_1) B(t_2) T^B_{3,4} B(t_3) B(t_4) \rangle$$

$$- 4 A_1(t_1) A_2(t_2) A_2(t_3) A_2(t_4) \langle B(t_1) T^B_{2,3,4} B(t_2) B(t_3) B(t_4) \rangle$$

$$- 4 A_1(t_1) A_1(t_2) A_1(t_3) A_2(t_4) \langle T^B_{-1,2,3} B(t_1) B(t_2) B(t_3) B(t_4) \rangle \Big\}$$

In equation (A-1), the operators $T^B_{-1,2}$, $T^B_{3,4}$, $T^B_{2,3,4}$, and $T^B_{-1,2}$ act only upon the operators with the corresponding time arguments. T^B and T_-^B order all four B operators that occur. We wish to compare equation (A-1) to $\frac{1}{2} W_2^2$ obtained by squaring equation (IV-4).

$$\frac{1}{2} W_2^2 = \frac{1}{8\hbar^4} \int_0^t dt_1 \int_0^t dt_2 \int_0^t dt_3 \int_0^t dt_4 \Big\{ A_1(t_1) A_1(t_2) A_1(t_3) A_1(t_4) \tag{A-2}$$

$$\times \langle T_{-1,2}^B B(t_1) B(t_2) \rangle \langle T_{-3,4}^B B(t_3) B(t_4) \rangle$$

$$+ A_2(t_1) A_2(t_2) A_2(t_3) A_2(t_4) \langle T_{1,2}^B B(t_1) B(t_2) \rangle \langle T_{3,4}^B B(t_3) B(t_4) \rangle$$

$$+ 2 A_1(t_1) A_1(t_2) A_2(t_3) A_2(t_4) \langle T_{-1,2}^B B(t_1) B(t_2) \rangle \langle T_{3,4}^B B(t_3) B(t_4) \rangle$$

$$+ 4 A_1(t_1) A_1(t_2) A_1(t_3) A_2(t_4) \langle B(t_1) B(t_3) \rangle \langle B(t_2) B(t_4) \rangle$$

$$- 4 A_1(t_1) A_1(t_2) A_1(t_3) A_2(t_4) \langle T_{-1,2}^B B(t_1) B(t_2) \rangle \langle B(t_3) B(t_4) \rangle$$

$$- 4 A_1(t_1) A_2(t_2) A_2(t_3) A_2(t_4) \langle B(t_1) B(t_2) \rangle \langle T_{3,4}^B B(t_3) B(t_4) \rangle \Big\}$$

By relabeling the dummy indices in equation (A-2) and treating the A's as c-numbers, it is easy to obtain

$$\frac{1}{2} W_2^2 = \frac{1}{4!\hbar^4} \int_0^t dt_1 \int_0^t dt_2 \int_0^t dt_3 \int_0^t dt_4 \tag{A-3}$$

$$\times \Big\{ A_1(t_1) A_1(t_2) A_1(t_3) A_1(t_4) \Big[\langle T_{-1,2}^B B(t_1) B(t_2) \rangle \langle T_{-3,4}^B B(t_3) B(t_4) \rangle$$

$$+ \langle T_{-1,3}^B B(t_1) B(t_3) \rangle \langle T_{-2,4}^B B(t_2) B(t_4) \rangle + \langle T_{-1,4}^B B(t_1) B(t_4) \rangle \langle T_{-2,3}^B B(t_2) B(t_3) \rangle \Big]$$

$$+ A_2(t_1) A_2(t_2) A_2(t_3) A_2(t_4) \Big[\langle T_{1,2}^B B(t_1) B(t_2) \rangle \langle T_{3,4}^B B(t_3) B(t_4) \rangle$$

$$+ \langle T_{1,3}^B B(t_1) B(t_3) \rangle \langle T_{2,4}^B B(t_2) B(t_4) \rangle + \langle T_{1,4}^B B(t_1) B(t_4) \rangle \langle T_{2,3}^B B(t_2) B(t_3) \rangle \Big]$$

$$+ 6 A_1(t_1) A_1(t_2) A_2(t_3) A_2(t_4) \Big[\langle T_{-1,2}^B B(t_1) B(t_2) \rangle \langle T_{3,4}^B B(t_3) B(t_4) \rangle$$

$$+ \langle B(t_1) B(t_3) \rangle \langle B(t_2) B(t_4) \rangle + \langle B(t_1) B(t_4) \rangle \langle B(t_2) B(t_3) \rangle \Big]$$

$$- 4 A_1(t_1) A_1(t_2) A_1(t_3) A_2(t_4) \Big[\langle T_{-1,2}^B B(t_1) B(t_2) \rangle \langle B(t_3) B(t_4) \rangle$$

$$+ \langle T_{-1,3}^B B(t_1) B(t_3) \rangle \langle B(t_2) B(t_4) \rangle + \langle B(t_1) B(t_4) \rangle \langle T_{-2,3}^B B(t_2) B(t_3) \rangle \Big]$$

$$- 4 A_1(t_1) A_2(t_2) A_2(t_3) A_2(t_4) \Big[\langle B(t_1) B(t_2) \rangle \langle T_{3,4}^B B(t_3) B(t_4) \rangle$$

$$+ \langle B(t_1) B(t_3) \rangle \langle T_{2,4}^B B(t_2) B(t_4) \rangle + \langle B(t_1) B(t_4) \rangle \langle T_{2,3}^B B(t_2) B(t_3) \rangle \Big] .$$

By comparing equations (A-1) and (A-3), we see that $W_4 = 0$ if

$$\langle B(t_1)B(t_2)B(t_3)B(t_4)\rangle = \langle B(t_1)B(t_2)\rangle\langle B(t_3)B(t_4)\rangle \qquad \text{A-4}$$

$$+\langle B(t_1)B(t_3)\rangle\langle B(t_2)B(t_4)\rangle + \langle B(t_1)B(t_4)\rangle\langle B(t_2)B(t_3)\rangle$$

We now show that such a relation is satisfied if B is the position coordinate of a single harmonic oscillator. As mentioned above, if this condition is met for a single oscillator, it is also satisfied for a collection of an arbitrary number of oscillators.

We express B in the language of second quantization,

$$B(t) = \left(\frac{\hbar}{2m\omega}\right)^{1/2}\left(a e^{-i\omega t} + a^{+} e^{i\omega t}\right) \qquad \text{A-5}$$

Then since

$$\langle B(t_1)B(t_2)B(t_3)B(t_4)\rangle = Z^{-1}\sum_n e^{-\frac{n\hbar\omega}{KT}}\langle n|B(t_1)B(t_2)B(t_3)B(t_4)|n\rangle$$

we see that of all the possible products of creation and destruction operators, only those where the number of creation operations is equal to the number of destruction operators actually contribute. Thus,

$$\langle B(t_1)B(t_2)B(t_3)B(t_4)\rangle = \left(\frac{\hbar}{2m\omega_0}\right)^2\Big\{\langle a e^{-i\omega t_1} a e^{-i\omega t_2} a^{+} e^{i\omega t_3} a^{+} e^{i\omega t_4}\rangle \qquad \text{A-6}$$

$$+\langle a e^{-i\omega t_1} a^{+} e^{i\omega t_2} a e^{-i\omega t_3} a^{+} e^{i\omega t_4}\rangle + \langle a e^{-i\omega t_1} a^{+} e^{i\omega t_2} a^{+} e^{i\omega t_3} a e^{-i\omega t_4}\rangle$$

