***2. Interactions with an external ‘perturbation’***

In a light-harvesting complex our ‘system’ of coupled chromophore electronic excitations are further coupled to a thermal environment or ‘bath’. Although people tend to think of this bath as the protein scaffold, lipid bilayer, water, etc. What we actually mean by the bath is the set of nuclear vibrational modes of the chromophores themselves. In this respect each chromophore is its own immediate bath and since vibrations on one molecule do not strongly effect vibrations on another one, we can think of each chromophore having its own independent bath. The wider environment (protein, etc.) plays a thermodynamic role. It dampens and randomizes our molecular vibrations according to its temperature. To understand this we will have to combine quantum mechanics with statistical mechanics, something known as ***the theory of open quantum systems***. Before we consider this though we will consider a much simpler set-up, one in which our system interacts with a small, deterministic external interaction.

*2.1 A two-level system interacting with light*

Let us consider two coupled chromophores. Since we do not explicitly include the ground state this constitute a system of two excitonic states. Let us assume that this system interacts with light. Our Hamiltonian is,

where is our system-light interaction term. We will use a semi-classical approach in which we treat the system quantum mechanically and we treat light as an oscillating electric field. We assume that our interaction term has the form,

where sets the magnitude of the interaction and is the frequency of oscillation. Moreover, we are going to assume that the frequency of the light is close to ***resonance*** with the energy gap between our two excitonic states,

Lastly, we will assume that the system exists in some general pure state as described by Eqn. (35). Substituting this into the Schödinger equation gives,

If we remember that the basis states has no time-dependence and that they are eigenstates of ,

If we multiply Eqn. (57) by either or we get two differential equations,

where we have used the fact that the excitonic states are orthonormal and we define,

We call these interaction ***matrix elements***. Our task is now to solve Eqns. (58) and (59). Our first step is to consider the case when Clearly we have,

In the absence of an interaction and have no explicit time-dependence. We are going to assume that the interaction gives them a time-dependence and we propose the trial solutions,

Inserting, Eqn. (63) into Eqn. (58) we get,

which simplifies to,

Similarly,

Since we have assumed that it is implied that and . This means that the light only induces transitions between the two excitonic states and not between the these states and the ground state. Therefore we may assume that and,

Next we explicitly write out the time-dependence of the interaction matrix elements,

Similarly,

The next thing we do is remember that we assumed that the frequency of the light was *close to* resonance with the energy gap between the excitonic states. We can therefore assume that . Next we invoke something known as the ***Rotating Wave Approximation*** (RWA). The reason for this name is technical and not actually very helpful. In essence we have to realize that the frequency is generally very large so that oscillates very rapidly compared to the time-dependence of . Therefore, these oscillations are so fast that they actually average out to zero, , on the timescale of . Therefore,

These equations are simplified but still coupled to each other. If we take the derivative of Eqn. (73) we get,

Substituting in Eqn. (74),

Where we have used the fact that . Eqn. (76) is a very familiar second order differential equation with a simple general solution,

where we have defined the ***Rabi frequency***,

and is an arbitrary phase. Remember that we cannot observe these amplitudes directly, merely the probabilities over repeated measurements. Since the amplitudes are now explicitly time-dependent,

So,

and by the conservation of probability,

Finally, to get rid of we have to assume a set of initial conditions. Let’s assume that at the system is in the lowest energy exciton state, . This gives . We see that the probabilities oscillate with the Rabi frequency with a phase lag of . What this means is that probability is moving backwards and forwards between the two exciton states. This is known as ***a coherence*** between our two excitonic states. If we switch to the site basis we will see very complex behaviour,

Putting in our solutions,

Using the same assumptions as in Eqn.(42)-(47), the double angle formula,

and the identity,

we get,

We plot this in Fig. 2 and see that the system is also oscillatory but in a far less trivial manner. This illustrates that in this case working in the exciton basis is the much better choice.

**Conclusions**

(1) When we include an interaction with an external agent into our Hamiltonian the exciton states are no longer eigenstates.

(2) Interaction with the light field causes reversible, oscillatory movement of energy between the excitonic levels. This phenomenon is known as ***optical pumping*** and the resulting oscillation is known as ***a coherence****.*

(3) Since we only have two states the dynamics are entirely reversible, we need further coupling to additional ‘bath’ states to see ***dephasing of the coherence*** and ***dissipation of energy***.

