***6. System Bath Interactions***

In the last section we started to think about how a stochastic external environment may affect a simple quantum system (namely a QHO). We used the simplest possible description of our environment, a ***thermal bath***. This is simply an infinitely large space at constant temperature. It has no internal structure, no internal dynamics but simply acts a source and sink for energy. This is a poor representation of the actual phenomena we are trying to study.

Our ***system*** consists entirely of electronic transitions between the inter-pigment excitonic states. These electronic transitions are strongly-coupled to the vibrational motion of the nuclei, which is coupled to the random motions of the protein binding pocket, which are coupled to rest of the protein, and so on and so forth. Although these various vibrational and thermal degrees of freedom collectively represent our ***environment***, there sharp boundary. We have to develop a more sophisticated description that takes into account the hierarchical structure of the environment. We are going to start by considering how our pigments vibrations are perturbed by the vibrations in the protein binding pocket. We are going to describe the nuclear vibrations as a QHO. These will be coupled to a set of thermal QHOs representing the protein binding pocket coupled to the wider thermal environment. Here we track our vibrational oscillator and refer to it as the ***relevant oscillator***. The thermal oscillators are collectively termed the ***harmonic environment*** or ***harmonic bath***. The effect of the harmonic bath is to ***damp*** the relevant oscillator resulting in dissipation.

*6.1 The Caldeira-Legget Model*

The relevant oscillator is described by the ***system Hamiltonian***,

where is the momentum operator and is the effective mass of the oscillator. is the potential energy terms which we do not specify other than to say it is obviously a function of the displacement of the oscillator . Here we use instead of since we are now explicitly dealing with a molecular vibrational normal mode. is generally used to denote a ***normal coordinate*** while is reserved for Cartesian coordinates. The infinitely large set of thermal oscillators constitutes the bath,

Each thermal oscillator has momentum, , Cartesian displacement, , natural frequency, , and effective mass, . As always the circumflexes indicate operators which will now drop. The ***system-bath interaction*** is currently undefined but must depend on the displacements of both the relevant and thermal oscillators,

Where the curly braces, , indicate a multiple set. We will assume that the ***coupling is linear***,

The negative sign is assigned purely because it makes our life easier later. We may do this since the ***coupling constant***, , are as yet undefined. The total Hamiltonian is defined,

Let us gather terms that depend on ,

We now define,

As the ***effective potential of the relevant oscillator*** under the influence of the harmonic bath,

Where we can think of,

as the ***effective potential of the th bath oscillator*** under the influence of the relevant oscillator. Eqn. (420) is known as the ***Caldiera-Legget Hamiltonian*** and its basic assumption is the linearity of the system-bath couplings.

**Conclusions**

The Hamiltonian for the entire ***super-system*** is a sum of ***system***, ***bath*** and ***system-bath interaction*** terms,

The assumption of ***linearity*** in the system-bath interaction defines the ***Caldiera-Legget Hamiltonian***,

*6.2 The correlation function of the quantum bath*

Possessing our Hamiltonian, we are now in a position to derive our equations of motion. However, we will first derive some useful rules. The ***canonical commutation relation*** states that,

This is true for any pair of ***conjugate variables*** but position and momentum are relevant to the task at hand. We can easily prove by considering the action of this commutator on some arbitrary spatial wave function,

Let us consider a generalization,

where is an integer. We have

Therefore,

Similarly, it can be shown that,

although the proof is a little more complicated. Let us work in the Heisenberg representation in which the implicit time dependence is transferred to the operators ( and ). According to Eqn. (121),

where we have used the fact that and commute, and commute (they coverer separate coordinate spaces) and commutes with itself. Using Eqn. (427),

We now take the derivative of Eqn. (430),

Where we have used the fact that commutes with and itself. We will take each term in turn. We can evaluate the first term by considering its effect on an arbitrary function,

Therefore,

The second term can be evaluated using Eqn. (426),

Lastly,

where we have used the identity

and the canonical commutation relation in Eqn. (422). Combining these terms,

By exactly the same logic,

where we have used the identity,

Next,

We now have two coupled second-order differential equations that describe the motion of the relevant oscillator and the harmonic bath,

It is a considerable challenge to solve these equations of motion. We will assume that and are not operators but variables. In other words, we solve these equations for the case of a classical oscillator in a classical harmonic bath. We can then quantize our solution by replacing variables with operators. We start by solving Eqn. (441). Since it is a second order ***inhomogeneous differential equation*** it will have solution,

is known as the ***homogeneous part*** or ***complimentary function*** and is the general solution to the homogenous differential equation,

or,

is a ***particular solution*** to Eqn. (441), also known as the ***inhomogeneous part***. The homogeneous equation Eqn. (443) has general solution,

The coefficients, , can be generally expressed in terms of the initial conditions,

and,

Therefore,

and,

Therefore, complimentary function is,

Note that the is still a general solution to the homogeneous function as we have not specified values for or .