(continued)

$$+\langle a^{+}e^{i\omega t_1}a^{+}e^{i\omega t_2}ae^{-i\omega t_3}ae^{-i\omega t_4}\rangle+\langle a^{+}e^{i\omega t_1}ae^{-i\omega t_2}a^{+}e^{i\omega t_3}ae^{-i\omega t_4}\rangle$$

$$+\langle a^{+}e^{i\omega t_1}ae^{-i\omega t_2}ae^{-i\omega t_3}a^{+}e^{i\omega t_4}\rangle\}$$

$$=\left(\frac{\hbar}{2m\omega}\right)^2\left\{e^{-i\omega(t_1+t_2-t_3-t_4)}\langle aaa^{+}a^{+}\rangle\right.$$

$$+e^{-i\omega(t_1-t_2+t_3-t_4)}\langle aa^{+}aa^{+}\rangle+e^{-i\omega(t_1-t_2-t_3+t_4)}\langle aa^{+}a^{+}a\rangle$$

$$+e^{i\omega(t_1+t_2-t_3-t_4)}\langle a^{+}a^{+}aa\rangle+e^{i\omega(t_1-t_2+t_3-t_4)}\langle a^{+}aa^{+}a\rangle$$

$$\left.+e^{i\omega(t_1-t_2-t_3+t_4)}\langle a^{+}aaa^{+}\rangle\right\}$$

We now use the commutation relations,

$$[a,a^{+}]=1$$

$$[a,a]=[a^{+},a^{+}]=0$$

to write

$$\langle aaa^{+}a^{+}\rangle=\langle[a,a]a^{+}a^{+}\rangle+\langle a[a,a^{+}]a^{+}\rangle+\langle aa^{+}[a,a^{+}]\rangle+\langle aa^{+}a^{+}a\rangle \qquad \text{A-7}$$

$$=2\langle aa^{+}\rangle+\langle aa^{+}a^{+}a\rangle$$

But

$$\langle a a^+ a^+ a\rangle = Z^{-1}\,\mathrm{tr}\{e^{-\beta H} a a^+ a^+ a\}$$

$$= Z^{-1}\,\mathrm{tr}\{a e^{-\beta H} a a^+ a^+\}$$

$$= Z^{-1}\,\mathrm{tr}\{e^{-\beta H}(e^{\beta H} a\, e^{-\beta H}) a a^+ a^+\},\ \beta = \frac{1}{KT}$$

and since $e^{\beta H} a e^{-\beta H} = e^{-\beta\hbar\omega} a$, we can write

$$\langle a a^+ a^+ a\rangle = e^{-\beta\hbar\omega}\langle a a a^+ a^+\rangle \qquad \text{A-8}$$

Substituting equation (A-7) into (A-8), we find

$$\langle a a a^+ a^+\rangle = 2\langle a a^+\rangle + e^{-\beta\hbar\omega}\langle a a a^+ a^+\rangle$$

Then,

$$\langle a a a^+ a^+\rangle = \frac{2}{1 - e^{-\beta\hbar\omega}}\langle a a^+\rangle \qquad \text{A-9}$$

The other thermal averages in equation (A-6) can be simplified in this way. We obtain

$$\langle a a^+ a a^+\rangle = \frac{1}{1 - e^{-\beta\hbar\omega}}\left(\langle a a^+\rangle + \langle a^+ a\rangle\right) \qquad \text{A-10}$$

$$\langle a a^+ a^+ a\rangle = \frac{2}{1 - e^{-\beta\hbar\omega}}\langle a^+ a\rangle \qquad \text{A-11}$$

$$\langle a^+ a^+ a a\rangle = -\frac{2}{1 - e^{\beta\hbar\omega}}\langle a^+ a\rangle \qquad \text{A-12}$$

$$\langle a^+ a a^+ a \rangle = -\frac{1}{1-e^{\beta\hbar\omega}}\left(\langle a^+ a\rangle + \langle a a^+\rangle\right) \qquad \text{A-13}$$

and

$$\langle a^+ a a a^+ \rangle = -\frac{2}{1-e^{\beta\hbar\omega}}\langle a a^+\rangle \qquad \text{A-14}$$

Now $\langle a^+ a \rangle$ is the average occupation number of an oscillator in thermal equilibrium. Thus,

$$\frac{1}{e^{\beta\hbar\omega}-1} = \langle a^+ a\rangle \qquad \text{A-15}$$

and

$$\frac{1}{1-e^{-\beta\hbar\omega}} = \frac{e^{\beta\hbar\omega}}{e^{\beta\hbar\omega}-1} = \frac{1}{e^{\beta\hbar\omega}-1} + 1 = \langle a^+ a\rangle + 1 \qquad \text{A-16}$$

Substituting equations (A-15) and (A-16) into (A-9) through (A-14), we have

$$\langle a a a^+ a^+ \rangle = 2\langle a a^+\rangle\langle a a^+\rangle \qquad \text{A-17}$$

$$\langle a a^+ a a^+ \rangle = \langle a a^+\rangle\left(\langle a a^+\rangle + \langle a^+ a\rangle\right) \qquad \text{A-18}$$

$$\langle a a^+ a^+ a \rangle = 2\langle a a^+\rangle\langle a^+ a\rangle \qquad \text{A-19}$$

$$\langle a^+ a^+ a a \rangle = 2\langle a^+ a\rangle\langle a^+ a\rangle \qquad \text{A-20}$$

$$\langle a^+ a a^+ a \rangle = \langle a^+ a\rangle\left(\langle a^+ a\rangle + \langle a a^+\rangle\right) \qquad \text{A-21}$$

and

$$\langle a^{+}aaa^{+}\rangle = 2\langle a^{+}a\rangle\langle aa^{+}\rangle \qquad \text{A-22}$$

Using these results in equation (A-6), we obtain

$$\langle B(t_1)B(t_2)B(t_3)B(t_4)\rangle = \left(\frac{\hbar}{2m\omega}\right)^2\Big\{2\langle aa^{+}\rangle\langle aa^{+}\rangle e^{-i\omega(t_1+t_2-t_3-t_4)} \qquad \text{A-23}$$

$$+\langle aa^{+}\rangle\left(\langle aa^{+}\rangle+\langle a^{+}a\rangle\right)e^{-i\omega(t_1-t_2+t_3-t_4)} + 2\langle aa^{+}\rangle\langle a^{+}a\rangle e^{-i\omega(t_1-t_2-t_3+t_4)}$$

$$+2\langle a^{+}a\rangle\langle a^{+}a\rangle e^{i\omega(t_1+t_2-t_3-t_4)} + \langle a^{+}a\rangle\left(\langle a^{+}a\rangle+\langle aa^{+}\rangle\right)e^{i\omega(t_1-t_2+t_3-t_4)}$$

$$+2\langle a^{+}a\rangle\langle aa^{+}\rangle e^{i\omega(t_1-t_2-t_3+t_4)}\Big\}$$

It is this last form that we wish to compare to

$$\langle B(t_1)B(t_2)\rangle\langle B(t_3)B(t_4)\rangle + \langle B(t_1)B(t_3)\rangle\langle B(t_2)B(t_4)\rangle \qquad \text{A-24}$$

$$+\langle B(t_1)B(t_4)\rangle\langle B(t_2)B(t_3)\rangle$$

The first term can be written

$$\left(\frac{\hbar}{2m\omega}\right)^2\left(\langle a^{+}e^{i\omega t_1}a\,e^{-i\omega t_2}\rangle + \langle a\,e^{-i\omega t_1}a^{+}e^{i\omega t_2}\rangle\right)$$

$$\times\left(\langle a^{+}e^{i\omega t_3}a\,e^{-i\omega t_4}\rangle + \langle a\,e^{-i\omega t_3}a^{+}e^{i\omega t_4}\rangle\right)$$

(continued)

$$= \left(\frac{\hbar}{2m\omega}\right)^2 \Big(\langle a^+ a\rangle \langle a^+ a\rangle e^{i\omega(t_1 - t_2 + t_3 - t_4)} + \langle a^+ a\rangle \langle a a^+\rangle e^{i\omega(t_1 - t_2 - t_3 + t_4)}$$

$$+ \langle a a^+\rangle \langle a^+ a\rangle e^{i\omega(t_1 - t_2 - t_3 + t_4)} + \langle a a^+\rangle \langle a a^+\rangle e^{-i\omega(t_1 - t_2 + t_3 - t_4)} \Big)$$

