***4. The Density Operator and Density Matrix***

Our ultimate goal is to develop a theory of excitation relaxation within a network of strongly-coupled chromophore electronic transitions which are each coupled to a stochastic bath composed (in part) of the nuclear vibrations. Although there is no exact theory of such a system we will develop a standard approach based on a 2nd order perturbative treatment of the system bath interaction. To do this we will have to introduce the idea of the ***reduced density operator/matrix***.

*4.1 The Density Operator formalism for a closed system*

We have seen that the wave function formalism is too inflexible to describe a system coupled to a stochastic bath. We initially prepare our system in a ***pure system state*** and it is possible to write down a wave-function as a linear super-position of well characterized system eigenstates. However, once our system interacts with the stochastic bath the system state becomes entangled with a huge number of poorly-characterized bath states. It therefore becomes impossible to express our system state in the basis of system eigenstates. To an observer focussing only on the system it appears to evolve into a classical stochastic system and the best description possible is a ***statistical mixture***. This process is called ***dephasing*** and although it is generally fast compared to biological timescales it is not instantaneous. Simple theories (such as Forster) that assume our system *starts* as a statistical mixture neglect the initial quantum behaviour. This is an incorrect approach as certain coherent effects, such as delocalized excitonic states can actually last long enough to have a significant impact on the dynamics of the system. We therefore need a representation that is flexible enough to characterize the transition from pure state to statistical mixture. This representation is the ***Density Operator/Matrix***.

To start we are going to re-centre our theory not on the wave function but on physical observables. Let us assume we have a closed system described by some pure state which is expressed in some basis of eigenstates as in Eqn. (29). The physical observables of this system are given by the expectation value of their associated operators. In the Schrodinger represntation,

Since form a known and complete basis of eigenstates (which are by definition time-independent) we can assume that the matrix elements, , are also known (and also, by definition, time-independent). Therefore, the dynamics of our observables are completely and directly defined by the pairwise products of the complex amplitudes . Therefore, it may be more intuitive to develop a quantum description of our system in terms of rather than the wave function. Let us define an operator which, for historical reasons, we will call the ***density operator***,

If we expand the wave function, , in terms of some basis of eigenstates we get,

We can then compute the matrix elements in the same basis,

Therefore, we can re-write Eqn. (243) in term of elements of the ***Density Matrix***,

Where . If we consider the product of two matrices, , then the elements of the resulting matrix are defined,

Therefore,

where the ***trace*** is defined as the sum over the diagonal elements of a matrix.

The interpretation of the density matrix is rather straight forward. The diagonal elements are,

and are essentially the probabilities of observing the system in basis state . Any time dependence they possess is entirely explicit. Since we are dealing with a closed system,

The off-diagonal elements are defined,

and exhibit unitary evolution in addition to any explicit time-dependence. The off-diagonal elements represent the degree to which our system is a linear superposition of eigenstates and . In other words, they quantify the ***coherence*** between and in our system. As such the diagonal elements of are known as ***populations***  and the off-diagonal elements are known as ***coherences***.

At the moment the density matrix and the wave function representations of our closed system are entirely equivalent. However, the density matrix representation is the only one that can be generalized to handle ***statistical mixtures***. So far we have assumed that our system is prepared in some pure state. However, this implies that the tools we use to prepare the system are somehow completely free of error or uncertainty. Let us assume that there are a range of possible pure states, , in which our system can find itself after preparation, each with an associated probability . This reflects a ***statistical uncertainty*** in which we, as the people carrying out the experiment, don’t know for certain which pure state we have prepared. However, the system is in one of these pure states and not some coherent super-position or more than one pure state. We will illustrate this difference now.

