***5. Stochastic Dynamics and the Reduced Density Operator***

So far our discussions of quantum systems have been limited to closed systems. That is systems that are completely defined by a countable set of basis states. We have dealt with external interactions in a rather superficial way, with a time-dependent potential/perturbation inducing transitions/coherences between these states. To do this there must be energy exchange between our system and some external environment but we have never given any detailed description of this environment. Even when we discussed Forster theory we glossed over the system-environment interaction. We simply stated that it determines the donor and acceptor line shapes and acts a thermal bath into which we can instantaneously and irreversibly dump reorganization energy. This is obviously unrealistic, just like our relevant system the environment can exist in various different states.

The problem we encounter is that our environment typically contains a very large number of degrees of freedom that we do not (or cannot) track experimentally. The prime example would be the ever-fluctuating nuclear configurations of our molecules. These movements strongly influence our electronic transitions but cannot themselves be precisely tracked. However, we assign certain statistical properties to these fluctuations. They will have some average value and some statistical variance. They may be strongly-correlated to each other and therefore more like actual vibrations. Alternatively, they could be only very weakly correlated and therefore essentially just jerky, random movements. Quantifying such properties statistically allows us to develop a ***stochastic*** description of our environment and system-environment interaction. We will do this here by introducing two important concepts, the ***equilibrium quantum harmonic oscillator*** and the ***spectral density*** for bath induced fluctuations.

*5.1 The Quantum Harmonic Oscillator*

The *bath* in our case consists of the random nuclear motion of our chromophores. Providing these momentary distortions are not too severe they will be some linear combination of ***normal distortions***. The nuclear configuration of our chromophores can therefore be thought of as a set of ***quantum harmonic oscillators*** (QHOs) that undergo fluctuations due their random interaction with the wider thermal environment (the protein, water, lipid, etc.). However, we will first discuss the properties of a fully deterministic (i.e. isolated) QHO.

The Hamiltonian for a QHO is,

where and are the momentum and displacement of the oscillator respectively, is its effective mass and is the natural frequency of the oscillator. The circumflexes over , and simply indicate operators and are hereafter dropped. The eigenstates of the QHO satisfy,

where,

and,

There derivation of these solutions, along with the spatial wave function, , can be found in any undergraduate text on quantum mechanics. Here we simply quote it,

Here we have defined a ***dimensionless coordinate***,

is a normalization constant,

and are the ***Hermite polynomials***,

The key point for us is that the QHO has an infinite number of states which are equally-spaced by an amount . This ‘ladder’ of states allows us to introduce the concept of ***second quantization***. We can define ***raising*** ***and lowering operators*** that have the following effect,

where the coefficients simply ensure correct normalization. We can now introduce the concept of energy ***quanta*** or ***particles***. denotes a state with ‘vibrational particles’ (termed ***phonons***). As more particles are added the energy increases, as particles are removed the energy decreases. contains no particles and therefore is the ground state of the QHO. This leads to the obvious property,

In terms of particles the action of on is to ***create*** an additional particle. Similarly the action of on destroys or ***annihilates*** a particle. Therefore we refer to and as ***creation and annihilation operators***. We touched on these briefly when calculating resonance coupling in Chapter 3. If we consider the successive action of both operators,

Therefore, the states are eigenstates of the combined operator with eigenvalues equal to the number of phonons. Therefore is called the ***number operator***. We can therefore write our QHO Hamiltonian as,

If we reverse the order we get,

This leads to the famous ***commutation relation for bosonic operators***,

We use the term ‘bosonic’ to mean particles with ***integer spin*** such as the spin-less (spin-0) phonons. We can also define creation and annihilation operators for ***fermions*** (such as electrons). They have a similar effect but obey the fermionic anti-commutation relation,

We mention this just in passing for completeness and will discuss them in more detail when they are required.

Our energy eigenstates, which we can alternatively think of as ***particle number states***, define a complete basis. Since we are dealing with an isolated oscillator we can define some general pure state,

We can then transform to the density matrix representation as in Eqn. (246),

This gives us no new information but does set us up for the next section when we start thinking in terms of ***statistical mechanics***.

**Conclusions**

(1) The eigenstates of the QHO form an infinite, evenly spaced ‘ladder’ of states,

(2) We can alternatively view these as ***phonon number states***,

(3) The eigenstates are Gaussian functions multiplied by ***Hermite polynomials***. The order of the Hermite polynomial increases with energy.