(4) Reversible movement of energy is also present within the site basis, although it is much more complex to express mathematically. This illustrates the principle of ***choosing the most reasonable basis*** for the problem at hand.

***Figure 2:*** *The evolution of the occupation probabilities in the site basis for a coupled homodimer being driven by a resonant light field. We assume that* simply for clarity.

*2.2 The interaction representation*

Before we develop a more general approach to external interactions we have to develop a more useful representation of quantum mechanics. Everything we have considered so far has been in the so-called ***Schrödinger******representation***. We were see that there are actually several different *representations* of quantum mechanics that are entirely equivalent but more or less useful in different situations.

**2.2.1 The Schrödinger Representation**

In the Schödinger representation it is assumed that the operators associated with the observables have no *implicit* time dependence. The implicit temporal evolution of observable quantities is due to the temporal evolution of the wave function. It is still possible to have operators with *explicit* time dependence due to some external interaction. For example, if we consider an isolated harmonic oscillator the expectation value of the momentum, , oscillates sinusoidally in time. This is due to the *implicit* time dependence of . The operator is time-independent. Now imagine an external interaction disturbs the oscillator. The time evolution of is now due to the *implicit* time-dependence of the wave function and the *explicit* time-dependence of the operator. For reasons that will become clear, we will henceforth refer to the *implicit* time dependence as ***unitary evolution*** and the *explicit* time-dependence simply as ***time dependence***.

The unitary evolution of the wave function is governed by the Scrödinger equation,

where is some general Hamiltonian. If our Hamiltonian has no time-dependence (as in our spin-boson Hamiltonian in Eqn. (1)) then Eqn. (88) has the general solution,

where the exponential operator is defined by an infinite Taylor expansion,

For the special case of being an energy eigenstate (in our case an excitonic state) then Eqn. (89) becomes,

This leads us naturally to the concept of the ***unitary time evolution operator***,

which propagates the wave function from some initial state, , to its current state, . Things get more complicated for a time-dependent Hamiltonian,

This has a general solution,

so,

We could naively apply a similar Taylor expansion in analogy with Eqn. (90) giving,

However, we are not properly treating as an operator. For the last term on the right-had side of Eqn. (97) we are integrating over both possible time-orderings of the two Hamiltonian operators and . This is only correct if and commute which is not generally true. The correct approach is to enforce ***strict time-ordering***,

where we enforce . We give this the symbolic notation,

where is known as the ***time-ordered exponential***.

has a number of useful properties:

**(1) Step-wise decomposition:** If the time-evolution is deterministic then the time evolution should depend only on the initial and final point,

**(2) Time Continuity:**

**(3) Time reversal:** The inverse of the time-evolution operator is the ***time reversal operator***.

Therefore,

**(4) Unitarity:** Cleary this is a unitary transformation meaning the inverse of the operator is equal to the Hermitean conjugate,

For a time-independent Hamiltonian,

while more generally,

where the operators act to the left.

We can define an equation for motion for the time-evolution operator which is formally equivalent to the Schrödinger equation but has certain advantages. Let consider time-evolution over an infinitesimally small time range, . So small in fact that we can assume that the Hamiltonian is time-independent even if it strictly isn’t and can truncate the Eqn. (90) after first order,

Remembering the property of stepwise decomposition,

Rearranging,

In the limit of ,

For the time-reversal operator,

This is entirely equivalent to the Schrödinger equation but has the advantage of not being dependent on the actual wave function. Typically, we can generally write down a Hamiltonian (and therefore, in principle, construct ) while we rarely know the functional form of the wave function itself. However, in the Schrödinger representation the Taylor expansion in Eqn. (90), or the time-ordered exponential in Eqn. (99), is rarely convergent. The means that in most practical cases we cannot directly obtain the dynamics of our system from the Hamiltonian. To do this we have to develop alternative representations and develop the idea of a ***perturbation***.