How would we expect such statistical uncertainty to be reflected in a physical measurement? For a pure state a physical observable is associated with and expectation value . If our pure state is an eigenstate of then is well defined quantity. If our pure state is a superposition of eigenstates then is the *average* value that you will measure in repeated experiments. If we are not totally certain which pure state,, our system is in then the average value of our observable over many measurements will be a ***statistical average*** of the possible expectation values ,

Now in building a description of this uncertain statistical mixture we may be tempted to write,

where the operator meaning ‘possibly equal to’. If we now try to calculate the expectation value we get,

which is clearly not correct. The reason for this is that the object described in Eqn. (254) would be some coherent superposition of states and not a statistical mixture. We now consider the density operator and try,

As before,

where we have used the completeness of our basis states, . Eqns. (255) and (257) show us something very important: The density matrix formalism is capable of representing statistical mixtures and the wave function formalism is not. Therefore, we will restate Eqn. (256) as the general definition of the density operator,

The matrix elements are defined,

where is the amplitude of eigenstate in the pure state . The diagonal elements are, as before, the occupation probabilities or ***populations*** of the basis states,

Due to the conservation of probability,

This is true whether describes a pure state or a statistical mixture. However, let us consider the sum of the *square of the* populations,

If describes a pure state, , then,

However, if describes a statistical mixture of pure states (which are not necessarily orthogonal, then,

and since,

therefore measures the ***statistical uncertainty*** in our system.

**Conclusions**

(1) For a pure state the wave function and density matrix descriptions are completely equivalent.

(2) If a system is prepared in a ***statistical mixture*** of pure states then only the density matrix representation is applicable.

(3) The diagonal elements are the ***populations*** of the basis states while the off-diagonal elements are the ***coherences*** between basis states.

(5) Conservation of probability,

(6) Degree of statistical uncertainty,

*4.2 The Liouville-von Neumann Equation*

We formally defined the density operator/matrix in terms of a wave function of statistical distribution of wave functions which are in turn defined by the complex amplitudes in the eigen basis expansion. Generally, we don’t need this level of detail and to describe measurements on a physical system it is sufficient to know the evolution of the density matrix without then trying to reconstruct some set of wave functions. To do this we need to define an equation of motion for the density operator/matrix,

Using the definition of the Schrodinger equation in Eqn. (9),

This leads to the famous Liouville-von Neumann equation,

where we have used the ***commutator*** and the Hamiltonian may have some explicit time dependence, *.* We can obtain a general solution by integrating Eqn. (268),

This is a ***recursive solution*** as the solution depends on itself. We can expand this iteratively by substituting Eqn. (269) into itself,

where we have made the trivial substitution in the first term on the right hand side for the sake of consistency. We recursively substitute again and again to obtain the infinite series

In more condensed notation,

Note that we are correctly treating and as operators by enforcing strict time-ordering. It can be shown that this expression can be rewritten as,

and I leave it as an exercise to differentiate Eqn. (273) to re-obtain the Liouville-von Neumann equation. This may seem mathematically cumbersome but we can develop a slightly more compact notation using the notion of ***super-operators***. Let us rewrite Eqn. (268) as,

Where is the ***Liouvillian*** super-operator which acts on an operator as,

Similarly, we define our solution in terms of a super-operator analogue to the ***time evolution operator***,

where is a ***propagator*** which propagates an operator in time according to,

As we shall see later, the ***Liouville space*** formulation becomes particularly useful when dealing with open systems.

Let us now consider how the density matrix elements, i.e. the populations and coherences, evolve in time. The general solutions given in Eqn. (272) and equivalently in Eqn. (277) are of limited use since the series expansion in is not generally rapidly convergent (since is not rapidly convergent). To do this we will have to invoke perturbation theory and obtain approximate solutions which are specific to particular problems. For the moment we can consider the simplest possible case of an isolate system with a time-independent Hamiltonian. For simplicity let us define ,

Therefore,

This tells us that the populations,

are constant and the coherence between any two states oscillates (unitary evolution) with a frequency determined by their energy difference,

Importantly, the coherences do not degrade over time. The degradation, known as ***coherence dephasing***, occurs when we have an ***open system***.

