# Quantum Statistical Response Functions

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# 1. Introduction

Many experiments that one would like to describe theoretically have a common (idealised) form: one starts by perturbing the system one wants to study by an external agent (such as a laserpulse) and after a certain time interval one probes the system by measuring one of its dynamical variables such as its polarisation (dipole moment). In other words the dynamical *response* of the system to an external perturbation is measured. Often the system of interest, such as a liquid, is macroscopic in nature and it becomes impossible to describe the motion of all its individual constituents in full detail and one has to resort to the methods of statistical (quantum)mechanics. In this case it is often profitable to divide the system into two parts, a small subsystem (hereafter simply called "the system") which is described in full detail (e.g. a molecule in a liquid) and the rest of the system (called "the environment" or "the bath") which is treated only statistically and which interacts with the system proper. At the start of the experiment one assumes that the system and the bath are in stationary equilibrium and can be described by equilibrium thermodynamics. The external perturbation then excites the system in various ways, taking it out of statistical equilibrium. Subsequently the system interacts with the bath and will tend to loose (*dissipate)* its excess energy to its environment and will eventually return (*relax*) back to thermodynamic equilibrium. One can now study this relaxation process by measuring the value of some observable of the system as function of the delay since the system was excited (the dynamic response function of this observable), thus obtaining information about the system bath interaction (the intermolecular forces in a liquid for example). If the delay is long enough one expects the system to have relaxed to equilibrium and one simply measures the equilibrium value of the response (which usually vanishes, e.g. the average dipole moment of a molecule in a liquid is zero, due to random orientations).

In this short course we will discuss the theoretical tools which are needed to describe the type of experiment discussed above. There are apparently three ingredients we will have to treat which are absent in the description of the groundstate properties of isolated molecules.

- We will have to decide how to describe a quantum system statistically rather than by specifying its wavefunction.
- We will have to describe the time dependent interaction with the external perturbing agent and the subsequent influence of this perturbation on the properties of the system as a function of time.
- Finally we will have to study the interaction of the system with its environment and decide on how to model the relaxation processes introduced above.

We will start with a brief summary of the quantum description of isolated systems and then we will address each of these three problems in turn and study how they come together in the description of quantum statistical response.

## 2. Summary of Quantum Mechanics

*The Postulates of Quantum Mechanics*

Quantum mechanics can be based on the following abstract postulates with which the reader is assumed to be familiar and which are repeated here in order to set the stage for subsequent developments.

A. The state of a quantum system is fully described by a vector in a (usually infinitely dimensional) vector space (Hilbert space). This state vector is often but not always represented by a wavefunction. The vector space has an inner product which is called the *overlap* of two state vectors.

B. The observables (measurable quantities) of a quantum system are described by (Hermitian) operators working in this Hilbert space.

C. All measurements of an observable A have one of the eigenvalues $a_n$ of the corresponding operator **A** as their result.

$$\mathbf{A}|n\rangle = a_n|n\rangle \tag{1}$$

The corresponding eigenvector $|n\rangle$ is called an eigenstate of the operator. The eigenstates form a complete orthonormal set of states in the Hilbert space, i.e. *any* state vector can be expressed as a linear combination of these eigenvectors:

$$|\ \rangle = \sum_n |n\rangle\langle n|\ \rangle$$
$$\langle n|m\rangle = \delta_{nm} \tag{2}$$

It is in principle impossible to predict which of the eigenvalues will be measured, even if the state (state vector) of the system is exactly known. Quantum mechanics can only predict the probability with which a particular eigenvalue can be found. Note that this indeterminacy has *nothing* to do with an incomplete knowledge of the state of the system and is unrelated to the statistical description of macroscopic systems by statistical mechanics to be treated later.

D. The probability $P(a_n)$ of measuring an eigenvalue $a_n$ in a system described by a state vector $|\ \rangle$ is given by the square of the overlap of $|\ \rangle$ with the eigenstate $|n\rangle$ corresponding to the eigenvalue $a_n$:

$$P(a_n) = \left|\langle n|\ \rangle\right|^2 \tag{3}$$

E. From a knowledge of the state vector at any point in time, one can predict the state vector at a later time through the time dependent Schrödinger equation:

$$i\frac{\partial|\ \rangle}{\partial t} = \mathbf{H} \tag{4}$$

where **H** is the operator of the total energy (the Hamiltonian).