**2.2.2 The Heisenberg Representation**

An entirely equivalent but in a sense ‘opposite’ representation is one in which all time-dependence (both unitary and explicit) is carried by the operators associated with the observable quantities. The wave function itself is assumed to by rigidly static. We can use the time-reversal operator to ‘remove’ the unitary evolution from the wave function,

We develop an alternative notation,

where and indicate ‘Heisenberg’ an ‘Schrodinger’ respectively and we have assumed . We tend not to bother with the index as it is assumed we are in the Schrodinger representation unless otherwise stated.

Let us now consider an observable associated with operator with some time dependence. Following repeated measurements we will record an ***expected value***,

Where we now define the operator in the Heisenberg representation,

The first thing we notice is that the Schrodinger and Heisenberg representations coincide at ,

We can also derive an equation of motion, the **Heisenberg equation**, . For generality let us assume that both the operator and the Hamiltonian have some time-dependence in the Schrodinger representation,

Using Eqns. (110) and (111),

where we have exploited the unitarity of the time evolution operator, and,

Defining the commutator,

we obtain the Heisenberg equation,

Often it is written in terms of expectation values rather than the operator itself,

If our observable has no time-dependence () then,

This shows that if commutes with () then is not time-dependent.

This representation benefits from the fact that we can, in principle, describe the time evolution of observable quantities without knowledge of the wave function or the time evolution operator. However, the most useful representation by far is one that can be considered intermediate between the Heisenberg and Schrodinger representations: the ***interaction representation***.

**2.2.3 The Interaction Representation**

The reason that the previous definitions of the time evolution operator are very slowly convergent or not convergent at all is due to the fact that we treat the entire Hamiltonian as a single object. It is much more useful to split our Hamiltonian into a ‘system’ and ‘interaction’ term,

where we have assumed, for generality, that our Hamiltonian has some time-dependence. is the Hamiltonian of our system in the absence of the external interaction, while is our ***interaction Hamiltonian***. How we make this partition is a matter of choice and depends very much on the particular problem being studied. We will discuss this in more detail in subsequent sections but for now it is enough to know that both and can have some time-dependence.

Let us, for the moment, consider on its own. The associated time-evolution operator is,

We define the ***interaction representation*** as,

and,

Essentially we have removed the unitary evolution associated with from the wave function and transferred it to the operators. The wave function retains only the time-dependence associated with the interaction, (hence the name of the representation). We can think of this as an intermediate representation between those of Schrodinger and Heisenberg. If we substitute Eqn. (125) into the Schrodinger equation,

The left hand side gives,

Therefore,

Multiplying by from the right by,

Using Eqn. (126) gives,

where is the interaction Hamiltonian in the interaction representation. Eqn. (131) is the Schrodinger equation in the interaction representation. It has the solution,

Where we define the unitary time-evolution operator of the interaction,

We are now going to derive one of the most important equations in quantum mechanics. First we acknowledge that all representations coincide at . Therefore,

We now see that,

Comparing this to Eqn. (92) we get,

This shows that the total unitary evolution of the wave function is a combination of unitary evolution under the influence of the system and the evolution due to the interaction. We will use this to develop the following,

If we expand this we get,

Since the unitary operator does not depend on any of the integration variable (, , etc.) we can bring them into the integrals. Additionally we will use the definition of the interaction representation of operators in Eqn. (126),

If we remember,

We get,

We can write this more generally as,

This is incredibly profound and we will describe how so in the next section. Essentially, we have separated the unitary evolution associated with the non-interacting Hamiltonian and the time evolution associated with the interaction.

Lastly, because we will use it later, we can derive an equation of motion for observable quantities as we did for the Heisenberg representation. If we differentiate Eqn. (126),

Using Eqns. (110) and (111),

**Conclusions**

(1) In the **Schrodinger representation** the unitary evolution of the system is carried by the wave function. Operators associated with observable quantities are time independent unless they carry an explicit time dependence due to an external interaction.

(2) In the **Heisenberg representation** the wave function (or state vector in Heisenberg’s formulation) is rigidly static and all time dependence is carried by the operators.

(3) In the **Interaction picture** the Hamiltonian is split into non-interacting and interacting terms. The time-dependence associated with the non-interacting term is transferred to the operators while the wave function retains the time-dependence of the interaction.

(4) All representations coincide at some initial time, .