Similarly, the second term of equation (A-24) is equivalent to

$$\left(\frac{\hbar}{2m\omega}\right)^2 \Big(\langle a^+ a\rangle \langle a^+ a\rangle e^{i\omega(t_1 - t_3 + t_2 - t_4)} + \langle a^+ a\rangle \langle a a^+\rangle e^{i\omega(t_1 - t_3 - t_2 + t_4)}$$

$$+ \langle a a^+\rangle \langle a^+ a\rangle e^{-i\omega(t_1 - t_3 - t_2 + t_4)} + \langle a a^+\rangle \langle a a^+\rangle e^{-i\omega(t_1 - t_3 + t_2 - t_4)} \Big)$$

The last term of equation (A-24) is equal to

$$\left(\frac{\hbar}{2m\omega}\right)^2 \Big(\langle a^+ a\rangle \langle a^+ a\rangle e^{i\omega(t_1 - t_4 + t_2 - t_3)} + \langle a^+ a\rangle \langle a a^+\rangle e^{i\omega(t_1 - t_4 - t_2 + t_3)}$$

$$+ \langle a a^+\rangle \langle a^+ a\rangle e^{-i\omega(t_1 - t_4 - t_2 + t_3)} + \langle a a^+\rangle \langle a a^+\rangle e^{-i\omega(t_1 - t_4 + t_2 + t_3)} \Big)$$

Thus,

$$\langle B(t_1) B(t_2)\rangle \langle B(t_3) B(t_4)\rangle + \langle B(t_1) B(t_3)\rangle \langle B(t_2) B(t_4)\rangle \qquad \text{A-25}$$

$$+ \langle B(t_1) B(t_4)\rangle \langle B(t_2) B(t_3)\rangle$$

$$= \left(\frac{\hbar}{2m\omega}\right)^2 \Big\{ 2 \langle a a^+\rangle \langle a a^+\rangle e^{-i\omega(t_1 + t_2 - t_3 - t_4)}$$

(continued)

$$+\langle aa^{+}\rangle\left(\langle aa^{+}\rangle+\langle a^{+}a\rangle\right)e^{-i\omega(t_1-t_2+t_3-t_4)}$$

$$+2\langle aa^{+}\rangle\langle a^{+}a\rangle e^{-i\omega(t_1-t_2-t_3+t_4)}+2\langle a^{+}a\rangle\langle a^{+}a\rangle e^{i\omega(t_1+t_2-t_3-t_4)}$$

$$+\langle a^{+}a\rangle\left(\langle a^{+}a\rangle+\langle aa^{+}\rangle\right)e^{i\omega(t_1-t_2+t_3-t_4)}$$

$$+2\langle a^{+}a\rangle\langle aa^{+}\rangle e^{i\omega(t_1-t_2-t_3+t_4)}\Big\}$$

By comparing equation (A-23) to (A-25), we see that the desired decomposition equation (A-4) has been proven. This result is a special case of Wick's theorem for finite temperatures.[33]

APPENDIX B

ESTIMATE OF RATE OF CONVERGENCE OF EARLIER-LATER EXPANSION

The usefulness of the earlier-later expansion of Chapter V depends upon the accuracy involved in the truncation of the series expansion of $U(t,t'')$ (equation (VI-9)). While no rigorous criterion for convergence has been developed, we can make a rough calculation using the oscillator as our system which may serve as a basis for comparing the relative importance of the k=1 term of equation (VI-11) to the k=0 term.

The calculation we have in mind is as follows:

i) Approximate equation (VI-9) by neglecting terms for which $k > 1$. That is, we let

$$\mathcal{U}(t,t'') = T_{-}^{A_1} T^{A_2}\left\{ A_1(t'')\left(1 + W_{\ell} + W_{e,\ell}\right) e^{W(t'')} \right\} \qquad \text{B-1}$$

We then make some rather crude approximations concerning the reservoir correlation function $< B(t)B(t') >$ to further simplify $U(t,t'')$.

ii) The resulting expression for $U(t,t'')$ is substituted into equation (VI-4) to obtain

$$\hat{F}_1 = e^{-iH_{s_2}t/\hbar} \langle S_{i_1}| \int_0^t dt'' \langle B(t'')B(t)\rangle \, \mathcal{U}(t,t'') |S_{i_2}\rangle \, e^{iH_{s_1}t/\hbar} \qquad \text{B-2}$$

Using our assumptions concerning the reservoir, we may perform the time integrations and find F_2 by taking the hermitian adjoint of $\hat{F}_1$.

iii) The quantity $\hat{F}_1 - \hat{F}_2$ is substituted into equation (V-1),

$$\frac{d\rho_s(t)}{dt} = -\frac{i}{\hbar}[H_s, \rho_s(t)] + \frac{1}{\hbar^2}[A, \hat{F}_1 - \hat{F}_2] \qquad \text{B-3}$$

Upon taking diagonal matrix elements of this result using free oscillator states, we may compare the contributions to the oscillator transition rates of the k=0 term of equation (B-1) to the k=1 terms.

In order to proceed with the calculation, some specification of the reservoir correlation function must be made. Our choice is

$$\langle B(t'')B(t)\rangle = \begin{cases} B^2 & , \ |t-t''| < t_c \\ 0 & , \ |t-t''| \geq t_c \end{cases} \qquad \text{B-4}$$

where t_c is sufficiently small that system operators may be considered constant over comparable time intervals. This representation of the reservoir correlation function may be the weakest part of this discussion. In general, $\langle B(t'')B(t)\rangle$ is not real but satisfies

$$\langle B(t'')B(t)\rangle = \langle B(t)B(t''+i\hbar\theta)\rangle$$

and

$$\langle B(t'')B(t)\rangle = \langle B(t)B(t'')\rangle^*$$

whereas in our case,

$$\langle B(t'')B(t)\rangle = \langle B(t)B(t'')\rangle$$

and is real.

The factor $< B(t'')B(t) >$ in equation (B-2) allows us to consider values of $U(t,t'')$ only slightly removed from $U(t,t)$. Since by hypothesis we imagine that system operators are essentially constant over this interval, we replace $e^{W(t'')}$ and $A_1(t'')$ by $e^{W(t)}$ and $A_1(t)$, respectively. Further, although we require that t be much greater than t_c, we also imagine that t is small enough that the system is still in its initial state. That is,

$$\rho_s(t) = |S_i\rangle\langle S_i|$$

But from equation (IV-7),

$$\rho_s(t) = e^{-iH_{s_i}t/\hbar}\langle S_{i_1}| T_-^{A_1} T^{A_2} e^{W(t)} |S_{i_2}\rangle e^{iH_{s_i}t/\hbar}$$

Thus, $e^{W(t)} \simeq 1$ and we can write equation (B-1) as

$$U(t,t'') \cong \left(1 + T_-^{A} T^{A_2} W_e + T_-^{A_1} T^{A_2} W_{e,\ell}\right) A(t) \qquad \text{B-5}$$

This is to be substituted into the expression for F_1. After replacing W_1 and $W_{e,1}$ by equations (VI-7) and (VI-8) and performing the now trivial time ordering, we obtain

$$\hat{F}_1 = \int_0^t dt'' \langle B(t'')B(t)\rangle\, |S_i\rangle\langle S_i|\, A(0) \qquad \text{B-6}$$

$$-\frac{1}{\hbar^2}\int_0^t dt'' \langle B(t'')B(t)\rangle \int_{t''}^{t} dt_1 \int_{t''}^{t_1} dt_2 \Big\{ \langle B(t_2)B(t_1)\rangle\, |S_i\rangle\langle S_i|$$