Conclusions:

(1) The dynamics of an isolated system are totally determined by the Liouville-von Neumann equation,

(2) The general time-evolution is defined by the ***propagator***,

(3) For a closed system the populations of states do not evolve in time. The coherences between states oscillate continuously with frequency,

*4.3 Perturbation theory in the density matrix formalism*

As with the wave function formalism of pure states the solution of our equations of motion for the density operator is too general to be of any real use. For all but the simplest cases the true solution depends on an infinite series expansion that either does not converge or converges very slowly. For real systems we must obtain an approximate solution via perturbation theory. The key to developing this is, as in our wave function-based approach, the ***interaction representation***. Let us assume that our Hamiltonian can be decomposed as,

where we have dropped the circumflexes used to indicate operators. is our non-interaction system Hamiltonian and is an explicitly time-dependent external perturbation. This is an example of a ***closed system***. The eigenstates of represent the complete basis meaning that they are not coupled to any additional external states. The perturbation is some external (classical) field which can input energy to the system but contains no states that can be populated. According to Eqn. (126) the density operator in the interaction representation is defined,

Equivalently,

Using Eqn. (268),

We can use the product rule to fist evaluate the left hand side of Eqn. (285),

Using Eqns. (110) and (111),

Therefore, Eqn. (286) reduces to,

We now do two things. Firstly, we express in the interaction representation and then with multiply by from the left and from the right,

This leads to our final equation of motion,

We can use this to generate our perturbation expansion. In exact analogy with Eqn. (272) we have the general solution,

Providing we partition our Hamiltonian correctly (so that is a small perturbation) then the series in Eqn. (291) should be rapidly convergent. This means that a (hopefully) accurate description of our dynamics can be obtained with a truncated form of the propagator. Let us consider some low order truncations.

**4.3.1 First Order Perturbation Theory**

Truncating Eqn. (291) after gives,

We can define the ***first order correction*** to the unitary evolution as,

We can expand out the commutator,

and convert back to the Schrodinger picture, remembering that all representations coincide at ,

So,

Finally we realize that and ,

This may look like a lot of mathematical nonsense but actually it has a very clear interpretation. What we have to remember is the density operator is an operator of the form which means that we have to consider how both and evolve in time. is affected by operators acting on from the left and is affected by operators from the right. Let us start with the first term on the left hand side of Eqn. (297). We have the chain of operators,

Let us assume that the system starts out the lowest energy eigenstate . This means that the density operator is in the initial pure state . The matrix elements will be,

meaning that state is exclusively populated and there are no coherences between states. If we look at Eqn. (298) then the only thing acting on from the right is , meaning simply experiences unitary evolution over the time range . However, is acted on from the left by . Therefore, from experiences unitary evolution un the influence of . Then at experiences an interaction due to the action of which cause a transition to . It then resumes unitary evolution under the action of . Let us now look at the matrix elements of ,

where

The diagonal elements is,

It should now be obvious that the second in Eqn. (297) shows the revered situation, with experiencing the interaction and simply undergoing unitary evolution. The overall evolution of the density matrix is a superposition of both ***trajectories***. We can draw these conceptually using ***double sided Feynman diagrams*** as shown in Fig. 4 The difference between these two ***diagrams***, and is actually trivial, with the second merely being the complex conjugate of the first. Conjugate pairs of diagrams are a defining feature of the perturbation expansion and generally it is sufficient to draw only one (the left handed diagram by convention). The existence of its conjugate partner is implied.

The matrix elements of the first order correction (Eqn. (297)) in full are therefore,

Fig. 4 seems to imply that the interaction is instantaneous but it can have an extended and complicated time-dependence. Let us assume however that the interaction is somehow impulsive. For example, it could be a very sharp and very precisely timed laser pulse,

where the -function means that the pulse interacts with our system at precisely . Eqn. (303) becomes,