*Projection Operators*

Note that the expression $|n><n|$ in equation (2) can be considered as an operator working on the state vector $|\ >$, the result being a vector proportional to $|n>$ with a coefficient equal to the overlap $<n|\ >$, i.e. the projection of the vector $|\ >$ on the vector $|n>$. The operator $|n><n|$ is therefore called the *projection* operator on the state $|n>$. The completeness relation (2) can then be written in terms of these projection operators as:

$$\sum_n |n\rangle\langle n| = 1 \tag{5}$$

Similarly one can write any operator **A** in terms of its eigenvalues and eigenvectors:

$$\mathbf{A}|\ \rangle = \sum_n \mathbf{A}|n\rangle\langle n|\ \rangle = \sum_n a_n|n\rangle\langle n|\ \rangle \qquad \mathbf{A} = \sum_n a_n|n\rangle\langle n| \tag{6}$$

We can then derive a compact expression for the average value measured for an observable using (3) and (6):

$$\langle\mathbf{A}\rangle = \sum_n P(a_n)a_n = \sum_n \langle\ |n\rangle a_n\langle n|\ \rangle = \langle\ |\mathbf{A}|\ \rangle \tag{7}$$

*The Schrödinger Picture*

Equation (4) can be formally solved as

$$|\ (t)\rangle = e^{-iH(t-t_0)}|\ (t_0)\rangle \quad U(t,t_0)|\ (t_0)\rangle$$

$$i\frac{\partial}{\partial t} U(t,t_0) = \mathbf{H}U(t,t_0) \tag{8}$$

where $U(t,t_0)$ is called the *evolution operator*, which propagates the state vector from time $t_0$ to a later time $t$.

In this formulation of quantum mechanics, called the *Schrödinger Picture* the operators are independent of time, while all the dynamical information is carried by the state vector.

*The Heisenberg Picture*

An alternative equivalent (in fact the oldest) formulation of quantum mechanics is obtained by transforming all operators and all state vectors with the unitary operator $U$ of equation (8):

$$\mathbf{A_H}(t) = U^\dagger(t,t_0)\mathbf{A}U(t,t_0) \qquad |\ _H\rangle = U^\dagger(t,t_0)|\ (t)\rangle = |\ (t_0)\rangle \tag{9}$$

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In this Picture the state vector is independent of time, but the operators evolve in time according to the *Heisenberg Equation* of motion, found by combining (8) and (9):

$$\frac{\partial \mathbf{A_H}(t)}{\partial t} = i\left[\mathbf{H}, \mathbf{A_H}(t)\right] \tag{10}$$

Since $U$ is unitary, the equation for the average value (7) remains valid in all pictures.

*The Interaction Picture*

For our purposes it is most useful to use a Picture intermediate between the Schrödinger and Heisenberg Pictures, called the Intermediate or Interaction Picture. In this formulation the total Hamiltionian is split into an unperturbed part $\mathbf{H_0}$ and a (possibly time dependent) perturbation $\mathbf{H}(t)$. We transform all operators and state vectors with the evolution operator $U_0$ corresponding to $\mathbf{H_0}$ in the spirit of equation (9). As a consequence all the unperturbed dynamics is cast into the operators, while the state vector only evolves in time under the influence of the perturbation:

$$\mathbf{A}_I(t) = U_0^{\dagger}(t,t_0)\mathbf{A}\,U_0(t,t_0) \qquad \left|\,_I(t)\right\rangle = U_0^{\dagger}(t,t_0)\left|\,(t)\right\rangle$$

$$i\frac{\partial \left|\,_I\right\rangle}{\partial t} = \mathbf{H}_I(t)\,_I(t) \qquad\qquad \frac{\partial \mathbf{A}_I(t)}{\partial t} = i\left[\mathbf{H}_0, \mathbf{A}_I(t)\right] \tag{11}$$

For the evolution operator in the Interaction Picture we now have from (11)

$$i\frac{\partial}{\partial t}U_I(t,t_0) = \mathbf{H}_I(t)U_I(t,t_0) \qquad \left|\,_I(t)\right\rangle = U_I(t,t_0)\left|\,_I(t_0)\right\rangle \tag{12}$$

