***3. Forster’s Theory of Resonant Energy Transfer***

Before we start discussing more complex theories of energy relaxation we are going to consider Forster theory. The essence of this theory is the assumption that the inter-chromophore resonance couplings are much weaker than the coupling between each chromophore and its respective bath. It can formally be derived from Redfield theory, which treats the system-bath interaction perturbatively. You arrive at Forster theory by further relegating the inter-chromophore couplings to a similar perturbative treatment. Here we will present a phenomenological argument for the structure of Forster theory, reserving the formal derivation until we discuss more general theories.

*3.1 Occupation probabilities, rate constants and equations of motion*

Since we are treating the inter-molecular interaction perturbatively (i.e. not as part of our relevant system), Our system Hamiltonian is,

for which the eigenstates are the single-molecule excited states, . Therefore, the only sensible option is to work in the site basis. Its seems tempting to think that our next step is obvious. We define some initial conditions,

and then propagate it in time using an appropriately truncated time-evolution operator. However, the stochastic nature of the system bath-interaction does not allow for this. The reason being is that our small number of system states, , are coupled to a huge bath of whose exact microscopic state we are completely unaware. Any interaction between the two will lead to them becoming entangled and so it becomes impossible to write down a wave-function in terms of only the system states,

Because we are only paying detailed attention to the system degrees of freedom what we end up with is not a pure state but a ***statistical mixture***.

With each site in our complex we will associated an ***occupation probability***, , which tells us the likelihood that the excitation is located on site at time . We can define a ***vector of probabilities***,

It is extremely important to remember that this does not imply the existence of some wave-function,

This would be a pure state which we cannot define only in terms of system states. Instead we develop a stochastic picture of ***excitation hopping*** between the localized excited states. Let us assume that we have prepared our system in some initial state, . This could be an excitation initially localized on a particular chromophore, ,

or possibly an equilibrium distribution,

where is the inverse temperature. We can also define a set of ***coupled equations of motion***,

Such a set of equations actually describes any system of coupled first-order processes they are known as the ***Master Equations*** due to their enormous applicability in science. is the rate constant for the transfer of population ***from*** ***to***  and is the rate at which site is deactivated to the ground state. Since we do not explicitly include the ground state in any of our theories is generally just treated as a phenomenological decay rate. The values can be taken from fluorescence decay measurements. For example is a typical value for chlorophyll. The ***transfer rates*** (sometimes known as ***Forster rates***) are given by Fermi’s golden rule which I will repeat here,

Obviously we know what these various terms mean in a general sense but we will explain what they each mean in this particular context in the following sections. For the moment we will assume that these parameters are known and focus on solving the equations of motion.

For a system of chromophores Eqn. (186) represents a set of coupled, linear ordinary differential equations (ODEs). They do not have a general analytical solution and so one must use ***numerical analysis*** to generate a solution. This is made tractable by rewriting Eqn. (186) in matrix form,

where is an ***transfer matrix***. Its diagonal elements are defined,

and off-diagonal elements,

Eqn. (188) has the general solution,

However, this solution is too general to be of any real use. is a ***matrix exponential*** and is highly non-trivial to evaluate if is not diagonal. Generally it is defined in terms of an infinite power series,

We simplify this expression using ***matrix diagonalization***. For a general square matrix there exists a set of vectors, , that satisfy the relation,

where is an ***eigenvector*** of and is the ***eigenvalue***. An matrix will have eigenvectors each with an associated eigenvalue. We can collect them into a single expression,

where is a matrix whose columns are the eigenvectors and diagonal matrix of eigenvalues,

For the matrix there exists and inverse matrix,

where diagonal unit or identity matrix. If we multiply Eqn. (194) from the left by then we get,

or inversely,

This is a very important expression. It tells us that a non-diagonal representation can be transformed to a diagonal one. is therefore known as either the ***transformation matrix*** or the ***diagonalizing matrix***. Let us use this to simplify our matrix exponential,

Using the identify relationship,

where, since is diagonal,

We can now re-write Eqn. (191) in a form that is trivial to evaluate computationally,

where,

Generally, the time evolutions of the individual populations are not observable. We can, indirectly, observe the decline of the total population,