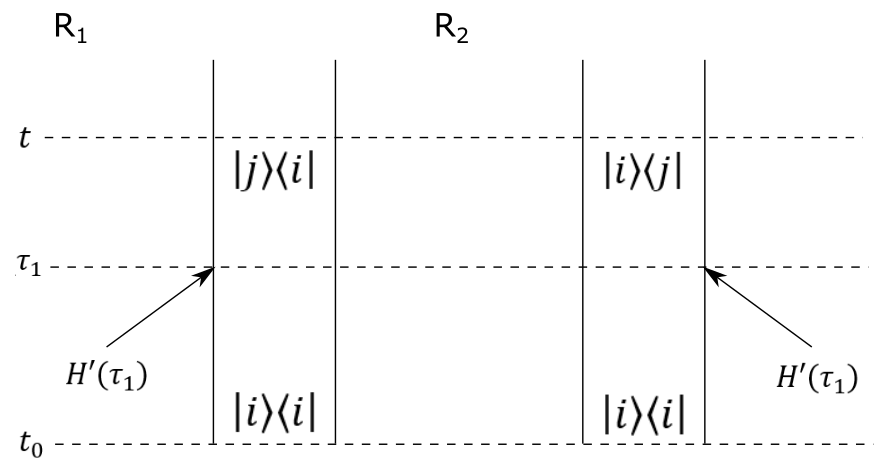


Figure 4: The two double sided Feynman diagrams associated with a first order perturbation. In this example the eigenstate is initially populated. The action of the interaction at then creates a coherence between eigenstates and . The difference between the two diagrams R1 and R2 is trivial (R2 is simply the complex conjugate of R1). It is important to remember that although these diagrams imply an impulsive interaction as a specific time we actually integrate over all possible values of . The interaction may be extended and have a complicated time-dependence.

If we assume that the interaction matrix elements are real then,

where . The time argument implies that is our start time so the formal definition is,

Cleary the diagonal elements of Eqn. (307) are zero while the off-diagonal elements oscillate with frequency . In other words, ***a first order interaction creates a coherence between two eigenstates***.

**4.3.2 Second Order Perturbation Theory**

Generally we define our system/experiment in such a way that the expansion in Eqn. (291) converges as rapidly as possible. Never-the-less, some symmetry in our system or a deliberate experimental choice often means that we must consider higher order perturbations. For example, ‘non-linear’ spectroscopic techniques are designed to explore 3rd and even 5th order interactions between light and matter. When considering system-bath interactions in our light-harvesting complexes the statistical treatment of the bath (in terms of two-point correlation functions) means that we must consider 2nd order perturbations. The 2nd order () term in Eqn. (291) is,

As before, we obtain our diagrams by expanding the commutator,

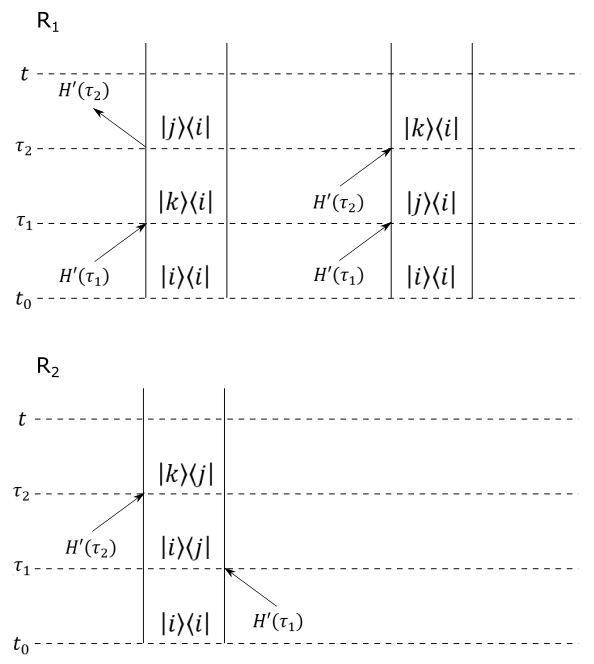
and switching back to the Schrodinger representation (which I will leave as an exercise since it is straightforward but long-winded),

We have two pairs of terms which are related by complex conjugation,

In subsequent discussions we will only discuss and explicitly with the understanding that they come with conjugate partners. In the past we have called these terms ‘diagrams’ which is not strictly accurate when we go above first order. Since we have more than one interaction each term is a general description of a collection of different (but related) processes, which depend on the specific system being studied and the experimental set-up you are using. This is illustrated in Fig. 5. If we assume that our system is initially in the ground state, , then the first interaction can only be absorption (energy entering our system). However, the second interaction can be either an absorption or an emission (energy leaving the system). Even so this representation is still very general as we make no assumptions about how , and are related (in some situations they may label the same state). These diagrams can be further subdivided when one considers specific systems and experimental set-ups.