It is now easy to make an expansion in orders of the perturbation for the evolution in the Interaction Picture by integrating equation (12) iteratively :

$$U_I(t,t_0) = 1 + (-i)\int_{t_0}^{t} d\tau_1 \mathbf{H}_I(\tau_1) + (-i)^2 \int_{t_0}^{t} d\tau_2 \int_{t_0}^{\tau_2} d\tau_1 \mathbf{H}_I(\tau_2)\mathbf{H}_I(\tau_1) + \ldots =$$

$$1 + \sum_{n=1} (-i)^n \int_{t_0}^{t} d\tau_n \int_{t_0}^{\tau_n} d\tau_{n-1} \ldots \int_{t_0}^{\tau_2} d\tau_1 \mathbf{H}_I(\tau_n)\mathbf{H}_I(\tau_{n-1})\ldots\mathbf{H}_I(\tau_1) \tag{13}$$

This expansion is the basis for all developments in Time Dependent Perturbation Theory and is of course most useful if the perturbation is small, so that we can limit ourselves to the first few terms in (12).

*Response Functions*

Let us use equation (12) to calculate the response discussed in the introduction in the case of a system that can be described by a state vector. In particular we perturb the system with some time dependent perturbation $\mathbf{H}(t)$ and we ask ourselves what average value we will measure for some property $\mathbf{A}$ at some later time $t_1$. We will

limit ourselves here to the *linear response,* i.e. we take the perturbation into account to first order only. For the average value of **A** at $t_1$ we have from (7)

$$\langle \mathbf{A} \rangle_{t_1} = \langle \psi(t_1) | \mathbf{A} | \psi(t_1) \rangle = \langle \psi_I(t_1) | \mathbf{A}_I(t_1) | \psi_I(t_1) \rangle \tag{14}$$

while from (13) we find for the state vector in the Interaction Picture

$$| \psi_I(t_1) \rangle = U_I(t_1, t_0) | \psi_I(t_0) \rangle = U_I(t_1, t_0) | \psi(t_0) \rangle = | \psi(t_0) \rangle - i \int_{t_0}^{t_1} d\tau_1 \mathbf{H}_I(\tau_1) | \psi(t_0) \rangle \tag{15}$$

Putting (14) and (15) together we find

$$\langle \mathbf{A} \rangle_{t_1} = \langle \psi(t_0) | \mathbf{A}_I(t_1) | \psi(t_0) \rangle + i \int_{t_0}^{t_1} d\tau \langle \psi(t_0) | [\mathbf{H}_I(\tau), A_I(t_1)] | \psi(t_0) \rangle \tag{16}$$

The first term is just the average value of **A** in the absence of a perturbation, while the second term represents the contribution to the change in the average of **A** that is linear in the perturbation, i.e. the linear response. Higher order response functions can easily be derived by using (13) to higher order.

### 3. Quantum Statistical Mechanics, The Density Operator

*Definition and Properties of the Density Operator*

The theory in the previous section for the response function depends critically on a knowledge of the unperturbed state vector and cannot therefore be used for macroscopic systems or systems that interact with a bath, since in these situations one can never actually determine the state vector. However, often it is possible to specify the *probability* that the system can be described by a certain state vector. For example if a system is in contact with an external heat bath at a temperature $T$, thermodynamics tells us that the probability of finding the system in a state with energy $E_n$ is proportional to the well know Boltzmann factor:

$$p_n \quad e^{-E_n/kT} \tag{17}$$

If one wants to evaluate the average value of some observable **A** in such a case one has to deal with *two* kinds of probabilities, first the inherent quantum mechanical probabilities that are always present and second the probabilities due to our lack of knowledge of the precise quantum state the system is in. If $p_n$ is the probability that the system is in the state $|_n\rangle$ the average value for a property **A** is found as:

$$\langle \mathbf{A} \rangle = \sum_n p_n \langle _n |\mathbf{A}| _n \rangle \tag{18}$$

The statistical state of the system is clearly defined by the combination of the probabilities $p_n$ and the corresponding state vectors $|_n\rangle$. This total state information can conveniently and compactly be summarised by introducing a new object, the *density operator*, defined as a weighted sum of projectors on the state vectors $|_n\rangle$:

$$\rho = \sum_n p_n |_n\rangle\langle _n| \tag{19}$$

The average value (18) can then be written in terms of this density operator as:

$$
\langle \mathbf{A} \rangle = \sum_n p_n \langle _n |\mathbf{A}| _n \rangle = \sum_m \sum_n p_n \langle _n |\mathbf{A}| m \rangle\langle m| _n \rangle =
$$
$$
\sum_m \sum_n \langle m| _n \rangle p_n \langle _n |\mathbf{A}| m \rangle = \sum_m \langle m|\rho\mathbf{A}| m \rangle \quad Tr\rho\,\mathbf{A} \tag{20}
$$

