***8. Perturbative theories of Energy Transfer***

When we considered the harmonic oscillator in a harmonic bath we derived all of the phenomena that are relevant to energy transfer in antenna systems: Population relaxation and coherence dephasing driven by the system-bath interaction. Moreover, we found that the system-bath interaction was completely defined by the spectral density function. We are now going to take these ideas and apply them to an excitonic manifold coupled to a bath. In the framework of ***second order perturbation theory*** we will derive the ***Redfield Equations***. We will then derive to very important theoretical frameworks for modelling photosynthetic antennae: ***Förster Theory*** and ***Modified Redfield Theory***.

*8.1 The Redfield Equations*

Let us start utterly generally by assuming we have a system, a bath, and some coupling between them. In the interaction representation the total density operator satisfies,

where the functional dependence on time indicates the interaction representation,

As in the previous section we integrate Eqn. (555),

And substitute this back into Eqn (555),

We do this simply because we wish to perform a trace over the bath and express the system-bath interaction in terms of a correlation function. We have an initial conditions term in . We can discard this for two reasons. If the bath is harmonic (as in the previous Section) then this term is linearly dependent on the bath coordinates. Therefore, they will average to zero when we perform the bath trace. Even if we assume some non-harmonic bath we can argue that in a stochastic system the initial conditions will be ‘forgotten’ in a finite (and usually very short) time. Therefore,

We can perform the bath trace to get,

This is formally correct (i.e. not perturbative) but not in any way useful. We must make a series of approximations to render this into a form that can be used for actual simulations. Eqn. (560) looks a little like second-order perturbation theory. However, the fact that we have a derivative of on the left-hand-side and not itself indicates that it is not. We have simply expanded it in a way that makes our subsequent treatment more straight-forward. The first approximation we make is, as before, that the bath is at constant equilibrium,

Next we have to make some assumptions regarding the form of the system-bath interaction. Let us assume that the coupling is linear in both the system and the bath,

where is a coordinate of the bath and is some operator of the system. It usually takes the form of a projector,

where are system eigenstates. is a coupling constant and is an ***index of expansion*** only until we specify some basis (which we do next section). As always, we immediately drop the circumflexes indicating operators. We can expand the commutator in our trace,

We remember three things here:-

(1) Since and span different Hilbert spaces they commute with each other.

(2) Since and span the system and is a constant they can be taken out of the bath trace.

(3) The trace operation is symmetric with respect to cyclic permutation.

Therefore,

As before the trace defines the bath correlation function,

Where we have defined the correlation function,

We are going to use the properties,

and,

and assign the entirety of Eqn. (566) to the actions of a ***rate super-operator***, ,

We therefore have our equation of motion in the interaction representation,

Despite these approximation, Eqn. (570) still treats the system-bath interaction in a non-perturbative manner. As such it contains a memory effect and is extremely difficult to solve. We can simply this by making the ***Markov approximation*** which assumes that the system-bath interaction is a weak perturbation and varies very slowly. This is the same assumption at the heart of perturbation theory and so this is entirely equivalent to invoking ***second-order perturbation theory***. The Markovian form of Eqn. (571) is,

At this stage we convert back to the Schrödinger representation. It is straight-forward but very long and tedious to show that,

where all (super) operators are now implicitly understood to be in the Schrödinger representation. The rate super-operator is now,

where we define the system time-evolution operator,

This is the ***Redfield equation*** and we can define the ***Redfield relaxation super-operator***,

This gives us,

Lastly, we note that this is an ***integrodifferential equation*** meaning that it still must be solved in order to obtain the dynamics. We leave it in this form until we have a specific problem in mind.

**Conclusions**

The basic assumptions of the Redfield equation,

are:-

(1) The system bath interaction is bilinear in both the system and the bath.

(2) The bath is at constant equilibrium.

(3) The reduced system dynamics are Markovian.

This is formally equivalent to perturbation theory to the second order in the system-bath interaction.

(

(3) The dynamics are Markovian. This

*8.2 The Relaxation of Excitons*

Eqn. (576) simplifies considerably when we express it in some suitable basis. Of course this means rendering a totally general equation into something rather specific to the problem at hand. The whole point of this long journey was to derive a suitable theory for modelling energy relaxation in a light-harvesting complex. The eigenstates of this system are the single-exciton states which are defined in Eqn. (2) in Section 1 but we repeat here,

where are the single-molecule states and are the exciton coefficients. Note, in the following derivation there will be multiple indices. We therefore adopt the convention that ***lowercase letters are used for site indices*** while ***capital letters are used for exciton indices***. This basis has the advantage of diagonalizing the system Hamiltonian but we are of course free to use whichever basis is most convenient. We first construct our system Hamiltonian in the site basis which is simply our spin-boson Hamiltonian. This is listed in Eqn. (1) but we repeat (in a slightly more condensed form,

The bath is assumed to be harmonic and therefore has a Hamiltonian of the form,

where and represent the momenta and displacements of the bath oscillators respectively. We’re not really very interested in this part and we don’t need to specify it in any more detail. The system-bath interaction is, like before, assumed to be linear in both the system and the bath. Moreover, we assume that the interaction is diagonal in the site basis which is essentially the assumption that the fluctuations on different chromophores are not coupled to each other,

where is the normal displacement of the nuclear degrees of freedom of molecule and is a coupling constant. Eqn. (581) is actually ***linearly couples the nuclear vibrations to fluctuations in the electronic energy gap***. Here we are simply assuming such a mapping but it can be derived from the ***displaced oscillator model*** of molecular excitations. We will derive this latter when addressing spectroscopy.