*2.3 Time-dependent perturbation theory*

The Schrodinger (Eqn. (99)) and Interaction (Eqn. (142)) representations of the time-evolution operator are entirely equivalent. If we include terms up to infinite order () in the time-ordered exponential then both give an exact description of the dynamics. This is impossible and we must truncate this expansion at some finite (and in practice low) order to get an approximate solution. Only the interaction representation has the flexibility needed to do this we have to invoke the concept of a ***perturbation***.

Let us consider a system with a well-defined (and known) basis of eigenstates. For us this will be our coupled chromophore electronic excitations. Now we consider an external interaction that is weak compared to the interactions within our system (in our case our resonant couplings ). What we mean by *weak* is that it does not completely disrupt the system and the original non-interacting eigenstates are still a good basis for the description of the interacting system. We define our Hamiltonian as,

where is our weak interaction or ***perturbation***. How we separate these terms depends entirely on the system and process you are studying. For example, in a light-harvesting complex we have to think carefully.

(1) One could say that our system is actually just the isolated chromophore electronic transitions and the couplings, , is our perturbation. As we will see later this leads to Förster theory. It is now well known that this is not a good description of light harvesting complexes due to the couplings being rather strong. The exciton basis is generally the appropriate one.

(2) The light field in optical spectroscopy can definitely be treated as a perturbation. In fact the response function formulation of the theory of spectroscopy is based on 1st and 3rd order perturbation theory. However, as long as we are not trying to model ultra-fast time-resolved spectroscopy, the light field basically just prepares our system in some initial state (e.g. creating an excited state via absorption) and the subsequent energy relaxation is independent of it. We can often relegate the light interaction to something that simply defines our initial conditions.

(3) The electronic-vibrational coupling is often (as a first approximation at least) treated as a perturbation. Coupling of our exciton states to the vibrational modes of the chromophores has the effect of introducing irreversibility and dissipation into our dynamics but it is assumed to not destroy the exciton states themselves. For light-harvesting complexes an entirely perturbative treatment of the system-bath interaction is not sufficient and several ‘modified’ theories include part of it explicitly within the system Hamiltonian.

Let us assume that we have split our Hamiltonian in some way that is appropriate to the problem. By this we mean that we have chosen to be small enough so that we can truncate our time-ordered exponential in Eqn. (142) is convergent at low orders.

**2.3.1 Zeroth order perturbation theory or just ignoring the interaction**

I add this only for completeness and to establish a vocabulary. The simplest thing we can do is simply ignore the summation in Eqn. (142 ) to give,

We call this ***zeroth order*** since we ignore . Essentially we are just ignoring the interaction and assuming that the wave function experiences only unitary evolution due to .

**2.3.2 First order perturbation theory and Fermi’s Golden rule.**   
The expansion in the time-evolution operator is truncated after ,

By looking at the chain of operators in the integrand of Eq. (147) we can develop an intuitive way of think about this. Consider the chain of operations,

(1) The system starts (at ) in some initial state and evolves unitarily under the influence of until time .

(2) At the system experiences the external interaction, , which induces a transition to a new state .

(3) then evolves unitarily under the influence of until time .

This type of visualization technique leads to the idea of representing system evolution via ***one-sided*** ***Feynman diagrams*** (see Fig. 3). Naïve reading of these diagrams would seem to imply that the interaction is impulsive. However, it is important to remember that we integrate over all possible times in the interval .

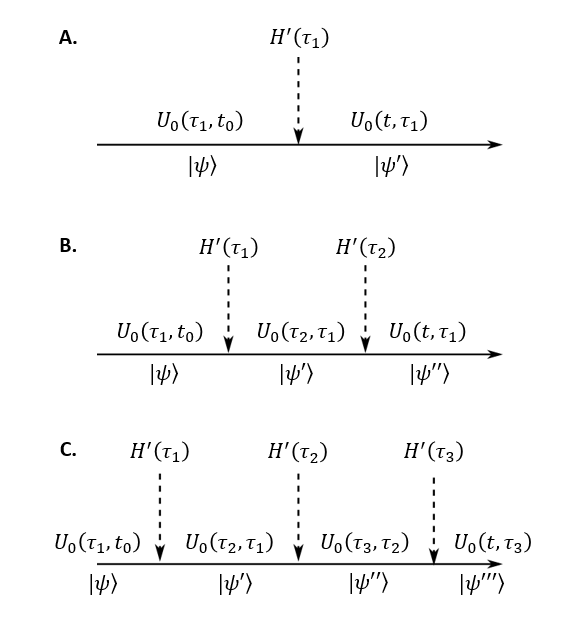
First order perturbation theory is possibly one of the most widely used approximations in physics. We will now discuss the derivation of Fermi’s golden rule. Let us assume that we have a manifold of eigenstates of , , and our system is prepared so it in state at Although we don’t know the specifics of the interaction we do know that it will cause our system to evolve from an eigenstate to some pure super-position state. We can say that the interaction ***creates a coherence between our excitonic states*** or that it ***causes a transfer of amplitude from***  ***to the other eigenstates***. Our initial state is,