In the last line we have defined the trace of an operator as the sum of all its diagonal elements in any complete set of states (the value does not depend on which complete set we choose). The density operator in fact contains all information that can be known about the system, e.g. also the probability of measuring a particular eigenvalue $a_n$ for the property **A** can be expressed with the help of this operator (see eq. (3)):

$$P(a_n) = \sum_m p_m P_m(a_n) = \sum_m \langle n | \, _m \rangle p_m \langle \, _m | n \rangle = \langle n | \rho | n \rangle =$$

$$\sum_{mq} \langle q | \, _m \rangle p_m \langle \, _m | n \rangle \langle n | q \rangle = Tr\rho | n \rangle \langle n | \tag{21}$$

So this probability is equal to the trace of the density operator and the projector on the eigenstate of **A** corresponding to the particular eigenvalue $a_n$, or alternatively by the diagonal matrix elements of the density operator in the eigenstate basis of the operator **A**.

The density operator can be defined by giving its matrix elements in any complete basis, the so called *density matrix*. The diagonal elements of the density matrix are known as *populations* (they correspond, according to (21), to the probability of finding the system in the corresponding state), while the off-diagonal elements are known as the *coherences*.

For the trace of the density operator itself we find

$$Tr\rho = \sum_m \sum_n \langle m | \, _n \rangle p_n \langle \, _n | m \rangle = \sum_n p_n \langle \, _n | \, _n \rangle = \sum_n p_n = 1 \tag{22}$$

since the probability to find any state should be unity.

If all the $p_n$ in (19) except one (say for $| \, \rangle$) vanish, the density operator in fact reduces to the projector on the state that has probability 1:

$$\rho = | \, \rangle \langle \, | \tag{23}$$

The density operator formalism becomes then superfluous but remains correct. In such a case one says the system is in a *pure* state, while the more general case (19) the system is said to be in a *mixed* state. It is easy to recognise if a given density operator corresponds to a pure state or not by taking the trace of its square. We have

$$Tr\rho^2 = \sum_n p_n^2 \quad \sum_n p_n = 1 \tag{24}$$

since all probabilities are smaller than unity. Only if all $p_n$ in (24) vanish except one, can the equality be reached, in which case the state is pure and the density operator is a projection operator (23) with the characteristic property

$$\rho^2 = \rho \tag{25}$$

In the case of a system in contact with a heat bath at temperature *T*, as in equation (17) (the system is then said to be described by the *canonical ensemble),* we can write a very compact expression for the density operator:

$$\rho = \frac{1}{Z} \sum_m | \, _m \rangle e^{-E_m / kT} \langle \, _m | = \frac{1}{Z} e^{-H/kT} \sum_m | \, _m \rangle \langle \, _m | = \frac{1}{Z} e^{-H/kT}$$

$$Z = Tr e^{-H/kT} = \sum_m \langle \, _m | e^{-H/kT} | \, _m \rangle = \sum_m e^{-E_m/kT}$$

$$\tag{26}$$

Here $Z$ is a normalisation factor ensuring that the trace of the density operator equals unity. In fact it plays an important role in statistical thermodynamics, where it is known as the *partition function* and it can be shown that if it is known as a function of temperature and volume, then all other thermodynamic quantities can be derived from it.

*Time Dependence of the Density Operator, The Liouville Equation*

From the Schrödinger equation (4) we easily derive the corresponding equation determining the time dependence of the density operator:

$$\frac{\partial \rho}{\partial t} = \sum_m |\partial_m/\partial t\rangle p_m \langle_m| + \sum_m |_m\rangle p_m \langle \partial_m/\partial t| =$$
$$-iH\sum_m |_m\rangle p_m \langle_m| + i\sum_m |_m\rangle p_m \langle_m|H = -i[H,\rho(t)]$$

(27)

This equation for the evolution in time of the density operator is known as the (quantum) *Liouville Equation*. Note the change of sign compared to the Heisenberg Equation (10) for an arbitrary operator in the Heisenberg Picture. Equation (27) is actually in the Schrödinger Picture, where the state vectors and hence the density operator change in time, while the operators describing observables are time independent.