(continued)

$$\times A(0)A(t_2-t)A(t_1-t)\Big\} - \frac{1}{\hbar^2}\int_0^t dt''\langle B(t'')B(t)\rangle \int_{t''}^{t} dt_1 \int_{t''}^{t_1} dt_2 \Big\{\langle B(t_1)B(t_2)\rangle$$

$$\times A(t_1-t)A(t_2-t)|S_i\rangle\langle S_i| A(0)\Big\}$$

$$+ \frac{1}{\hbar^2}\int_0^t dt''\langle B(t'')B(t)\rangle \int_{t''}^{t} dt_1 \int_{t''}^{t_1} dt_2 \Big\{\langle B(t_1)B(t_2)\rangle A(t_2-t)|S_i\rangle\langle S_i|$$

$$\times A(0)A(t_1-t)\Big\} - \frac{1}{\hbar^2}\int_{t''}^{t} dt_1 \int_0^{t''} dt_2 \Big\{\langle B(t_2)B(t_1)\rangle |S_i\rangle\langle S_i|$$

$$\times A(0)A(t_2-t)A(t_1-t)\Big\}$$

$$- \frac{1}{\hbar^2}\int_0^t dt''\langle B(t'')B(t)\rangle \int_{t''}^{t} dt_1 \int_0^{t''} dt_2 \Big\{\langle B(t_1)B(t_2)\rangle A(t_1-t)A(t_2-t)$$

$$\times |S_i\rangle\langle S_i| A(0)\Big\} + \frac{1}{\hbar^2}\int_{t''}^{t} dt_1 \int_0^{t''} dt_2 \Big\{\langle B(t_1)B(t_2)\rangle A(t_2-t)$$

$$\times |S_i\rangle\langle S_i| A(0)A(t_1-t)\Big\}$$

$$+ \frac{1}{\hbar^2}\int_0^t dt''\langle B(t'')B(t)\rangle \int_{t''}^{t} dt_1 \int_0^{t''} dt_2 \Big\{\langle B(t_2)B(t_1)\rangle A(t_1-t)$$

$$\times |S_i\rangle\langle S_i| A(0)A(t_2-t)\Big\}$$

We have followed our practice of dropping subscripts when a final order is obtained. The changed time arguments are a result of manipulating the $e^{\pm iH_s t/\hbar}$ factors. The next step is to recognize that the correlation functions combined with the limits of integration will restrict the possible values of t_1 and t_2 to within t_c of t so that we make the approximations

$$A(t_2-t) \cong A(0), \quad t-t_c \le t_2 \le t$$

and

$$A(t_1-t) \cong A(0), \quad t-t_c \le t_1 \le t$$

Then using $< B(t_1)B(t_2) > = < B(t_2)B(t_1) >$, we write

$$\hat{F}_1 = \int_0^t dt'' \langle B(t'')B(t)\rangle |S_i\rangle\langle S_i| A(0) \tag{B-7}$$

$$-\frac{1}{\hbar^2}\int_0^t dt'' \int_{t''}^t dt_1 \int_{t''}^{t_1} dt_2 \Big\{\langle B(t'')B(t)\rangle \langle B(t_2)B(t_1)\rangle$$

$$\times\Big(|S_i\rangle\langle S_i| A^3(0) + A^2(0)|S_i\rangle\langle S_i| A(0) - 2A(0)|S_i\rangle\langle S_i| A^2(0)\Big)\Big\}$$

$$-\frac{1}{\hbar^2}\int_0^t dt'' \int_{t''}^t dt_1 \int_0^{t''} dt_0 \ \langle B(t'')B(t)\rangle\langle B(t_2)B(t_1)\rangle$$

$$\times\Big(|S_i\rangle\langle S_i| A^3(0) + A^2(0)|S_i\rangle\langle S_i| A(0) - 2A(0)|S_i\rangle\langle S_i| A^2(0)\Big)\Big\}$$

$$= \int_0^t dt'' \langle B(t'')B(t)\rangle |S_i\rangle\langle S_i| A(0) - \frac{1}{\hbar^2}\int_0^t dt'' \int_{t''}^t dt_1 \int_0^{t_1} dt_2 \Big\{\langle B(t'')B(t)\rangle$$

$$\times\langle B(t_2)B(t_1)\rangle\Big(|S_i\rangle\langle S_i| A^3(0) + A^2(0)|S_i\rangle\langle S_i| A(0) - 2A(0)|S_i\rangle\langle S_i| A^2(0)\Big)\Big\}$$

We find $\hat{F}_2$ by taking the hermitian adjoint of $\hat{F}_1$. After a reordering of the variables of integration so that $\int_0^t dt'' \int_{t''}^t dt_1 \int_0^{t_1} dt_2$ is replaced by $\int_0^t dt_1 \int_0^{t_1} dt'' \int_0^{t_1} dt_2$, we have

$$\hat{F}_1 - \hat{F}_2 = \int_0^t dt'' \langle B(t'')B(t)\rangle \Big\{ |S_i\rangle\langle S_i| A(0) - A(0)|S_i\rangle\langle S_i| \Big\} \qquad \text{B-8}$$

$$- \frac{1}{\hbar^2} \int_0^t dt_1 \int_0^{t_1} dt'' \int_0^{t_1} dt_2 \Big\{ \langle B(t'')B(t)\rangle \langle B(t_2)B(t_1)\rangle$$

$$\times \Big(|S_i\rangle\langle S_i| A^3(0) - A^3(0)|S_i\rangle\langle S_i| + 3A^2(0)|S_i\rangle\langle S_i| A(0) - 3A(0)|S_i\rangle\langle S_i| A^2(0) \Big) \Big\}$$

By using equation (B-3), we may perform the integrations to obtain

$$\int_0^t dt'' \langle B(t'')B(t)\rangle = B^2 t_c$$

and

$$\int_0^t dt_1 \int_0^{t_1} dt'' \int_0^{t_1} dt_2 \langle B(t'')B(t)\rangle \langle B(t_2)B(t_1)\rangle = \frac{1}{2} B^4 t_c^3$$

Hence,

$$\hat{F}_1 - \hat{F}_2 = B^2 t_c \Big\{ |S_i\rangle\langle S_i| A(0) - A(0)|S_i\rangle\langle S_i| \Big\} - \frac{B^4 t_c^3}{2\hbar^2} \qquad \text{B-9}$$

$$\times \Big\{ |S_i\rangle\langle S_i| A^3(0) - A^3(0)|S_i\rangle\langle S_i| + 3A^2(0)|S_i\rangle\langle S_i| A(0) - 3A(0)|S_i\rangle\langle S_i| A^2(0) \Big\}$$

To get an idea of the relative importance of the term linear in t_c compared to the term proportional to t_c^3, we return to the oscillator problem. We wish to calculate the contributions to the transition rate due to these terms at a time when the oscillator is certainly in the n^{th} free state. That is, when

$$\langle a|\rho_s|b\rangle = \delta_{an}\delta_{bn}$$

The transition rate out of this state at time t is given by equation (VI-1),

$$\frac{d\langle n|\rho_s|n\rangle}{dt} = \frac{1}{\hbar^2}\langle n|\,[q, \hat{F}_1-\hat{F}_2]\,|n\rangle \qquad \text{B-10}$$

$$= \frac{1}{\hbar^2}\left(\frac{\hbar}{2m\omega_0}\right)^{1/2}\sum_m\left(\langle n|a+a^+|m\rangle\langle m|\hat{F}_1-\hat{F}_2|n\rangle - \langle n|\hat{F}_1-\hat{F}_2|m\rangle\langle m|a+a^+|n\rangle\right)$$

$$= \frac{1}{\hbar^2}\left(\frac{\hbar}{2m\omega_0}\right)^{1/2}\Big[(n+1)^{1/2}\left(\langle n+1|\hat{F}_1-\hat{F}_2|n\rangle - \langle n|\hat{F}_1-\hat{F}_2|n+1\rangle\right)$$

$$+ n^{1/2}\left(\langle n-1|\hat{F}_1-\hat{F}_2|n\rangle - \langle n|\hat{F}_1-\hat{F}_2|n-1\rangle\right)\Big]$$

where we have used equations (V-6) through (V-11). It is easily shown that $\hat{F}_1-\hat{F}_2$ is anti-hermitian. It follows that

$$\langle n|\hat{F}_1-\hat{F}_2|n+1\rangle = -\langle n+1|\hat{F}_1-\hat{F}_2|n\rangle^*$$