The decay is due to the non-zero dissipation rates, , is monotonic but is not generally mono-exponential. As such it does not have a single excitation lifetime but we can still define the ***mean excitation decay time***,

where,

The sum is over the elements of the vector . This sum is invariant to ***cyclic permutation*** of the order or matrices/vectors in the product so we can say,

We gain nothing mathematically by doing this but it is a more intuitive representation of . Let us consider the case where (i.e. a system of uncoupled chromophores). In this case,

In this case Eqn. (205) reduces to,

For the uncoupled case the mean excitation lifetime is just the sum of the lifetimes of the individual chromophores, weighted by their initial population. We can now see that Eqn. (205) is similarly a weighted sum of ***effective*** lifetimes weighted by ***effective*** initial populations. The inter-chromophore energy transfer ***mixes*** the decay lifetimes. It is important to remember that this is NOT a quantum mechanical mixture but a statistical one.

**Conclusions**

(1) The interaction between the chromophores and a stochastic bath means that we cannot define a system wave-function.

(2) The system state evolves into a ***statistical mixture*** characterized by a vector of occupation probabilities.

(3) The evolution is describe by a set of coupled differential equations, the ***Mater Equations***.

(4) The matrix representation allows us to numerically solve the Master Equations for an arbitrary network of coupled chromophores.

*3.2 The coupling matrix element*

The Forster rates depend on the matrix element,

Our interaction Hamiltonian is, most generally, the intermolecular two-electron interaction. To compute this matrix element we are going to use a bit of quantum chemistry. It is important to remember that the analysis is self-contained and may re-use symbols and terminology we have previously employed when discussing different things. Moreover, we are here going to explicitly consider the electronic ground state of the chromophores.

Physically, the inter-molecular coupling is an interaction between electronic transitions on neighbouring molecules. Let us consider a pair of chromophores, and . The initial state of this system corresponds to in its excited state and in its electronic ground state,

The action of the coupling is to move the excitation from to ,

To properly define the single-molecule states we have to consider both electronic and vibrational degrees of freedom. In the Born-Oppenheimer approximation we can assume that these degrees of freedom are separable,

where is the electronic wave function which is an explicit function of the electronic coordinates, , and is parametrically dependent on the nuclear coordinates, . is the nuclear (vibrational) wave-function. In practice we go a little further and make the ***Condon*** or ***Crude adiabatic approximation***,

where indicates that the electronic wave-function is calculated for the ground state geometry.

Before we evaluate our matrix element we need a more formal definition of the interaction Hamiltonian. Essentially this Hamiltonian quantifies the ***two-electron interaction*** between the single-molecule electronic vibrations. Chemically, an electronic transition is represented as the movement of electrons between ***molecular orbitals*** (MOs). However, it is more convenient to work in the basis of ***atomic orbitals*** (AOs). In the ***second quantization*** representation,

where annihilates (creates) an electron of spin in the AO and the factor of corrects for double counting. is the notoriously complex ***four centre integral***,

The indices , , and count atomic orbitals but we have yet to assign them to any of the molecules. As such Eqn. (215) contains all possible two electron interactions. For example would be the internal electron-electron interaction of molecule . There are two terms within Eqn. (215) that are relevant to inter-molecular energy transfer,

The first term is the ***Coulomb interaction*** and the ***Coulomb integral*** is defined,

The second term is the ***Exchange interaction*** and the ***Exchange integral*** is defined,

and the negative sign is picked up due to reordering of the operators. The exchange integral is only significant at very close inter-pigment separations and is generally neglected. We can now evaluate our matrix element,

If we substitute in Eqn. (215)

Here we have defined the elements of the ***spin-density matrix*** in the AO basis,

Generally, the expectation value in Eqn. (220) is independent of the spin-index and so we define

as the elements of the ***transition density matrix*** in the AO basis.

where is the ***purely electronic Coulomb coupling.*** How we calculate is discussed elsewhere but Eqn. (222) can, in principle, be evaluated exactly. However, it is extremely computationally expensive and approximations must be made. Firstly, there are several techniques to make the transition density matrix approximately diagonal (formal matrix diagonalization does not reduce computational cost),

where,

is the electron density associated with AO . Although simplified Eqn. (224) is still very difficult to evaluate. A further, and widely used, approximation is the ***monopole approximation* in** which we assume the electronic densities are -functions centred on the atomic nuclei,