For a system in thermal equilibrium described by (26) the density operator is seen to be a function of the Hamiltonian and hence it commutes with the Hamiltonian. Equation (27) then tells us that the density operator and hence all average values are in fact constant in time as is to be expected for a system in stationary thermal equilibrium. If we apply an external perturbation, the density operator will no longer commute with the total Hamiltonian (including the perturbation) and (27) then tells us that the density operator will start to evolve. After the perturbation is switched off we will see later that the system will return to equilibrium (26) provided it is coupled to a heat bath at temperature $T$.

Again we can formally solve (27) using the evolution operator $U$ of equation (8):

$$\rho(t) = U(t,t_0)\rho(t_0)U^\dagger(t,t_0)$$

(28)

*The Liouville Superoperator*

By a notational trick one can make the Liouville Equation for the density operator (27) look exactly like the Schrödinger Equation for the state vector (4). To this purpose one introduces the *Liouville superoperator or Liouvillian* **L**, i.e. a mathematical object that turns an operator into another operator, just like an ordinary operator turns a state vector into another state vector. It is defined by its action on an arbitrary operator **A**:

$$\mathsf{L}\,\mathbf{A} \quad [\mathbf{H},\mathbf{A}]$$

(29)

The Liouville Equation can then be written in complete analogy with (4) as

$$\frac{\partial \rho}{\partial t} = -i\mathsf{L}\ \rho \tag{30}$$

$$\rho(t) = \mathsf{U}(t,t_0)\rho(t_0) \quad \mathsf{U}(t,t_0) = e^{-i\mathsf{L}(t-t_0)}$$

where in analogy with (8) we have also introduced a superoperator evolution operator that obeys the differential equation (compare 8)

$$\frac{\partial \mathsf{U}(t,t_0)}{\partial t} = -i\mathsf{L}\ \mathsf{U}(t,t_0) \tag{31}$$

Although these notations do not introduce anything new, they have the advantage that many of the equations valid for state vector dynamics can be taken over if one replaces state vectors by density operators and Hamiltonians by Liouvillians.

*A simple two state example, Density Operator versus State Vector*

Let us as a simple example consider a system with only two energy levels *a* en *b* (a concrete example would be the two energy levels of a spin 1/2 particle, Zeeman split by a magnetic field). For simplicity we choose the zero of energy so, that the energies are symmetrically distributed around zero. The matrix of the Hamiltonian in the basis of its two eigenstates |a> and |b> is then simply:

$$\mathbf{H} = \begin{array}{cc} 0 & \\ 0 & - \end{array} \tag{32}$$

We now consider the system in two different statistical states, with two different density matrices. First assume that at time *t=0* the system is in a pure state described by the state vector | > or the equivalent density operator | >< |. If | > is given by

$$| \ \rangle = \frac{1}{\sqrt{2}}\left(|a\rangle + |b\rangle\right) \tag{33}$$

the corresponding density matrix in the basis of the eigenstates |a> and |b> reads

$$\rho_1 = \frac{1}{2}\begin{array}{cc} 1 & 1 \\ 1 & 1 \end{array} \tag{34}$$

On the other hand we consider a mixed state of the system at time *t=0* in which there is a probability 1/2 that the system is in state |a> and 1/2 that it is in |b>. In that case the density matrix in the eigenstate basis is given by

$$\rho_2 = \frac{1}{2}\begin{array}{cc} 1 & 0 \\ 0 & 1 \end{array} \tag{35}$$

Note that according to (21) in both cases the probability of measuring the energy   or -   is equal to 1/2. Nevertheless the two density matrices describe different physical situations. If we are given the matrices in (34) and (35), then according (24) and (25) we can immediately verify that (34) refers to a pure state, while (35) does not:

$$Tr\rho_1^2 = 1 \quad Tr\rho_2^2 = \frac{1}{2} \qquad \rho_1^2 = \rho_1 \quad \rho_2^2 \quad \rho_2 \tag{36}$$