Therefore,

$$\frac{d\langle n|\rho_s|n\rangle}{dt} = \frac{2}{\hbar}\left(\frac{\hbar}{2m\omega_0}\right)^{1/2} \mathrm{Re}\Big\{(n+1)^{1/2}\langle n+1|\hat{F}_1-\hat{F}_2|n\rangle - n^{1/2}\langle n|\hat{F}_1-\hat{F}_2|n-1\rangle\Big\} \qquad \text{B-11}$$

The job, then, is to evaluate

$$\langle n|\hat{F}_1-\hat{F}_2|n-1\rangle$$

and

$$\langle n+1|\hat{F}_1-\hat{F}_2|n\rangle$$

Replacing $|S_i>$ and A(0) by $|n>$ and q, respectively, equation (B-8) becomes

$$\hat{F}_1-\hat{F}_2 = B^2 t_c\Big\{|n\rangle\langle n|q - q|n\rangle\langle n|\Big\} - \frac{B^4 t_c^3}{2\hbar^2} \times\Big\{|n\rangle\langle n|q^3 - q^3|n\rangle\langle n| + 3q^2|n\rangle\langle n|q - 3q|n\rangle\langle n|\Big\}$$

Hence,

$$\langle n+1|\hat{F}_1-\hat{F}_2|n\rangle = -B^2 t_c\langle n+1|q|n\rangle + \frac{B^4 t_c^3}{2\hbar^2}\Big(\langle n+1|q^3|n\rangle + 3\langle n+1|q|n\rangle\langle n|q^2|n\rangle\Big)$$

and

$$\langle n|\hat{F}_1-\hat{F}_2|n-1\rangle = B^2 t_c \langle n|\underset{b}{q}|n-1\rangle - \frac{B^4 t_c^3}{2\hbar^2}$$

$$\times\left(\langle n|\underset{b}{q}^3|n-1\rangle + 3\langle n|\underset{b}{q}^2|n\rangle\langle n|\underset{b}{q}|n-1\rangle\right)$$

But

$$\langle n+1|\underset{b}{q}|n\rangle = (n+1)^{1/2}\left(\frac{\hbar}{2m\omega_0}\right)^{1/2}$$

$$\langle n|\underset{b}{q}|n-1\rangle = n^{1/2}\left(\frac{\hbar}{2m\omega_0}\right)^{1/2}$$

$$\langle n|\underset{b}{q}^2|n\rangle = (2n+1)\left(\frac{\hbar}{2m\omega_0}\right)$$

$$\langle n+1|\underset{b}{q}^3|n\rangle = (3n+3)(n+1)^{1/2}\left(\frac{\hbar}{2m\omega_0}\right)^{3/2}$$

and

$$\langle n|\underset{b}{q}^3|n-1\rangle = 3n\,n^{1/2}\left(\frac{\hbar}{2m\omega_0}\right)^{3/2}$$

Thus,

$$\langle n+1|\hat{F}_1-\hat{F}_2|n\rangle = -B^2 t_c (n+1)^{1/2}\left(\frac{\hbar}{2m\omega_0}\right)^{1/2}$$

$$+\frac{B^4 t_c^3}{2\hbar^2}(n+1)^{1/2}(9n+6)\left(\frac{\hbar}{2m\omega_0}\right)^{3/2}$$

and

$$\langle n|\hat{F}_1-\hat{F}_2|n-1\rangle = B^2 t_c n^{1/2}\left(\frac{\hbar}{2m\omega_0}\right)^{1/2}$$

$$-\frac{B^4 t_c^3}{2\hbar^2}n^{1/2}(9n+3)\left(\frac{\hbar}{2m\omega_0}\right)^{3/2}$$

Hence,

$$\frac{d\langle n|\rho_s|n\rangle}{dt} = -\frac{2}{\hbar^2}\left(\frac{\hbar}{2m\omega_0}\right) B^2 t_c (2n+1)$$
$$\times\left[1 - 3\,\frac{B^2 t_c^2}{\hbar^2}\left(\frac{\hbar}{2m\omega_0}\right)\left(\frac{3n^2+3n+1}{2n+1}\right)\right] \qquad \text{B-12}$$

To obtain some insight into this result, we use first order perturbation theory to calculate the probability that an oscillator that started out in the nth free state is still in that state at time t while the reservoir may have made any transition possible. That is, we calculate

$$P_n = 1 - \frac{1}{\hbar^2}\sum_{n'}\sum_{E_i}\sum_{E_j}\Big\{Z^{-1}e^{-\theta E_i}$$
$$\times\int_0^t dt_1\int_0^t dt_2 \langle E_i|\langle n|q(t_1)B(t_1)|n'\rangle|E_j\rangle\langle E_j|\langle n'|q(t_2)B(t_2)|E_i\rangle|n\rangle\Big\}$$

where we average over the initial reservoir states and sum over final reservoir and system states. Using the completeness of the E_j and n' states, we find

$$P_n = 1 - \frac{1}{\hbar^2}\int_0^t dt_1\int_0^t dt_2 \langle n|q(t_1)q(t_2)|n\rangle\langle B(t_1)B(t_2)\rangle$$

where we have used

$$\langle B(t_1)B(t_2)\rangle = \sum_{E_i} Z^{-1}e^{-\theta E_i}\langle E_i|B(t_1)B(t_2)|E_i\rangle$$

The integration with respect to t_2 may be performed by using the same reasoning as before; $< B(t_1)B(t_2) >$ is non-zero only for t_2 close to t_1 so we replace $q(t_2)$ by $q(t_1)$. Then,

$$P_n = 1 - \frac{1}{\hbar^2}\int_0^t dt_1 \langle n|q^2(t_1)|n\rangle \int_{t_1-t_c}^{t_1+t_c} dt_2\, B^2$$

$$= 1 - \frac{2t_c B^2}{\hbar^2}\int_0^t dt_1 \langle n|q^2(t_1)|n\rangle$$

But $q^2(t_1) = e^{iH_s t_1/\hbar}\, q^2\, e^{-iH_s t_1/\hbar}$. Hence,

$$\langle n|q^2(t_1)|n\rangle = \langle n|q^2|n\rangle = (2n+1)\left(\frac{\hbar}{2m\omega_0}\right)$$

and

$$P_n = 1 - \frac{2t_c t}{\hbar^2}(2n+1)\left(\frac{\hbar}{2m\omega_0}\right)B^2$$

Thus,

$$\frac{dP_n}{dt} = -\frac{2B^2 t_c}{\hbar^2}\left(\frac{\hbar}{2m\omega_0}\right)(2n+1)$$

Comparing this result to equation (B-12), we see that the k=1 terms of equation (B-1) contribute an amount roughly proportional to the probability that the oscillator undergoes a transition in a time interval of length t_c. So long as a combination of the shortness of the reservoir relaxation time and the weakness of the interaction strength works to make this probability small, we may make the truncation of equation (VI-11) with some confidence.

APPENDIX C

RELATION BETWEEN IMPROVED APPROXIMATE DENSITY OPERATOR EQUATION OF MOTION AND SECOND ORDER TIME DEPENDENT PERTURBATION THEORY

In this appendix, we show that the equation of motion for the reduced density operator derived in Chapter VI may be obtained by second order perturbation theory. In order to do so, we restrict ourselves to those times of observation for which second order perturbation theory is accurate. To obtain the greater generality of our method, one would have to stipulate that the reservoir possesses no memory of system transitions but that, in turn, would be contrary to the physical reality that makes it necessary to go beyond first order perturbation theory in the first place. The purpose of this derivation then, is not to confirm our previous work which is correct for arbitrary times, but to demonstrate that the physical processes considered in the first approximation to the earlier-later expansion are just those involved in second order perturbation theory.