*5.2 The QHO at Thermal Equilibrium with its Environment*

Let us assume that our QHO is embedded in an environment with which it can exchange energy but not matter. Such as system is termed ***closed*** (as opposed to an ***isolated system*** which can exchange neither energy nor matter with the environment). Let us further assume that the environment is infinitely large and is at a constant temperature, . We call this a ***thermal environment***. Left to itself the QHO will reach thermal equilibrium. The density matrix for a equilibrium state will be diagonal,

where the diagonal elements, , are the probabilities of finding the system in a particle vibrational level, . For a pure state the probabilities are given by the square of the complex amplitudes. However, the system will not be in a pure state due to its interaction with a random thermal environment. It is properly described as a ***statistical mixture***. We are not going to present a detailed review of statistical physics. We are simply going to state that the probabilities will be given by the ***Boltzmann distribution***,

where is the Boltzmann factor and,

Is the ***partition function***. In Eqn. (345) is there to ensure correct normalization. However, the partition function is of central importance in statistical physics as it can be used to derive all thermodynamic parameters relevant to our system. Using the series expansion of the exponential function and Eqn. (328) we can define the ***equilibrium density operator***,

Substituting Eqn. (329) into Eqn. (345) gives,

Similarly,

Using the convergence theorem,

we get,

Therefore,

Eqn. (352) is the probability of finding our QHO with energy or equivalently the probability that our QHO contains phonons. The ***mean number of phonons will be given by the first moment of*** ,

Using the identity,

gives,

This is the so called ***Bose-Einstein distribution*** which connects the mean number of phonons to the inverse temperature, . It lies at the heart of the quantum statistics of bosonic particles. It tells us that at low temperatures , meaning that the oscillator will be in its ground state. At high temperatures . This means that our oscillator can potentially contain an infinite number of photons.

While the energy/phonon number basis is a convenient diagonal representation we would also like to express the density matrix in the ***coordinate basis***. We are, after all interested in how the actual physical displacement, , of the QHO is affected by the thermal environment. To transform to the coordinate basis we use the completeness of the energy/particle number basis,

Using the definition of the QHO wave functions,

Evaluating the infinite summation in Eqn. (356) is very difficult and long winded. Suffice to say it can be ‘simplified’ to,

This is a very complicated expression but the first thing we notice is that because and are continuous then is also continuous. is therefore a function that tells us about the statistical properties of the oscillator. Let us start with the ‘diagonal’ terms or ***probabilities***,

This gives us the probability of finding our oscillator displaced from the equilibrium point by a distance . We see that this is a Gaussian function in . The general expression for a Gaussian function is,

where is the ***mean*** and is the ***variance***. Formally, the ***mean displacement will be given by the first moment of***  but since it is a Gaussian we can already tell that the ***mean displacement will be zero***,

This makes complete sense as our oscillator is harmonic, meaning the potential energy is symmetric for positive (extensions) and negative (compressions) displacements. Formally, the ***variance in the displacement is given by the second moment of***  but again, since it is a Gaussian, we can just read it from Eqn. (358),

This is not an intuitive expression so we can get more of a feel for Eqn. (361) if we consider the ***quantum and classical limits***. The ***classical limit*** is reached at high temperatures (),

The classical variance is therefore,

Eqn. (361) tells us that the fluctuations in the displacement of our oscillator increase linearly with temperature. Also, the inverse dependence on tells us that a ***stiff*** (i.e. high frequency) oscillator will show lower amplitude fluctuations than a ***loose*** (i.e. low frequency) one.

At the other extreme () we have the ***quantum limit*** where Eqn. (358) becomes,

where is simply the probability distribution of the QHO ground state. Therefore, in the low temperature (quantum) limit these fluctuations are due purely to quantum uncertainty. They are necessarily independent of temperature. The quantum variance in the displacement is,

and therefore entirely determined by the frequency (and mass) of the oscillator. The variance basically represents the ***spread*** of random displacements that are realized by our random oscillator. It actually has the dimensions of ***distance squared*** so we can define a typical ***length scale for our quantum fluctuations***,

Therefore,

It is worth noting that while the equilibrium density matrix of our QHO is diagonal in the basis of energy (particle number) eigenstates, it is not necessarily diagonal in the coordinate basis (as seen from Eqn. (355)). The off-diagonal elements are ***coherences between displacement***, i.e. they describe the QHO being in a quantum mechanical super-position of different displacement. This is what people are referring to when they talk (incorrectly) about quantum particles being in two places at the same time. Realistically, it just reflects the wave-like nature of quantum objects. Let us consider the high temperature () limit of Eqn. (357),

Clearly,

very rapidly with decreasing . Therefore, in the ***thermal limit***,

The exponential term in Eqn. (370) goes to zero very rapidly either with increasing temperature (i.e. decreasing ) or as gets larger. Essentially this means that,

Meaning that at high temperatures the equilibrium QHO just performs incoherent Gaussian fluctuations.

**Conclusions**

(1) A quantum oscillator at equilibrium with its environment will perform Gaussian fluctuations with a zero mean,

and a non-zero variance.

(2) In the ***thermal limit*** these fluctuations are purely classical (and diagonal) and depend on the temperature of the environment,

(3) In the ***quantum (low temperature) limit*** the fluctuations are still present but they are due to inherent quantum uncertainty rather than the thermal environment,

where,

is the fundamental ***length-scale*** of the quantum fluctuations.