We obtain a particular solution to Eqn. (441) by the method of ***Green’s function***. If we have a general differential equation,

where and are functions and is a ***general linear differential operator***, then Green’s function, , satisfies,

where is (as always) the Dirac -function. The solution to Eqn. (452) will be,

We can prove this simply by substituting Eqn. (454) into Eqn. (452),

where we have used ***Leibniz’s rule*** on the second line. For Eqn. (441) our differential operator is,

Therefore, our Green’s function must satisfy,

and our particular solution must have the form,

Since it is a particular function we must specify a particular set of initial conditions. Also, is not an independent function but is coupled to by Eqn. (440). We therefore need to enforce a causal relationship. We do this by assuming,

and

Eqn. (460) effectively means that the system-bath interaction is ‘switched on’ at . We can do this because the bath has a ***finite memory*** and therefore for finite times this continuity is ‘forgotten’. Eqn. (457) looks simple but the -function means it can’t just be directly integrated. We can solve it by performing a Fourier transform to the frequency domain,

Using the differentiation property of the Fourier transform,

we get,

or,

We can reverse transform this back to the time-domain which involves rearranging variables and using the Cauchy integration method for complex functions. However, we can just look up the answer in a table of Fourier transform pairs and apply our initial conditions,

where,

is the ***Heaviside step function***. Substituting this into Eqn. (458) yields our particular solution,

where the lower bound comes from . We will partially evaluate this integral by parts to make the final conclusion neater. Let us assume,

So that,

where,

Our solution to Eqn. (441) is now the rather cumbersome,

We can now substitute this into Eqn. (440),

If we define,

and rearrange,

Lastly we define,

to obtain the ***Langevin equation*** for an oscillator coupled to a harmonic bath,

Let us compare this to a general equation for a ***driven***, ***damped oscillator***,

We see that is a ***time-dependent driving term*** and characterizes ***friction*** or ***damping***. The term is the ***restoring force*** (gradient forces are the gradient of a potential) and describes the normal oscillatory motion in the absence of the bath. The final term, , characterizes the initial state of the oscillator when the system bath-interaction was ‘switched on’. Essentially the system-bath interaction has been ‘on’ for a very long time and so any initial state of the oscillator is ***forgotten*** in a finite time. In most situations we can neglect this term. Finally, although we derived Eqn. (468) for the classical case it also holds for the quantum case. We merely replace all position and momentum variable with their operator counterparts knowing that they obey the canonical commutation relation.

The analytical definitions in Eqns. (464) and (466) imply that the driving, , and friction, , terms are deterministic. However, while these definitions are formally correct, both of these terms will be stochastic. The bath contains, effectively, an infinite number of modes and we have no information regarding their initial positions, , or momenta, . We have to therefore develop a stochastic definition of these terms using correlation functions. As before, we start in the classical case.

Due to its stochastic nature we are going to term the ***fluctuating force***. We see from Eqn. (464) that is purely a property of the bath which we assume is at equilibrium. The classical equilibrium probability distribution of the bath is given by,

where, is the energy of the th bath oscillator, is the classical partition function of the bath. We assume that the bath oscillators are independent of one another and therefore the bath partition function is the product of the individual partition functions of each bath oscillator,

Since,

and in the classical case and are continuous variables,

This double Gaussian integral is actually straight forward to evaluate,

Therefore, we have the simple result for the classical partition function,

where is the number of oscillators within the bath. Practically, this is an uncountable number. However, it will not be present in the derived statistical quantities that we are interested in. The total probability distribution is therefore,

However, since the oscillators are independent their collective properties are completely defined by their individual properties. The probability distribution per oscillator or the ***classical probability density*** is,

We can describe the fluctuating force by its moments, the first of which is the ***mean force*** exerted on the relevant oscillator by the bath. Since we assume that the bath is at equilibrium this will be time independent,

where the last step comes from the fact we are integrating an odd function symmetrically about the origin. We could have guessed this result since it is obvious that the bath cannot exert some ***net force*** on our relevant oscillator. The ***generalized second moment*** gives us our correlation function,

Although this looks horribly complicated, it is obvious that the second term disappears due to symmetry. Therefore,

Remember that this is a classical result. If we look at the definition of the classical position correlation function of an oscillator in Eqn. (397) in the last section we see that,

There is a lot of indices but essentially the force correlation function is simply the weighted sum of the position correlation functions of each oscillator, the weighting being the square of the coupling constants, . However, we can also use Eqn. (466), the expression for the time dependent friction, to get,

Which is the ***classical fluctuation-dissipation theorem***. This is a vitally important result as it tells us that the equilibrium fluctuations in the bath dampen our relevant oscillator. Eqn. (480) implies that ***the full quantum mechanical correlation function*** is simply,

As before, it is instructive to look at the ***even and odd parts*** separately. The even part,

Is temperature dependent and in the high-temperature limit () reduces to the classical fluctuation,

The odd part,

is imaginary, temperature-independent and represents the pure quantum fluctuations. We can also define the spectral density in analogy with Eqn. (403) in Section 5,

and since our grand result in Section 5 is completely general

If we consider the high temperature limit of the symmetric part,

where,

is one form of the ***quantum fluctuation-dissipation theorem.*** Although quite condensed it tells us that the dissipative dynamics of the relevant oscillator are totally defined by the spectral density of the harmonic bath. As before this relation is actually very general.

Although this section is rather abstract it reveals a critically important and highly general result. The dynamics of our system can be thought of as deterministic motion (which is defined by its internal properties) that is damped and rendered stochastic by the bath. More importantly, the stochastic dynamics are determined by two things, the fluctuating force and the time-dependent friction, which we see are both ***completely defined by the spectral density of the bath***. In the next section we will use this gold nugget to develop a density matrix representation of our dissipative system.

**Conclusions**

(1) The equation of motion for the relevant oscillator is expressed (in addition to its internal properties) in terms of the ***time-dependent friction***, , and the ***fluctuating force***, ,

These determine the stochastic part of the dynamics of the relevant oscillator.

(2) The fluctuating force is completely defined by the correlation function,

(3) The time dependent friction is defined,

(4) We see that the stochastic dynamics of our system are completely determined by the spectral density of the bath.