while our final state is,

The final and initial states are connected by the action of the time evolution operator,

Substituting in Eqns. (149) and (150),

Because contains a general external interaction term we cannot write an exact expression for it. However, we will assume that it is weak enough for us to truncate the series expansion after 1st order,



***Figure 3:*** *Feynman diagram representations of the evolution of the wave function under a the influence of an external perturbation showing* ***A.*** *first order,* ***B.*** *second order and* ***C.*** *third order terms.*

To evaluate this let us multiply both sides of Eqn. (153) by and remembering that (time reversal and unitarity,

We can simplify this expression immensely by remembering that and by using the ***completeness*** of the eigen basis,

Now we remember that,

so that,

where the ***matrix element*** is defined,

And the first term on the right-hand side has vanished because we have stated that . Simplifying and letting the -functions pick out terms in the summation,

where . Let us think about probabilities instead of amplitude. The probability of observing the system in (the initially unoccupied) state is given by the square of Eqn. (159),

Physically this quantity is ***probability of finding our system in eigenstate at time given that it was in state at time*** *.* We use an alternative label and call it a ***transition probability***,

Without any loss of generality we can set . Let us now assume that the perturbation varies so slowly that it can be treated as effectively constant over the time interval ,

Using the standard integral,

We are almost at the final expression. In practice the handful of eigenstates that make up or system are coupled to a continuum of environmental states. Let us assume that is a system state and belongs to the continuum of environmental states. In this case we have to consider the probability of transfer from to any one of a huge number of states, , in the infinitesimal energy range . The useful quantity to describe this is the ***density of states***, , and the total number of states in this energy range are given by,

The total probability of transition from eigenstate to any other state is then,

To further simplify we rewrite our expression for in terms of an ***unnormalized*** ***sinc function***,

Therefore,

We can use some properties of our sinc function to simplify the integral in Eqn. (166),

The unnormalized sinc function has an interesting limiting property related to the definition of the ***Dirac delta function***,

where the factor of comes from the fact that our sinc function is not normalized. Rearranging Eqn. (169),

Since is far smaller than any possible timescale, , that we can probe experimentally then the limit in Eqn. (170) is indeed satisfied. Therefore,

Eqn. (172) tells us that the probability of a transition from state initial to a continuum state is proportional to , and . Let’s explain what each of these mean:

(1) is the ***matrix element of the interaction in the eigenstate basis***. Essentially, this quantity describes how two states, in this case and , are ***coupled by the interaction***. We therefore call the ***coupling between states and*** .  This makes clear sense the stronger the coupling between these states, the higher the probability of a transition from one to the other.

(2) is the ***density of states*** in the continuum, , that have the same energy, , as initial state . This amounts to a demand that that the transfer process must conserve energy. You can’t transition to a state that is lower or higher in energy. The may seem contrary to the basic principles of biochemistry but one has to remember that so far we have not considered a ***thermal*** environment which can act as a source of additional energy or a sink for excess energy. All of the theoretical arguments thus far can be assumed to refer to the ***zero temperature limit***.

(3) is the duration of the interaction. It suggests that the longer the interaction the more likely you are to have transitions between states. However, Eqn. (172) implies that increases linearly with which is clearly unphysical. is a probability and therefore . This is simply a side-effect of all the mathematical approximations we have made. We can still use Eqn. (172) but we must remember that it is only valid for small (i.e. short interactions).