Therefore,

In Eqn. (226) the are ***atomic orbital transition monopoles***. They are the partial charge associated with a particular AO . There are several of these associated with each atom. For example, in the MNDO formalism each ‘heavy’ (non-hydrogen) atom is associated with one -orbital and three orthogonal -orbitals. We can convert to ***transition atomic charges*** simply by summing over all AOs for a particular atom, ,

where,

However we choose to evaluate the coupling matrix element, we now define our rate constant,

We now have to realize something important. In the definition of our wave-functions in Eqns. (214) and (215) we have not only specified an electronic state but also some ***vibrational state*** on this electronic state. This vibrational state technically belongs to the ‘environment’. The rate constant as specified in Eqn. (229) is therefore not the total rate of energy transfer between chromophores but actually specifies a pair of specific ***vibronic states*** belonging to their respective chromophores. In this case the additional terms begin to make physical sense,

and,

are the ***Franck-Condon factors*** that are a measure of the overlap between equivalent vibrational levels on different electronic states. They basically define the relative amplitude of the different vibronic peaks associated with an electronic transition. The density of states, , is easy to define in terms of the ***conservation of energy***. Vibronic transitions and must have the same energy,

We can employ a standard identity for -functions,

Therefore,

where we have moved the Franck-Condon factors inside the integrals for a subsequent step (even though they are simply constants for a given pair of vibrational states. Next, we wish to know the the ***total transfer rate*** for the chromophore pair. Let us re-label the initially excited chromophore as and the finally excited chromophore as . The index now labels a particular vibronic transition of and labels a vibronic transition on . The total rate is then the sum over all possible combinations of and ,

where we have realized that in the ***Condon approximation*** (Eqns. (214) and (215)) the purely electronic coupling is the same for all pairs of vibronic states. Simplifying further,

We now realize that,

and,

are general expressions for the absorption spectrum of the ‘acceptor’, , and the fluorescence spectrum of the ‘donor’, . We now have the classic expression for the ***Forster rates***,

We note that the ***spectral overlap integral*** DOES NOT imply that a photon is emitted by the donor and then absorbed by the acceptor. This would be ***photon reabsorption*** which is a much slower process and while it does occur in leaves it is incidental to the process of light-harvesting. We simply use the overlap of spectral lines as a (measureable) proxy for the density of states. Even so Eqns. (237) and (238) are a little too general to be useful. They are defined in terms of vibrational wave functions and their projections onto electronic states. These are very hard to calculate from first principles and a better approach is to develop a phenomenological description of spectral line shapes. We will do this in detail in the next section but for the moment we will simply state it.

Expressing fluorescence and absorption spectra as some analytical function of energy/frequency is not generally possible. Even if we use some simplified ansatz function there is no such thing as a *general* expression for either or . It will be shown later that it is far more intuitive to express the Forster rate in terms of ***1st order optical response functions***,

where just means the real part of complex function and the response functions and are related to the spectral functions by a Fourier transform. The response functions benefit from having a simple functional form which can be evaluated numerically,

where is the ***frequency of the 0-0 transition*** of the donor/acceptor, , is the ***Stokes frequency shift*** of the fluorescence relative to absorption and is the so-called ***line broadening function***. It is important to remember that the line-broadening functions and the response functions themselves are complex functions (and so the ‘\*’ labels matter). The line-broadening functions are defined entirely by the system-bath interaction and their derivation needs extensive preparation. We will begin to develop this formalism in the next chapter.

**Conclusions**

(1) To correctly evaluate the interaction matrix element one must consider both the electronic and vibrational part of the wave-function (***vibronic transitions***).

(2) We can calculate the rate constant in terms of a ***purely electronic coupling***, , and a ***spectral overlap integral***,

This avoids the need for (the highly non-trivial) calculation of nuclear vibrational wave functions and then projecting them onto the electronic wave functions.

(3) The response function representation allows for straight-forward numerical evaluation of the spectral overlap integral.

(4) The response functions are totally defined by a 0-0 transition energy , a reorganization energy, and a line-broadening function, . The latter is non-trivial and is completely defined by the system-bath interaction.