In the exciton basis the system Hamiltonian transforms is diagonal,

Therefore,

For the relaxation term we have to transform the system-bath Hamiltonian,

Now we could go through the process of deriving the Redfield super-operator again but don’t really have to. We can use Eqn. (574) directly with a few minor changes. Firstly, the arbitrary indices now explicitly label states in the ***site basis***.Secondly, the only real difference is we have additional summation indices due to the excitonic expansion of . The excitonic coefficients are unaffected by the bath trace and they commute with all of the operators. Therefore,

Rearranging,

We now invoke an approximation (more of an observation really) by realizing that the dominant modes of the bath are the intra-molecular nuclear vibrations. The vibrational fluctuations of two different sites can therefore be assumed to be uncorrelated,

Therefore,

where we have defined the rank-4 excitonic correlation function,

where is the fluctuating site energy of site . This one-to-one mapping between the displacement and energy gap fluctuations is a direct result of Eqn. (581). We can now compute the matrix elements,

Making use of the orthogonality and completeness of the exciton basis,

and using matrix element notation and evaluating the -functions,

Since we are working in the basis of eigenstates of ,

Similarly,

Therefore,

We are now free to switch the letters we use for our summation indices,

One of the things we notice from Eqn. (589) is that the order of indices in the correlation function are no-longer meaningful. This is only true for the assumption of no correlation between the vibrations of different molecules. Therefore, our Redfield equation in the exciton basis is,

We now define the ***auxiliary spectral function*** as the half Fourier transform of the exaction correlation function,

Giving,

We can use the very condensed (but in my opinion not very useful) super-operator notation,

This is still a rather unwieldy equation but one thing that should be apparent is that the population evolution and the coherence dephasing a not separate as they were in the caser of the harmonic oscillator. This is a general feature of systems that have a countable number of arbitrarily-spaced energy levels. We are going to simplify this equation further by invoking the ***secular approximation*** which is a more tightly constrained for of the rotating wave approximation. We will first take some time to justify it. If we consider Eqn. (599) in the absence of an interaction it has the trivial solution,

If the interaction is a small perturbation, then we can approximately account for it by applying a slowly varying amplitude to Eqn. (600),

It just so happens that this slowly varying amplitude is the interaction representation of our interacting reduced density matrix. This is only approximately valid if we assume,

Essentially this means that the ***system-bath interaction is smaller than the level*** splitting. If we substitute Eqn. (601) into Eqn. (599) then,

Rearranging,

Integrating,

Since is slowly-varying the integral kernel will become highly-oscillating if is larger than or . We can therefore neglect such terms and retain only those that are ‘secular’, a word which originally meant ‘non-oscillating’. Unless our system is totally homogeneous, the only terms that survive will be those with (1) and and (2) and . The ***secular Redfield equations*** are therefore,

This (in my opinion) is not very useful notation. Essentially, it means the Eqn. (598) reduces to,

If we realize that the order of the indices in the auxiliary spectral functions are significant when we assume the vibrations of different molecules are uncorrelated,

This is an incredibly famous equation that describes the coherence dephasing and population relaxation of an excitonic manifold coupled to a uniform, equilibrium harmonic bath. One of the first things to notice about Eqn. (608) is that, as in our model of the harmonic oscillator, the coherence dephasing and the population relaxation are independent. This is due to the secular approximation. We can therefore look at these phenomena separately. The population relaxation is given by,

We can simplify this considerably. Firstly, consider,

Therefore,

Substituting

Therefore,

Since Eqn. (613) vanishes when ,

Therefore,

where,

If we assume that (i.e. ) then,

where is the spectral density of the bath fluctuations and is, as always, the inverse temperature. Due to the definition of the correlation function the transfer rates necessarily satisfy the ***detailed balance condition***,

Therefore,

or equivalently,

The interpretation of Eqn. (615) is very straightforward. The first term on the left hand side is the rate of population loss from state due to transfer to relaxation to other states. Conversely, the second term is the gain of population due to relaxation from other states. This is simply a Master Equation describing probability diffusion.

Since we do not explicitly include the ground state in this theory Eqn. (615) only includes relaxation within the manifold of excited states. It neglects inter-conversion to the ground state. We treat this in an ad hoc manner with some decay rate, ,

This decay rate of a given excitonic state will be a quantum mechanical mixture of the excitation lifetimes of the component chromophores/sites,

The evolution of the coherences is given by,

where, is the ***coherence dephasing super-operator***. Full secular Redfield equation can then be written as,

where the first term on the left hand side is the unitary evolution of the coherences, the second is the coherence dephasing and the third and fourth are the population relaxation.

**Conclusion**

The ***secular Redfield equation*** assumes that our manifold of excitonic states are very weakly coupled to a uniform harmonic bath at constant equilibrium. The resulting dynamics are a combination of ***unitary evolution***, ***coherence dephasing*** and ***populations relaxation***.

(1) The unitary evolution is purely under the influence of the system Hamiltonian,

(2) Coherence dephasing is caused by coupled to the bath,

where the dephasing super-operator is given in terms of the ***auxiliary spectral functions*** of the bath,

(3) The population relaxation is independent of the coherent dynamics,

where the relaxation rates are defined by the ***spectral densities*** of the bath,

and,

is an ad hoc population decay rate arising from ***lifetime mixing***.

*8.3 The ‘Modified’ Redfield Theory*