Moreover (35) and (36) will evolve differently in time. In fact one can easily verify by substitution into the equation of motion (27) and evaluating the commutator of (33) and (34) that at times other , $t=0$ (34) is given by:

$$\rho_1(t) = \frac{1}{2} \begin{array}{cc} 1 & e^{-i\ t} \\ e^{i\ t} & 1 \end{array} \tag{37}$$

On the other hand (35) obviously commutes with (33), so (27) then tells us (35) remains constant in time. In both cases the probabilities of measuring the energy or - are constant and equal to 1/2 at all times. However, the two distributions do differ for their predictions of other properties. For example consider a property *B* that only has off-diagonal matrix elements between our two energy eigenstates (in the spin example this might e.g. be the *x* component of the spin, if the magnetic field is in the *z* direction). For the average value of such a property we find using (20) and (35), (37):

$$\mathbf{B} = \begin{array}{cc} 0 & b \\ b & 0 \end{array} \tag{38}$$

$$\langle \mathbf{B} \rangle_1 = Tr\rho_1(t)\mathbf{B} = b\cos\ t \quad \langle \mathbf{B} \rangle_2 = Tr\rho_2(t)\mathbf{B} = 0$$

So while in the pure state the average value of *B* oscillates in time, it vanishes for all times in the mixed state, clearly demonstrating the physical difference of the two situations.

*Exercise*

Calculate the possible values for the property *B* above. What is the probability (as a function of time) of measuring each of these values in the statistical states studied above. Verify that the average values are indeed given by (38).

## 4. Quantum Statistical Response Functions

*Response Functions and the Density Operator*

In this chapter we will consider how to calculate the response functions we treated briefly in chapter 2 in the state vector formulation, when the system we study is described by a density operator rather than by a state vector. The problem we have to solve can be described as follows: At a time $t_0$ in the distant past the system is described by a density operator $\rho$ (usually the equilibrium operator (26)). Subsequently we disturb the system with a time dependent external perturbation $\mathbf{H}(t)$, such as one or more pulses of electromagnetic radiation. During the time the perturbation is present the density operator will evolve under the influence of both the unperturbed Hamiltonian $\mathbf{H}_0$ and the perturbation $\mathbf{H}(t)$. Finally we ask ourselves what the average value of some observable $\mathbf{A}$ will be when we measure it at some time $t$ in the future. Just as in chapter 2 the problem can most profitably be formulated in the Interaction Picture, where the density operator (and the state vectors from which it is constructed) only evolve under the influence of the perturbation $\mathbf{H}_I(t)$, while the operators describing observables are evolving with the unperturbed Hamiltonian $\mathbf{H}_0$. We easily derive from (11) and (27) the equations of motion in the Interaction Picture:

$$\frac{\partial \rho_I(t)}{\partial t} = -i\left[\mathbf{H}_I(t), \rho_I(t)\right]$$

$$\frac{\partial \mathbf{A}_I(t)}{\partial t} = i\left[\mathbf{H}_0(t), \mathbf{A}_I(t)\right] \qquad \mathbf{A}_I(t) = e^{i\mathbf{H}_0(t-t_0)}\mathbf{A}e^{-i\mathbf{H}_0(t-t_0)}$$

(39)

We can now use equation (39) to derive a perturbation expansion for the density operator in the Interaction Picture in powers of the perturbation $\mathbf{H}_I(t)$. To this purpose we can, to first order, replace the density operator on the right hand side of (39) by its unperturbed value at time $t_0$. It is then easy to integrate (39) and we find to first order:

$$\rho_I(t) = \rho_I(t_0) - i\int_{t_0}^{t} d\tau_1\left[\mathbf{H}_I(\tau_1), \rho_I(t_0)\right]$$

(40)

To find the density operator to arbitrary order, we substitute this first order solution back into (39) and integrate again. Proceeding iteratively in this way we obtain the time dependent perturbation theory expansion for the density operator:

$$\rho_I(t) = \rho_I(t_0) + \sum_{n=1}(-i)^n\int_{t_0}^{t} d\tau_n\int_{t_0}^{\tau_n} d\tau_{n-1}\ldots\int_{t_0}^{\tau_2} d\tau_1\left[\mathbf{H}_I(\tau_n),\left[\mathbf{H}_I(\tau_{n-1})\ldots,\left[\mathbf{H}_I(\tau_1), \rho_I(t_0)\right]\right]\right]$$

(42)