Since we are considering the problem where the cumulant expansion of Chapter IV is valid, we imagine that the reservoir variables obey the decomposition rule (see Appendix A)

$$\langle B(t_1)B(t_2)B(t_3)B(t_4)\rangle = \langle B(t_1)B(t_2)\rangle\langle B(t_3)B(t_4)\rangle + \langle B(t_1)B(t_3)\rangle\langle B(t_2)B(t_4)\rangle + \langle B(t_1)B(t_4)\rangle\langle B(t_2)B(t_3)\rangle \qquad \text{C-1}$$

For convenience, we introduce the interaction picture representation of the reduced density operator

$$\rho_s^I(t) = e^{iH_s t/\hbar}\rho_s(t)\, e^{-iH_s t/\hbar} \qquad \text{C-2}$$

To second order in perturbation theory, $\rho_s^I(t)$ may be obtained from its value at t=0 by evaluating

$$\begin{aligned}\rho_s^I(t) = \rho_s^I(0) &- \frac{i}{\hbar}\int_0^t dt_1\, tr_r\left[A(t_1)B(t_1), \rho^I(0)\right] \\ &- \frac{1}{\hbar^2}\int_0^t dt_1\int_0^{t_1} dt_2\, tr_r\left[A(t_1)B(t_1),\left[A(t_2)B(t_2), \rho^I(0)\right]\right] \\ &+ \frac{i}{\hbar^3}\int_0^t dt_1\int_0^{t_1} dt_2\int_0^{t_2} dt_3\left[A(t_1)B(t_1),\left[A(t_2)B(t_2),\left[A(t_3)B(t_3), \rho^I(0)\right]\right]\right] \\ &+ \frac{1}{\hbar^4}\int_0^t dt_1\int_0^{t_1} dt_2\int_0^{t_2} dt_3\int_0^{t_3} dt_4\, tr_r\Big[A(t_1)B(t_1),\Big[A(t_2)B(t_2),\Big[A(t_3)B(t_3), \\ &\qquad \left[A(t_4)B(t_4), \rho^I(0)\right]\Big]\Big]\Big]\end{aligned} \qquad \text{C-3}$$

where $\rho^I(0)$ is the full density operator of the combined system, reservoir plus system, at t=0 and tr_r denotes the trace over reservoir states. As in Chapter IV, we specify that, at t=0, the full density operator has the form

$$\rho^{I}(0) = \rho_s^{I}(0)\, Z^{-1} e^{-\theta H_r} \qquad \text{C-4}$$

where $\rho_s^I(0) = |S_i\rangle\langle S_i|$; Z^{-1} is the reservoir partition function; H_r is the reservoir Hamiltonian, and $\theta = \frac{1}{KT}$.

We assume that B(t) is a linear function of reservoir creation and destruction operators so that

$$Z^{-1} tr_r\, e^{-\theta H_r} B(t_1) = Z^{-1} tr_r\, e^{-\theta H_r} B(t_1)B(t_2)B(t_3) = 0$$

and equation (C-3) simplifies to

$$\rho_s^I(t) = \rho_s^I(0) - \frac{1}{\hbar^2}\int_0^t dt_1 \int_0^{t_1} dt_2\, tr_r \left[A(t_1)B(t_1),[A(t_2)B(t_2),\rho^I(0)]\right] \qquad \text{C-5}$$

$$+ \frac{1}{\hbar^4}\int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 \int_0^{t_3} dt_4\, tr_r \Big[A(t_1)B(t_1), \Big[A(t_2)B(t_2),$$

$$A(t_3)B(t_3),[A(t_4)B(t_4),\rho^I(0)]\Big]\Big]$$

We obtain the equation of motion by taking the time derivative of both sides of equation (C-5):

$$\frac{d\rho_s^I(t)}{dt} = -\frac{1}{\hbar^2}\int_0^t dt_2\, tr_r \left[A(t)B(t),[A(t_2)B(t_2),\rho^I(0)]\right] \qquad \text{C-6}$$

$$+ \frac{1}{\hbar^4}\int_0^t dt_2 \int_0^{t_2} dt_3 \int_0^{t_3} dt_4\, tr_r \left[A(t)B(t),\left[A(t_2)B(t_2),[A(t_3)B(t_3),[A(t_4)B(t_4),\rho_s^I(0)]]\right]\right]$$

By defining

$$\langle B(t_1)B(t_2)\rangle = Z^{-1}\, tr_r\, e^{-\theta H_r} B(t_1)B(t_2)$$

and using the cyclic invariance of the trace, it is a straightforward exercise to show that

$$tr_r\,[A(t)B(t),[A(t_2)B(t_2),\rho^I(0)]] \qquad \text{C-7}$$

$$= [A(t),\ A(t_2)\rho_s^I(0)\langle B(t)B(t_2)\rangle - \rho_s^I(0)A(t_2)\langle B(t_2)B(t)\rangle]$$

Similarly, by defining

$$\langle B(t_1)B(t_2)B(t_3)B(t_4)\rangle = Z^{-1}\, tr_r\, e^{-\theta H_r} B(t_1)B(t_2)B(t_3)B(t_4)$$

we can show that

$$tr_r\,[A(t)B(t),[A(t_2)B(t_2),[A(t_3)B(t_3),[A(t_4)B(t_4),\rho^I(0)]]]] \qquad \text{C-8}$$

$$= \langle B(t)B(t_2)B(t_3)B(t_4)\rangle [A(t),A(t_2)A(t_3)A(t_4)\rho_s^I(0)]$$

$$- \langle B(t_2)B(t)B(t_3)B(t_4)\rangle [A(t),A(t_3)A(t_4)\rho_s^I(0)A(t_2)]$$

$$- \langle B(t_3)B(t)B(t_2)B(t_4)\rangle [A(t),A(t_2)A(t_4)\rho_s^I(0)A(t_3)]$$

(continued)

$$+\langle B(t_3)\,B(t_2)\,B(t)\,B(t_4)\rangle\left[A(t),A(t_4)\,\rho_s^I(0)\,A(t_3)A(t_2)\right]$$

$$-\langle B(t_4)\,B(t)\,B(t_2)\,B(t_3)\rangle\left[A(t),A(t_2)\,A(t_3)\,\rho_s^I(0)\,A(t_4)\right]$$

$$+\langle B(t_4)\,B(t_2)\,B(t)\,B(t_3)\rangle\left[A(t),A(t_3)\,\rho_s^I(0)\,A(t_4)\,A(t_2)\right]$$

$$+\langle B(t_4)\,B(t_3)\,B(t_2)\,B(t)\rangle\left[A(t),\,A(t_2)\,\rho_s^I(0)\,A(t_4)\,A(t_3)\right]$$

$$-\langle B(t_4)\,B(t_3)\,B(t_2)\,B(t)\rangle\left[A(t),\,\rho_s^I(0)\,A(t_4)\,A(t_3)\,A(t_2)\right]$$

Substituting equations (C-7) and (C-8) into the expression for $d\rho_s^I(t)/dt$, we find

$$\frac{d\rho_s^I(t)}{dt}=\frac{1}{\hbar^2}\Big[A(t), \tag{C-9}$$

$$\rho_s^I(0)\int_0^t dt_2\langle B(t_2)\,B(t)\rangle A(t_2)-\int_0^t dt_2\langle B(t)\,B(t_2)\rangle A(t_2)\,\rho_s^I(0)$$

$$+\frac{1}{\hbar^2}\int_0^t dt_2\int_0^{t_2} dt_3\int_0^{t_3} dt_4\Big\{\langle B(t)\,B(t_2)B(t_3)B(t_4)\rangle A(t_2)\,A(t_3)\,A(t_4)\,\rho_s^I(0)$$

$$-\langle B(t_2)\,B(t)\,B(t_3)\,B(t_4)\rangle A(t_3)A(t_4)\,\rho_s^I(0)\,A(t_2)$$

$$-\langle B(t_3)\,B(t_2)\,B(t)\,B(t_4)\rangle A(t_2)\,A(t_4)\,\rho_s^I(0)\,A(t_3)$$

$$+\langle B(t_3)\,B(t_2)\,B(t)\,B(t_4)\rangle A(t_4)\,\rho_s^I(0)\,A(t_3)A(t_2)$$