(4) In the quantum limit there are coherences between different displacements but these rapidly fall to zero as the temperature increases,

*5.3 The Dynamics of a QHO at thermal equilibrium*

In the last section we talked about static properties of the equilibrium QHO such as its average displacement and the distribution of energies/phonon numbers. However, we also need to characterize its dynamical properties, i.e. how its displacement varies in time. The problem is that our QHO is subject to a ***stochastic force*** from the thermal environment and it is therefore impossible to write down analytical function for . The stochastic motion must be characterized in terms of a ***correlation function***,

Let us recall the QHO Hamiltonian in Eqn. (327) which is a composite operator of and . We can express these operators in terms of the creation and annihilation operators,

where is the length-scale defined in Eqn. (366). We can substitute these into Eqn. (327) just to show consistency,

Using the commutation relation in Eqn. (340),

We also have the inverse relations,

Let us focus on the coordinate operator, . We can transfer an explicit time dependence to it by transforming the ***Heisenberg representation***,

where and are the creation and annihilation operators in the Heisenberg representation. Let us look at the action of these operators on the particle number eigenstates using Eqns. (334) and (335),

Using the definition of the QHO energy eigenvalues in Eqn. (329),

Similarly,

Since we will use it later we will also consider,

and,

We are now in a position to derive an expression for our correlation function. We first need to realize that that we are dealing with operators and so,

Substituting in Eqn. (373),

We can evaluate these individual correlation functions using the definition of the trace and the completeness of the particle number basis,

Since the equilibrium density matrix is diagonal in the particle number basis and,

Similarly,

Using the same procedure,

The summation is simply the definition of the Bose-Einstein distribution defined in Eqn. (354),

Similarly,

Substituting these back into Eqn. (386),

In terms of basic constants,

This is perhaps one of the most important results in quantum physics. It describes how the fluctuations in our equilibrium QHO are dependent on temperature. Due to the principle of ***universality*** the environment of a quantum system can be described as an equilibrium QHO. We notice that this is a complex function with the following property,

The Imaginary part, , is independent of temperature while the real part, , has a very non-linear dependence. In the low temperature (quantum) limit,

Which is a complex function which is independent of temperature. This is the inherent ***quantum noise*** associated with the uncertainty principle. The thermal limit is entirely classical and linearly dependent on temperature,

This is a real-valued periodic function which we expect from a classical harmonic oscillator. Lastly, if we consider ,

we simply get the variance as previously given by Eqn. (362).

**Conclusions**

(1) The dynamics of the equilibrium QHO are fully determined by the ***displacement correlation function***,

(2) The low temperature limit gives us the correlation function for ***quantum noise***,

(3) The thermal limit gives the real-valued periodic correlation of the classical oscillator,

*5.4 The spectral density function*

The displacement correlation function completely defines the random Gaussian fluctuations of the oscillator due to the thermal environment and the inherent quantum noise. When one has a random temporal function then the obvious next step it to establish its frequency composition via ***Fourier analysis***. In the frequency domain,

where is a frequency ***variable*** and not to be confused with the natural frequency of the oscillator,. Evaluating this,

Remembering the definition of the -function,

we get,

The correlation function in the frequency domain is a Real function with both even and odd parts. The ***even part is also the temperature dependent part***,

The ***odd part is the pure characterization of the quantum oscillator***,

Strictly, the -function is only really defined in terms of the ***sifting effect*** it has on other functions inside an integral. Therefore, let us consider,

where is an arbitrary integrable function. Similarly, let us consider,

Since is an odd function,

We see that the integrals in Eqns. (404) and (406) give the same answer and so we can write the identity,

Therefore, we can write,

Let us now perform the ***inverse Fourier transform*** to reobtain the correlation function on the time domain,

This simplifies if we realize that each of these terms are either odd or even. Due to the bounds of the integral terms that are overall odd will integrate to zero. , and are all odd while is even. Therefore, the second () and third () terms are overall odd. Finally,

We have derived this definition of the correlation function from the assumption that our fluctuating system is a QHO. However, Eqn. (410) is rather general and is true for any function that satisfies,

and,

is the ***spectral density***. It completely characterizes the frequency composition of the fluctuations in our system due to its interaction with a stochastic environment. For a QHO is a simple -function since it possesses a single, well-defined natural frequency, . However, we define other spectral densities for more complicated systems at thermal equilibrium.

In the next section we are actually going to use the concept of the equilibrium QHO to define a more realistic model of the environment itself. Obviously a heat bath is far too a simplistic representation of our actual environment, which is primarily composed of the nuclear vibrations of the pigments. This leads to a ***hierarchical representation*** in which we have our system coupled to a set of local oscillators (our vibrational normal modes) which are in turn coupled to a wider thermal environment.

Conclusions

(1) The correlation function can be expressed in terms of the ***spectral density***,

(2) Although derived for the QHO this definition is true for any spectral density function that satisfies,

and,