Let us now consider the ***density matrix elements*** at second order. We will first consider and consider the completeness of our basis,

Using the orthonormality of our basis and remembering that ,

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**Figure 5:** Double sided Feynman diagrams for a second order perturbation. Assuming that the system starts in the ground state, the first interaction in all terms will be an absorption. For the second interaction can be either an absorption or an emission. Note that we do not make any assumptions about the relative energies (or even identities) of , and and therefore thee diagrams can be further sub-divided depending on the system being studied and the experimental set-up.

Knocking out the -functions and cleaning up,

Similarly,

We notice that Eqn. (317) and (318) are functionally identical apart from the absolute sign. This is simply because they are written in the most general form possible. Let us by simplify this by assuming that our system is composed of states , and in ascending order of energy. Let us consider the left most diagram of in Fig. 5. The density operator advances . Clearly, the only non-zero matrix element after this perturbation will be ,

For the right most diagram of in Fig. 5 the density operator advances and the only matrix element is,

For we can have the progression ,

We could also have ,

To explore the difference between these diagrams we will line them up and slightly change the order of indices in some of the transition frequencies. We will also

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Let us look in detail at how these interactions are reflected in the final form of the density matrix.

(1) For the absorption at and this contributes a term to the density matrix element. Then the emission at contributes a further (notice the difference in phase). Lastly, the unitary evolution of the resulting coherence, , contributes a factor of .

(2) For the absorption at and this contributes a term to the density matrix element. Then the absorption at contributes a further . Lastly, the unitary evolution of the resulting coherence, , contributes a factor of .

(3) For the absorption at and this contributes a term to the density matrix element. Then the absorption at contributes a further . Lastly, the unitary evolution of the resulting coherence, , contributes a factor of .

(4) For the absorption at and this contributes a term to the density matrix element. Then the absorption at contributes a further . Lastly, the unitary evolution of the resulting coherence, , contributes a factor of .

**The rules**

1. Each interaction is represented by an arrow contributes an interaction matrix element. A transition of the *ket* contributes while a transition of the *bra* contributes .
2. Each interaction also contributes a phase factor. An arrow pointing to the right contributes a phase factor while an arrow pointing to the left contributes .
3. The final subsequent unitary evolution of the resulting coherence, , contributes .

**4.3.3 Higher Order Perturbation Theory**

There are several systems/measurements that can only be understood in terms of 3rd, 4th and even 5th order perturbations. As stated before ‘non-linear’ spectroscopic techniques are based on 3rd (and more recently 5th) order interactions between the system and the light field. At third order the expansion of the nested commutator results in 6 terms which can be sub-divided into a hundreds of different diagrams. It is therefore impossible to discuss higher-order perturbation theory in general terms. Even if we are considering 3rd order optical measurements the diagrams that we must consider will differ depending on whether we are discussing Resonance Raman, Pump-Probe, 3 pulse photon echo, etc. We will leave this discussion for another time.

Conclusions:

(1) One can develop a diagrammatic representation of perturbation theory in analogy to the wave function representation.

(2) Interactions can act on both the ket (from the right) and the bra (from the left) necessitating ***double sided Feynman diagrams***.

(3) For 1st order perturbations a coherence is created by a single interaction.

(4) For higher order perturbations we must consider specific systems and experimental set-ups when constructing diagrams.

(5) There are simple rules for deriving the functional form of the resulting coherence without the need for exhaustive mathematical analysis.