(continued)

$$- \langle B(t_4)B(t)B(t_2)B(t_3)\rangle A(t_2)A(t_3)\rho_s^I(0)A(t_4)$$

$$+ \langle B(t_4)B(t_2)B(t)B(t_3)\rangle A(t_3)\rho_s^I(0)A(t_4)A(t_2)$$

$$+ \langle B(t_4)B(t_3)B(t)B(t_2)\rangle A(t_2)\rho_s^I(0)A(t_4)A(t_3)$$

$$- \langle B(t_4)B(t_3)B(t_2)B(t)\rangle \rho_s^I(0)A(t_4)A(t_3)A(t_2)\Big\}\Big]$$

We concentrate upon the integrand of the triple integral. Substituting the decomposition of equation (C-1), it becomes

$$\langle B(t)B(t_2)\rangle\Big\{\langle B(t_3)B(t_4)\rangle\big[A(t_2)A(t_3)A(t_4)\rho_s^I(0) - A(t_2)A(t_4) \qquad \text{C-10}$$

$$\times\rho_s^I(0)A(t_3)\big] + \langle B(t_4)B(t_3)\rangle\big[-A(t_2)A(t_3)\rho_s^I(0)A(t_4)$$

$$+ A(t_2)\rho_s^I(0)A(t_4)A(t_3)\big]\Big\} + \langle B(t_2)B(t)\rangle\Big\{\langle B(t_3)B(t_4)\rangle$$

$$\times\big[-A(t_3)A(t_4)\rho_s^I(0)A(t_2) + A(t_4)\rho_s^I(0)A(t_3)A(t_2)\big]$$

$$+ \langle B(t_4)B(t_3)\rangle\big[A(t_3)\rho_s^I(0)A(t_4)A(t_2) - \rho_s^I(0)A(t_4)A(t_3)A(t_2)\big]\Big\}$$

$$+ \langle B(t)B(t_3)\rangle\Big\{\langle B(t_2)B(t_4)\rangle\big[A(t_2)A(t_3)A(t_4)\rho_s^I(0) - A(t_3)A(t_4)$$

$$\times\rho_s^I(0)A(t_2)\big] + \langle B(t_4)B(t_2)\rangle\big[-A(t_2)A(t_3)\rho_s^I(0)A(t_4)$$

(continued)

$$+A(t_3)\,\rho_s^I(0)\,A(t_4)\,A(t_2)\Big]\Big\} + \langle B(t_3)B(t_4)\rangle \Big\{\langle B(t_2)B(t_4)\rangle$$

$$\times\Big[A(t_4)\,\rho_s^I(0)\,A(t_3)A(t_2) - A(t_2)A(t_4)\,\rho_s^I(0)\,A(t_3)\Big]$$

$$+\langle B(t_4)B(t_2)\rangle\Big[A(t_2)\,\rho_s^I(0)\,A(t_4)A(t_3) - \rho_s^I(0)\,A(t_4)A(t_3)A(t_2)\Big]\Big\}$$

$$+\langle B(t_1)B(t_4)\rangle\Big\{\langle B(t_2)B(t_3)\rangle\Big[A(t_2)A(t_3)A(t_4)\,\rho_s^I(0) - A(t_3)A(t_4)\,\rho_s^I(0)\,A(t_2)\Big]$$

$$+\langle B(t_3)B(t_2)\rangle\Big[A(t_4)\,\rho_s^I(0)\,A(t_3)A(t_2) - A(t_2)\,A(t_4)$$

$$\times\,\rho_s^I(0)\,A(t_3)\Big]\Big\} + \langle B(t_4)\,B(t)\rangle\Big\{\langle B(t_2)B(t_3)\rangle$$

$$\times\Big[A(t_3)\,\rho_s^I(0)\,A(t_4)\,A(t_2) - A(t_2)\,A(t_3)\,\rho_s^I(0)\,A(t_4)\Big]$$

$$+\langle B(t_3)B(t_2)\rangle\Big[A(t_2)\,\rho_s^I(0)\,A(t_4)A(t_3) - \rho_s^I(0)\,A(t_4)A(t_3)A(t_2)\Big]\Big\}$$

The next step is not obvious from a strategic point of view but it turns out that we need to factor from each term an A operator whose time argument is coupled to t in the correlation functions. For example, in the terms proportional to $< B(t)B(t_2) >$, we factor $A(t_2)$ to the left. In the terms proportional to $< B(t_2)B(t) >$, we factor $A(t_2)$ to the right. In the process, we add whatever commutators that are needed to take into account the non-commutivity of the A operators at different times. We obtain

$$\langle B(t)B(t_2)\rangle\, A(t_2)\Big\{\langle B(t_3)B(t_4)\rangle\,[A(t_3), A(t_4)\,\rho_s^I(0)]$$

$$-\langle B(t_4)B(t_3)\rangle\,[A(t_3), \rho_s^I(0)]\Big\}$$

$$+\langle B(t)B(t_3)\rangle\, A(t_3)\Big\{\langle B(t_2)B(t_4)\rangle\,[A(t_2), A(t_4)\,\rho_s^I(0)]$$

$$-\langle B(t_4)B(t_2)\rangle\,[A(t_2), \rho_s^I(0)\,A(t_4)]\Big\}$$

$$+\langle B(t)B(t_4)\rangle\, A(t_4)\Big\{\langle B(t_2)B(t_3)\rangle\,[A(t_2), A(t_3)\,\rho_s^I(0)]$$

$$-\langle B(t_3)B(t_2)\rangle\,[A(t_2), \rho_s^I(0)\,A(t_3)]\Big\}$$

$$+\Big\{\langle B(t_4)B(t_3)\rangle\,[A(t_3), \rho_s^I(0)\,A(t_4)]$$

$$-\langle B(t_3)B(t_4)\rangle\,[A(t_3), A(t_4)\,\rho_s^I(0)]\Big\}\langle B(t_2)B(t)\rangle A(t_2)$$

$$+\Big\{\langle B(t_4)B(t_2)\rangle\,[A(t_2), \rho_s^I(0)\,A(t_4)]$$

$$-\langle B(t_2)B(t_4)\rangle\,[A(t_2), A(t_4)\,\rho_s^I(0)]\Big\}\langle B(t_3)B(t)\rangle A(t_3)$$

$$+\Big\{\langle B(t_3)B(t_2)\rangle\,[A(t_2), \rho_s^I(0)\,A(t_3)]$$

$$-\langle B(t_2)B(t_3)\rangle\,[A(t_2), A(t_3)\,\rho_s^I(0)]\Big\}\langle B(t_4)B(t)\rangle A(t_4)$$

$$+\langle B(t)B(t_3)\rangle\langle B(t_2)B(t_4)\rangle\,[A(t_2), A(t_3)]\,A(t_4)\,\rho_s^I(0) - \langle B(t)B(t_3)\rangle$$

(continued)

$$\times\langle B(t_4)B(t_1)\rangle\left[A(t_2),A(t_3)\right]\rho_s^I(0)A(t_4)-\langle B(t_3)B(t_1)\rangle\langle B(t_2)B(t_4)\rangle$$

$$\times\left[A(t_2),A(t_3)\right]A(t_4)\rho_s^I(0)+\langle B(t_3)B(t_1)\rangle\langle B(t_4)B(t_2)\rangle\left[A(t_2),A(t_3)\right]$$

$$\times\rho_s^I(0)A(t_4)+\langle B(t_1)B(t_4)\rangle\langle B(t_2)B(t_3)\rangle\left[A(t_3),A(t_4)\right]A(t_2)\rho_s^I(0)$$

$$+\langle B(t_1)B(t_4)\rangle\langle B(t_2)B(t_3)\rangle\left[A(t_2),A(t_4)\right]A(t_3)\rho_s^I(0)-\langle B(t_1)B(t_4)\rangle$$

$$\times\langle B(t_2)B(t_3)\rangle\left[A(t_3),A(t_4)\right]\rho_s^I(0)A(t_2)+\langle B(t)B(t_4)\rangle\langle B(t_3)B(t_2)\rangle$$

$$\times\left[A(t_2),A(t_4)\right]\rho_s^I(0)A(t_3)-\langle B(t_4)B(t)\rangle\langle B(t_2)B(t_3)\rangle\left[A(t_2),A(t_4)\right]A(t_3)\rho_s^I(0)$$

$$-\langle B(t_4)B(t)\rangle\langle B(t_3)B(t_2)\rangle\left[A(t_3),A(t_4)\right]A(t_2)\rho_s^I(0)+\langle B(t_4)B(t)\rangle\langle B(t_3)B(t_2)\rangle$$

$$\times\left[A(t_3),A(t_4)\right]\rho_s^I(0)A(t_2)+\langle B(t_4)B(t)\rangle\langle B(t_3)B(t_2)\rangle\left[A(t_2),A(t_4)\right]\rho_s^I(0)A(t_3)$$