For the $n^{th}$-order response, i.e. the average value of the observable $\mathbf{A}$ at time $t$ we then find with the help of (20) (which remains valid in the Interaction Picture, prove this)

$$\langle \mathbf{A} \rangle_t^{(n)} = (-i)^n \int_{t_0}^{t} d\tau_n \int_{t_0}^{\tau_n} d\tau_{n-1} \ldots \int_{t_0}^{\tau_2} d\tau_1 \, Tr\mathbf{A}_I(t)\Big[\mathbf{H}_I(\tau_n),\Big[\mathbf{H}_I(\tau_{n-1})\ldots,\Big[\mathbf{H}_I(\tau_1),\rho_I(t_0)\Big]\Big]\Big] \quad (43)$$

As an important concrete example let the perturbation be due to an external time varying electric field *E(t)* interacting with the dipole moment operator μ of our system, so the interaction is $\mathbf{H}(t) = -\mu \, E(t)$. One then usually measures the resulting perturbed time varying dipole moment of the system, which (if macroscopic) will generate a measurable signal. The time dependent proportionality factors between the $n^{th}$ power of the applied electric field and the $n^{th}$ order contribution to the resulting dipole moment are called the *dynamic $n^{th}$ (hyper-)polarisabilities* or the *non-linear susceptibilities* and are the prototypical examples of optical response functions. From (43) we find for these susceptibilities :

$$\langle \mu_i \rangle^{(n)}(t) = \sum_{i_n i_{n-1} \ldots i_1} \int_{t_0}^{t} d\tau_n \int_{t_0}^{\tau_n} d\tau_{n-1} \ldots \int_{t_0}^{\tau_2} d\tau_1 \, \chi_{ii_n i_{n-1} \ldots i_1}(t,\tau_n,\tau_{n-1},\ldots,\tau_1) \, E_{i_n}(\tau_n)E_{i_{n-1}}(\tau_{n-1})\ldots E_{i_1}(\tau_1)$$

$$\chi_{ii_n i_{n-1} \ldots i_1}(t,\tau_n,\tau_{n-1},\ldots,\tau_1) = i^n \, Tr\mu_{Ii}(t)\Big[\mu_{Ii_n}(\tau_n),\Big[\mu_{Ii_{n-1}}(\tau_{n-1})\ldots,\Big[\mu_{Ii_1}(\tau_1),\rho_I(t_0)\Big]\Big]\Big]$$

$$(44)$$

Note that the $n^{th}$ order susceptibility in (40) is an $(n+1)^{th}$ order tensor with respect to the Cartesian directions. It also seems to depend on $n+1$ different times, but we shall see that in actual fact it only depends on the $n$ differences between these times. Note also that there is no commutator involving the latest (left most) dipole operator.

*Pictorial Representation*

In the case of an isolated system (no relaxation) that we are considering here, we can in fact give explicit expressions for these response functions in terms of energy eigenvalues and eigenstates of the system. Due to the commutators in (44) we will have to treat an increasing number $(2^n)$ of terms as we go to higher order. To keep track of all these terms it turns out to be advantageous to represent them in a pictorial way. In order to see how this pictorial representation comes about, let us work out one term of the second order response function given by (44) with *n=2*. One contribution would be e.g.

$$-Tr\mu_{Ii}(t)\mu_{Ij}(\tau_1)\rho_I(t_0)\mu_{Ik}(\tau_2) = -\sum_{abc} P(a)\langle c|\mu_{Ii}(t)|b\rangle\langle b|\mu_{Ij}(\tau_1)|a\rangle\langle a|\mu_{Ik}(\tau_2)|c\rangle$$

$$P(a) = \tfrac{1}{Z}e^{-E_a/kT}$$

$$(45)$$

where we have explicitly written out the trace and inserted the completeness relation (5) for the eigenstates of the unperturbed Hamiltonian. The density operator at the start of the experiment is assumed to be in thermal equilibrium and is therefore given by (26). We now use equations (8) and (11) to calculate the matrix elements of the Interaction Picture dipole moment operators:

$$\langle a|\mu_I(\tau)|b\rangle = \langle a|U_0^\dagger(\tau - t_0)\mu U_0(\tau - t_0)|b\rangle = \langle a|e^{i\mathbf{H_0}(\tau - t_0)}\mu e^{-i\mathbf{H_0}(\tau - t_0)}|b\rangle =$$

