***7. The Reduced Density Matrix Description of Dissipative Dynamics***

In the last section we derived a very important result: The dissipative dynamics of the system are completely defined by the spectral density of the system-bath interaction. Here it useful to again define what the spectral density actually is:-

***Spectral Density***: A function describing the distribution of oscillators (defined by their frequency and effective mass) in the bath, weighted by the coupling of each oscillator to the system.

We often choose to define everything in terms of the spectral density because it is experimentally measureable via techniques such as ***hole burning*** spectroscopy or it can be calculate using molecular dynamics. Of course, we could equally use the ***correlation function*** as the two map onto each other through the Fourier transform. We typically use the correlation function if we are deriving general rules from model assumptions. The reason we resort to a spectral density/correlation function description is because we have only a statistical knowledge of the system-bath interaction. Unfortunately, this means that we have ***no microscopic knowledge of part of the total super-system***. How then does one construct a density matrix for our system-bath super-system? The answer is that we don’t. We instead develop a ***reduced density matrix description of only the system degrees of freedom***.

*7.1. The Reduced Density Matrix*

Our total Hamiltonian is, as before,

If we first consider the non-interacting () case then we can factorize our total super-system density operator into system and bath sub-operators,

where and are the density operators for the uncoupled system and bath respectively. Of course when we cannot strictly perform such a factorization as the system and bath degrees of freedom are not independent of one another. However, we can produce a ***reduced density operator for the system*** by averaging over the degrees of freedom of the bath. In the uncoupled case,

Here denotes the trace over the bath degrees of freedom. does not depend on these degrees of freedom and so we can take it out of the trace and due to normalization. This is exact for the uncoupled case but we now define the ***reduced operator of the system*** as,

where is the full density operator of the interacting system-plus-bath super-system. contains all of the information on the system degrees of freedom. However, its dynamics will not be deterministic/reversible as it now subject to interaction with a large number of degree of freedom of which we have only a stochastic description. Effectively we have ***integrated out*** all of the microscopic information regarding the bath. We tend to drop the subscript in most discussions and assume that implicitly refers to the system.

We can now express the ***reduced density matrix elements*** in some appropriate basis. Let us assume that we have a basis, , that spans the system and a basis, , that spans the bath. The full density matrix would actually be a rank-4 matrix,

Therefore,

and we notice that spans only the system.

Conclusions

(1) We define the ***reduced density matrix*** of our system by tracing over the bath degrees of freedom,

*7.2 An oscillator in a harmonic bath*

As before, our model system will be a harmonic oscillator in a harmonic bath. Let us start with the Caldeira-Legget Hamiltonian and express the system momentum/coordinate in terms of bosonic operators,

where is the natural frequency of the relevant oscillator. This is quite a complex Hamiltonian and it actually serves us to consider the different terms separately. To do this we make a distinction between ***diagonal*** and ***off-diagonal fluctuations***.

**7.2.1 Off-diagonal fluctuations**

Let us first neglect the term in ,

and define a basis, , that spans only the system. These will be the particle number states of the oscillator. We first define an analogue of the Liouville-von Neumann equation for the total density matrix of our super-system. Firstly,

Let us consider the matrix element,

where is the matrix element of the bath Hamiltonian. Since the basis spans only the system,

Therefore,

Similarly,

Therefore,

Eqn. (503) contains the full time-dependence of the system-plus-bath, including the unitary evolution of the system and bath separately. It makes sense to remove this by switching to the interaction representation,

where is the full density matrix in the interaction representation. The matrix elements are,

We can substitute this into Eqn. (503). Let’s consider the left hand side first,

Now we consider the right hand side,

Equating Eqns. (506) and (507) and cancelling terms,

Rearranging,

If we define the bath operators in the interaction representation,

then,

The next step may seem a little odd but it vastly simplifies our final result. We first integrate Eqn. (511),

and we then substitute this solution back into Eqn. (511). Seemingly it will give us 20 rather complicated terms but we can argue that most of the can be neglected. Let us consider the first term on the right hand side of Eqn. (511),

This looks horrendous but there are three points to consider. Firstly, since the bath oscillators are independent of each other, their fluctuations are completely uncorrelated. Therefore, terms with in the double summation disappear. The first term also disappears since it contains a single power of and therefore averages out to zero,

Finally, we see that terms of the form,

since oscillates much more rapidly than . This is our old friend the ***rotating wave approximation***. This gives us,

By exactly the same logic we can evaluate all terms which we list in no particular order,

Although this is quite cumbersome we are now in a position to perform the trace over the bath coordinates. Let us define the reduced density operator in the interaction representation,

We also assume that, whatever happens to it, the bath is large enough to remain always at equilibrium. It is after all a heat bath, albeit a very structured one,

This gives us,

where we have taken advantage of the ***symmetry of the trace with respect to cyclic permutation***. Now, we are going to define the bath correlation function,

The complex conjugate is defined,

Therefore,

This looks very complicated but one can see from the indices that the different terms represent different processes. Let us consider the diagonal elements (the populations),

This describes the bath induced transfer of population between adjacent states of the relevant oscillator. The first two terms represent loss of population to the state below and above respectively. The third and fourth term accounts for gain of population from the lower and upper state respectively. Eqn. (523), subject to , describes the evolution of the coherences. The first thing we notice is that the dynamics of the coherence and the populations are de-coupled from each other. This is a quirk of the harmonic oscillator, specifically the fact that it possesses an infinite number of equally-spaced energy levels.