Finally, we can consider the transition ***probability per unit time*** also known as the ***rate constant***,

This is ***Fermi’s Golden Rule*** and is incredibly general in its applicability. We will find a use for it when developing ***Forster Theory***. The indices, , formally indicates that this rate constant refers to transfer ***from***  ***to*** . This notation emerges from our formal derivation. However, it can be a little counter intuitive and we often reverse the order of the indices,

**2.3.3 Higher order perturbation theory.**

It is important to remember that 1st order perturbation theory is not a general approach. For many problems, even with judicious partitioning of the Hamiltonian, higher-order (2nd, 3rd, etc.) terms in the expansion of the time evolution operator may be critically important. As with everything, it depends entirely on the problem at hand.

For example, let us take optical spectroscopy which can be described most generally as the interaction between a system of eigenstates (exciton states in our case) and a light field. We did previously consider a light field and introduced the concept of ***Rabi oscillations***. However, that was a somewhat idealized example of a perfectly sinusoidal light field with no start or finish (i.e. i.e. ). In real optical experiments you are dealing with illumination from an incoherent source or the action of a very short laser pulse. For this we need to treat the light interaction perturbatively.

One-photon absorption and fluorescence are ***first order processes*** meaning that they are completely described by 1st order perturbation theory. Because the time-evolution operator is linear in these techniques are known as ***linear absorption and fluorescence***. Non-linear spectroscopies are ***third order processes*** described by the term,

The chain of operators (illustrated in Fig. 3 c) indicates we can think of this as 3 successive interactions (at times ). Typically each of these interactions takes the form of a laser pulse hitting our sample and the type of non-linear techniques depends on how we arrange these 3 pulses. For example ***pump-probe spectroscopy*** is a common ***transient absorption*** technique. This technique uses two laser pulses (a pump and a probe).

(1) The first pulse carries out the first two interactions simultaneously (). The first interaction sets up a ***coherence*** (Rabi oscillation) between the ground and excited state.

(2) The second interaction ***populates*** the excited state, meaning that the system is in a meta-stable excited state.

(3) The third interaction occurs at some later time and can do several things: (i) Interact with an excited chromophore to create a coherence between the excited state and ground state leading to ***stimulated emission***. (ii) Interact with an excited chromophore to create a coherence between the excited state and an even higher excited state leading to ***excited state absorption***. (iii) Interact with a chromophore that didn’t interact with the initial pulse. This creates a coherence between the ground an excited state which is detected as linear absorption. This is a very small contribution when compared to normal steady state absorption. This ‘absorption deficit’ is known as the **ground state bleach**.

Many other techniques, differeing only in how we arrange our laser pulses, exist and form the family of ***third order spectroscopic methods***. For symmetry reasons ***even order optical effects* do not occur**. Fifth order optical spectroscopic techniques are now being explored but have yet to prove any value to the study of biological systems.

In later sections we will build a theory of energy transfer in light-harvesting complexes based on the idea of an initially excited manifold of excitonic-vibrational states interacting with a thermal bath. It is impossible to track the time-evolution of this bath due to the enormous number of degrees of freedom and the lack of experimental resolution. Such a bath performs stochastic (Gaussian) fluctuations which are mirrored in fluctuations in our chromophore site energies, . The effect of such a bath on the system is defined by the ***two point energy gap correlation function***,

which is defined in the site basis. This will be described in more detail later. For now it is enough to know that described the conditional probability of site (chromophore) having a site energy at time given that site has a site energy at . Since every chromophore has its own bath we assume that different sites are uncorrelated,

In other words it describes the pairwise correlation between different system-bath interactions. Clearly, the theoretical tools we are going to use will be based on ***second-order perturbation theory*** (see Fig. 3 b).

**Conclusions**

(1) Perturbation theory is based on the partitioning of our total Hamiltonian into a well characterized, time-independent ***non-interacting part*** and a small ***perturbation*** or ***interaction term***.

(2) may be considered a ‘perturbation’ if it is small enough for the eigenstates of to still be a good basis and for the expansion in the time-evolution operator to be rapidly convergent.

(3) ***Frist order perturbation theory*** leads to Fermi’s Golden Rule,

(4) A particular problem or experimental set-up may require high-order terms to be considered.