**The Excitation Relaxation Dynamics of Light-Harvesting Proteins**

***1. The dynamics of an isolated excitonic aggregate***

*1.1 The exciton basis*

Let us assume we have a system of coupled chromophores in a light-harvesting complex. Our ‘relevant system’ is composed of the electronic excitations of each chromophore. In this analysis we will not explicitly treat the ground state and so our system consists of spatially-localized (on their respective chromophores) excited electronic states. These states are coupled via the resonance interaction, , and we assume that these are strong enough to induce excitonic mixing (i.e. be included as part of the ‘system’) but not so strong that they completely distort the molecular excitations. For the moment we will completely ignore any external environment. The system is characterized by the *spin-boson Hamiltonian*,

where are the excitation energies of the individual chromophores and are the resonance couplings. The states are the energy eigenstates of the ***uncoupled*** chromophores and constitute the ‘site basis’. Due to the coupling the eigenstate of are not the basis states but a set of *excitonic states*,

where are the transformation coefficients and the set form the *exciton basis*. We are free to switch between the site and exciton bases and we can pick whichever is most convenient in a particular situation. The transformation is unitary, meaning,

and,

The exciton states represent the energy eigenstates of the of the system and have energy eigenvalues,

where and are the transformation matrix and system Hamiltonian expressed in the site basis.

*1.2 Superposition of states and time-dependence*

So far we have used the vector representation of our states. Here we will transform to the wave function representation,

Here,

is the spatial part of the wave-function obtained by projecting the exciton eigenstate on to an eigenstate of the position operator. The frequency,

defines the (very fast) oscillation of the phase of the wave-function. These basis states are eigenstates of the Time Independent Schrödinger Equation which, for the sake of completeness we will demonstrate. The Schrödinger Equation states,

Note, when is not used as an index it is *always* used to denote the imaginary number . Inserting our definition of ,

Separating time and space variables gives,

We have a function that is dependent only on time (left) equal to a function that is dependent only on space (right). Therefore, both the left and right hand sides of Eqn. (11) must equal the same constant, . From left and side,

Clearly and so,

Eqn. (14) is the Time Independent Schrödinger Equation where . Essentially, the only time-dependence that the basis state has is a trivial time-dependent phase, , which is actually unobservable. For example, we can define the probability distribution,

In other words the probability distribution is time-independent. Let us imagine we have prepared our system in a particular excitonic state, . Physically this means that the excitation is delocalized across several chromophores. However, when we ‘observe’ the excitation we will always find it on one of the chromophores. The probability of finding it on chromophore is given by,

Taking advantage of the *completeness* of the positional eigenstates,

we can say,

Expanding the exciton states in the site basis,

Now we separate out the trivial time dependence and rearrange a bit,

Since the orthonormality of the site basis dictates,

So we now see that are the chromophore ***occupation probabilities*.** In other words, they give the probability of finding the excitation on chromophore given that we prepared the system in exciton state . We notice that these probabilities are completely independent of time. This shows that, while the energy is delocalized across multiple chromophores, there is no ‘movement’ of energy from one part if the system to the other.

Let us consider observable properties more generally. Quantum mechanics tells us that we cannot predict the outcome of a single measurement. We are limited to predicting a statistical distribution of different possible outcomes which we will experimentally realize over repeated (identical) measurements. In this sense observable quantities are typically (but not always) are defined by an average and a variance. The exception to this is the concept of an eigenstate which has a well-defined value for a physical quantity. For example, an energy eigenstate (like our exciton states) has a well-defined energy, a momentum eigenstate has a well-defined momentum, etc. Generally, we are interested in calculating the average or ***expected*** value of a physical observable. All observables are associated with an operator (Energy is associated with the Hamiltonian). The ***expectation value*** of some observable, , is defined as,

where is the operator associated with observable (momentum, position, energy, etc.). Let us assume that is one of our exciton states and transform to the wave function representation,

Generally the operator acts only on the spatial part of the wave function so,

Which does not depend on time. Let us now expend the exciton state in the site basis,

This result encapsulates two really important concepts. Firstly, it shows that the coupling between chromophores does not only mix energies but all observable properties. Secondly, it shows that the observable properties of a single excitonic state have implicit no implicit time dependence. This last point is subject to the assumption that we have no interaction with any external degrees of freedom.