This expression is to be substituted for the integrand of the triple integral term of equation (C-9). The resulting complicated form may be considerably simplified by judiciously relabeling variables of integration and combining terms where possible. The end product is

$$\frac{d\rho_s^I(0)}{dt}=\frac{1}{\hbar^2}\Big[A(t), \qquad \text{C-11}$$

$$\int_0^t dt_2\left\{\rho_s^I(0)+\frac{1}{\hbar^2}\int_0^t dt_3\int_0^t dt_4\left[A(t_3),\langle B(t_4)B(t_3)\rangle\rho_s^I(0)A(t_4)\right.\right.$$

$$\left.\left.-\langle B(t_3)B(t_4)\rangle A(t_4)\rho_s^I(0)\right]\right\}\langle B(t_2)B(t)\rangle A(t_2)-\int_0^t dt_2\langle B(t)B(t_2)\rangle A(t_2)$$

(continued)

$$\times\left\{\rho_s^I(0)+\frac{1}{\hbar^2}\int_0^t dt_3\int_0^{t_3} dt_4\left[A(t_3),\langle B(t_4)B(t_3)\rangle\rho_s^I(0)A(t_4)-\langle B(t_3)B(t_4)\rangle A(t_4)\rho_s^I(0)\right]\right\}\Big)$$

$$-\frac{1}{\hbar^2}\rho_s^I(0)\int_0^t dt_2\int_0^t dt_3\int_0^{t_3} dt_4\ A(t_2)\Big\{\langle B(t_4)B(t)\rangle\langle T_-^B B(t_3)B(t_2)\rangle[A(t_4),A(t_3)]$$

$$-\langle B(t)B(t_4)\rangle\langle B(t_2)B(t_3)\rangle[A(t_4),A(t_3)]\Big\}$$

$$-\frac{1}{\hbar^2}\rho_s^I(0)\int_0^t dt_2\int_0^t dt_3\int_0^{t_3} dt_4\ A(t_2)\Big\{\langle B(t)B(t_4)\rangle\langle T^B B(t_3)B(t_2)\rangle[A(t_4),A(t_3)]$$

$$-\langle B(t_4)B(t)\rangle\langle B(t_2)B(t_3)\rangle[A(t_4),A(t_3)]\Big\}\rho_s^I(0)$$

But

$$\rho_s^I(0)$$

$$+\frac{1}{\hbar^2}\int_0^t dt_3\int_0^{t_3} dt_4\left[A(t_3),\langle B(t_4)B(t_3)\rangle\rho_s^I(0)A(t_4)-\langle B(t_3)B(t_4)\rangle A(t_4)\rho_s^I(0)\right]$$

is the first order expression for $\rho_s^I(t)$ and to the accuracy desired, may be replaced by $\rho_s^I(t)$. The triple integrals contain $\rho_s^I(0)$ which is the zeroth order approximation to $\rho_s^I(t)$ and since these terms are already small, we may also replace it by $\rho_s^I(t)$. Then,

$$\frac{d\rho_s^I(t)}{dt}=-\frac{1}{\hbar^2}\Big[A(t),\rho_s^I(t)\int_0^t dt_2\,A(t_2)\Big\{\langle B(t_2)B(t)\rangle \qquad \text{C-12}$$

$$-\frac{1}{\hbar^2}\int_0^t dt_3\int_0^{t_3} dt_4\langle B(t_4)B(t)\rangle\langle T_-^B B(t_3)B(t_2)\rangle[A(t_4),A(t_3)]$$

(continued)

$$+\frac{1}{\hbar^2}\int_0^t dt_3 \int_0^{t_3} dt_4 \langle B(t)B(t_4)\rangle \langle B(t_2)B(t_3)\rangle \left[A(t_4), A(t_3)\right]\Big\}$$

$$-\int_0^t dt_2\, A(t_2)\Big\{\langle B(t)B(t_2)\rangle + \frac{1}{\hbar^2}\int_0^t dt_3 \int_0^t dt_4 \langle B(t)B(t_4)\rangle \langle T^D B(t_3)B(t_2)\rangle \left[A(t_4), A(t_2)\right]$$

$$+\frac{1}{\hbar^2}\int_0^t dt_3 \int_0^{t_3} dt_4 \langle B(t_4)B(t)\rangle \langle B(t_2)B(t_3)\rangle \left[A(t_4), A(t_3)\right]\Big\}\rho_S^I(t)\Big]$$

which is identical to the interaction picture representation of the equation of motion for the reduced density operator as derived by the more rigorous treatment of Chapter VI.

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14. The doubling of the system space as a device has been employed by others. Schwinger in Ref. 5 makes a distinction between operators that propagate forward in time and those that propagate in the reverse sense. Louisell in Ref. 3 uses a disjoint system space in order to prove various operator theorems. R. P. Feynman and F. L. Vernon, Annals Physics, 24, 118 (1963) using Feynman's path integral techniques, double the integration variables for the path

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18. These ideas have been exploited extensively by R. P. Feynman in Ref. 15.

19. I am indebted to H. A. Gersch and R. F. Fox for introducing me to the general topic of cumulants. They jointly conducted a seminar in which several possible applications of the cumulant expansion were discussed. The papers by Kubo[35] and Glauber[34] give examples of the uses of cumulants in physics.

20. In effect, we are saying that system operators vary so little in the time interval $(t-t_c, t)$ that, if $t-t_c < t_1, t_2 < t$, then $[A(t_1), A(t_2)] = 0$.

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28. The proof of these theorems closely follows that of the theorems contained in equations (II-24) and (II-25).

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32. The general proof was found by J. F. Fernandez, Instituto Venezelano de Invesigaciones Cientificas, Caracas, Venezuela, and will be included in a paper to be published.

33. A. L. Fetter and J. D. Walecka, Quantum Theory of Many-Particle Systems (McGraw-Hill Book Co., New York, 1971).

34. R. J. Gauber, Lectures in Theoretical Physics, edited by W. E. Brittin and L. G. Dunham (Interscience, New York, 1959), Vol. 1.

35. R. Kubo, in Fluctuation, Relaxation, and Resonance in Magnetic Systems, edited by D. ter Haar (Oliver and Boyd, Edinburgh, Scotland, 1962).

VITA

Robert Estel Westerfield was born on December 16, 194[illegible] in San Diego, California. His early education was obtained in Arkansas and Florida. After graduating from high school, he served a four-year enlistment in the Air Force followed by another four years in the Marine Corps. During his second tour of duty, he discovered rather belatedly that he had more aptitude for the scholarly professions than for the martial arts (a feeling that became a certainty during a thirteen-month stay in Vietnam); he therefore matriculated at San Diego State University and was awarded a Bachelor of Science degree in Physics in June 1970. Graduate work immediately followed at the Georgia Institute of Technology where the Master's degree was earned in September 1971 and the requirements for the Ph.D. in Physics were satisfied by January, 1975. Since September 1974, he has been employed as a physicist at McMorrow Laboratories, Redstone Arsenal, Huntsville, Alabama by the U. S. Army.

Mr. Westerfield is married to the former Sonia F. Navarrete; they are the parents of two daughters, Marissa Anne and Christine Elizabeth.