The other things we notice is that the dynamics have ***a memory*** in the sense that doesn’t simply depend on the current state of the bath but also on its state at some earlier time. The is an example of ***non-Markovian dynamics*** and it is purely an effect of averaging over the bath. An isolated system does not exhibit a memory.The ***Markov approximation*** is to neglect this memory effect. Providing that our system-bath interaction is weak (and we often build our theory to ensure this) then the reduced density matrix is slowly varying in the interaction representation. This means we can take it out of the integral. Defining the complex, time-dependent quantities,

we get,

If we define the real quantities,

we have,

If we assume then Eqn. (530) describes the evolution of the coherences. The first line describes their decay under the influence of the bath. The second and third describe the transfer of coherences between different states. If we consider the populations,

These ***Markovian*** equations of motion are conceptually simple but the time dependent rates make them make it difficult to solve. However, we can remember that the bath correlation function dies down to zero quite quickly. So long as we are not interested in the dynamics at ultra-short timescales we can extend the integrals in Eqns. (525) and (526) to infinity. Let us first substitute ,

Letting (and switching variables) we can define the ***rate constants***,

We now use our standard definition of the correlation function in Eqn. (410) in Section 5,

Exploiting the symmetry of all spectral density and hyperbolic functions,

Similarly,

We see that these ***rate constant are real***. If we take the ratio of these two rate constants we derive the ***detail balance condition***,

This justifies the labels. is the rate constant from transfer to an upper state and is therefore subject to a Boltzmann penalty. is a downward rate. We now have our Master Equation for the reduced density matrix of our oscillator in a harmonic bath. Our population dynamics are,

This is a very important result. We have a system of energy level, which in this case belong to a single harmonic oscillator. Transitions between these levels are induced by the bath and the stochastic nature of the bath means we have to describe these transitions statistically, as the flow of probability between states. Coherent transport is also present but only for short times as the bath cause a decay of coherence (i.e. dephasing). The critical result is that these dynamics depend only on the distribution of states in the system, the initial state of the system, and the spectral density of the system-bath interaction.

**7.2.2 Diagonal fluctuations**

Off-diagonal fluctuations mean that they couple adjacent states of the relevant oscillator. This is due to the term. However, we can also consider ***diagonal*** (or ***energy***) ***fluctuations*** that do not couple adjacent states. These are described by a Hamiltonian of the form,

Clearly this gives us the matrix elements,

and,

The Liouville-von Neumann equation is then,

Moving to the interaction representation as before,

Our interactive solution is,

Which we substitute back into Eqn. (544),

Performing the trace over the bath,

We can separate the correlation function into ***real and imaginary parts***,

So,

The first thing we see is that,

Meaning that diagonal fluctuations effect only the coherences and do not result in population relaxation/transfer. We can invoke the Markov approximation,

where,

is known as the ***decay rate*** and,

is the ***frequency shift***. A formal Markovian solution is therefore,

So diagonal fluctuations simply cause decay in the coherences. In practice both types of fluctuations may be present and they will have different spectral densities.

This analysis, although somewhat abstract, encapsulates the essence of open quantum system theory. We have a set of states (in this case they belong to a harmonic oscillator) that define our system. We can imagine preparing our system in some pure state and in the absence of any interaction with a bath the subsequent dynamics are completely unitary. However, it is the interaction with the bath that causes a ***dephasing*** of this coherence and the evolution into a statistical mixture. Typically, this involves some irreversible transfer of population known as ***relaxation***. In the next section we are going to generalize this approach and develop several well know theories of energy transfer.

**Conclusions**

(1) ***Off-diagonal fluctuations*** in the bath cause ***population relaxation*** and ***coherence dephasing*** in the system. The latter is the result of the system becoming entangled with bath degrees of freedom that we are not observing.

(2) The reduced density matrix of the system possesses a ***memory of the previous state of the bath***. However, this is quickly forgotten and we may make the ***Markov approximation***,

(3) The dynamics depend only on the distribution of states within the system, the initial state of the system and the ***spectral density of the bath***.

(4) ***Diagonal fluctuations*** do not induce population relaxation but only coherence dephasing.