**Conclusions**

(1) The eigenstates of our system of coupled chromophores are the excitonic states and not the chromophore excited states.

(2) If the system is prepared in one of these exciton states then the probability of finding the excitation on a particular molecule is given by .

(3) The coupling mixes all observable properties.

(4) the observable properties of a single excitonic state have no implicit time-dependence.

*1.2 Superposition of states and time-dependence*

The ***principle of superposition*** tells us that if a differential equation (like the Schrödinger Equation) has a set of solutions then any linear combination of these solutions,

is also a solution (where are simply some set of expansion coefficients) . This applies to the quantum state of our system of coupled chromophores. We can define an arbitrary state of our system as,

It is important to remember that are just our excitonic basis states. We call a ***pure state*** and describe it as a ***coherent superposition*** of different excitonic states. We notice that this superposition is a purely quantum mechanical phenomenon and it is completely distinct from ***statistical mixtures*** of different states that arise when our system is coupled to a large, complicated environment. These pure states are generally what you prepare when you use a laser to excite a light-harvesting complex. Let us switch to the wave function representation,

We now transfer the time dependence from the basis state to the coefficient,

where,

We now define (with a bit of an abuse of notation) our pure state as,

By definition our basis states now have no time dependence whatsoever with the trivial time dependence contained in the expansion coefficients. Assuming we prepare our system in some superposition of exciton states, the probability of observing the excitation in one of these exciton states is,

Using Eqn. (28),

Therefore we interpret as the probability that the system will be observed in a exciton state and that this probability is not dependent on time. In other words, although our system is in a superposition of several excitonic states, there is no net flow of energy from one state to the other. We call the ***complex amplitudes*** and note that they have (at the moment) only a trivial dependence on time.

Sometimes, it can be more intuitive to work in the site basis rather than the exciton basis (it is easier to think of energy moving between different chromophores rather than abstract exciton states. Let us consider the probability of observing the excitation on a specific chromophore,

This is a bit abstract so let’s consider a simple 2-level system, that is a system of two chromophore states, , that couple to give two excitonic states, . Let us assume we prepare out system in the state,

In this case,

Using Eqn. (18) and realizing that the coefficients and are real,

where,

We see that this probability is time-dependent. To simplify further let us assume that our system is composed of two identical molecules () . This means that we have two excitonic states,

With eigen energies,

giving,

Let us also assume that we prepare our system in a symmetric superposition of these two exciton states,

This gives us,

and,

This is plotted in Fig. 1 and we see that the probabilities oscillate between 1 and 0 with a phase difference of . Physically, what this means is that we can think of the excitation oscillating backwards and forwards between the two chromophores. However, it is important to realize that this ‘motion’ is completely reversible and there is no net transfer of energy from one molecule to the other. This type of motion is known as ***coherent*** as it preserves the phase relationships between our basis states. In the absence of an interaction with an external environment the motion will always be coherent and effectively nothing happens.

**Conclusions**

(1) The energy eigenstates of our system of coupled chromophores are the excitonic states, which form a convenient basis to describe more general ***pure states*** of the system.

(2) We can also express this pure state in the ***site basis*** and in fact the two bases are entirely equivalent. We choose the one that is the most convenient.

(3) In the ***absence of an external interaction*** there is no transfer of energy between excitonic states.

(4) In the site basis we see that energy transfer between chromophores is oscillatory and reversible.

(5) To get irreversible, unidirectional energy transfer (such as we need in a light-harvesting complex) our ***chromophores must interact with an external environment***.

***Figure 1:*** *The evolution of the occupation probabilities in the site basis for a symmetric superposition of two excitonic states for a homodimer. We assume that* .