$$e^{i(E_a - E_b)(\tau - t_0)}\langle a|\mu|b\rangle \tag{46}$$

where in the last line we have expressed everything in the matrix elements of the ordinary, time independent, Schrödinger Picture dipole moment operator. Substituting (46) into (45) we find:

$$-Tr\mu_{Ii}(t)\mu_{Ij}(\tau_1)\rho_I(t_0)\mu_{Ik}(\tau_2) = - \sum_{abc} P(a)\langle c|\mu_i|b\rangle\langle b|\mu_j|a\rangle\langle a|\mu_k|c\rangle e^{i(E_a - E_b)(\tau_2 - \tau_1)}e^{i(E_c - E_b)(t - \tau_2)} =$$

$$- \sum_{abc} P(a)\langle c|\mu_i|b\rangle\langle b|\mu_j|a\rangle\langle a|\mu_k|c\rangle e^{i(E_a - E_b)t_1}e^{i(E_c - E_b)t_2} \tag{47}$$

Note that (47) indeed only depends on the two differences of the three times and in the last line we have made this explicit by introducing relative time coordinates:

$$t_1 \quad \tau_2 - \tau_1 \qquad t_{n-1} \quad \tau_n - \tau_{n-1} \qquad t_n \quad t - \tau_n \tag{48}$$

Also note that the time $t_0$ (a time before any interaction, see above) has completely dropped out of the equation. This is physically sensible, since the system was in thermodynamic equilibrium before the external perturbation acts and can not therefore evolve from $t_0$ until $\tau_1$, the time of the first interaction.

With equation (47) we now associate a picture (Figure 1) that summarises the physical process involved and from which we can derive the corresponding equation in an unambiguous way. These pictures are known as *Double Sided Feynman Diagrams*.
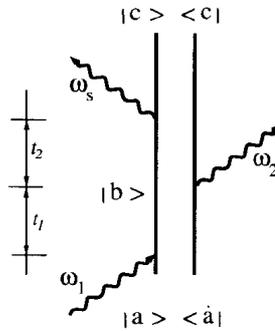


**Figure 1**

We read the diagram with time running from the bottom to the top. We start with the system in the state $|a\rangle\langle a|$ (the Boltzmann sum over $a$ is implicit). Subsequently the first interaction takes the system from the population $|a\rangle\langle a|$ into the coherence $|b\rangle\langle a|$. The left line in the diagram corresponds to the "ket" part of the operator, while the line on the right corresponds to the "bra" part. The interaction contributes a matrix element $<b|\mu|a>$ in (47) and is symbolised in the diagram by a wavy line (we ignore the arrow). Subsequently the system evolves freely for a time $t_1$ contributing a factor $exp(i(E_a-E_b))t_1$. Then the system again undergoes an interaction, taking it to the state $|b\rangle\langle c|$ and contributing a matrix element $<a|\mu|c>$ and a factor $-1$ coming from the

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commutator in (44). There is such a factor for every interaction on the right. Next the coherence evolves for a time $t_2$ contributing a factor $exp(i(E_c-E_b))t_2$. The final interaction takes the system from the coherence $|b><c|$ to the population $|c><c|$ and contributes a matrix element $<c|\mu|b>$. The total contribution is then obtained by summing the resulting expression over all the labels ($a$, $b$ and $c$ in this case).

Clearly every term in (44) can be represented by a similar diagram and conversely we can generate all the terms that contribute to the response function by enumerating all possible diagrams and associating an algebraic expression like (47) with each of them. The response function is then calculated as the sum of the contributions from all diagrams.

*General Rules for Double Sided Feynman Diagrams*

Let us summarise the general rules for associating and algebraic expression with a (double sided) Feynman diagram:

- For the $n^{th}$-order response function draw two lines representing the density operator and add $n$ wavy lines representing the interaction with the external perturbation connecting in all possible ways with either the left or the right line and in all possible time orderings. Add a final $(n+1)^{th}$ interaction representing the operator we measure the response of (**A** in (43)) on the *left only*. (We will always draw the arrow head pointing to the right except for the final one which points to the left, but we do not attach any significance to this convention.)
- Label all the lines between interactions with their energy level.
- Label all $n$ intervals between two successive interactions with a relative time coordinate $t_1$ $t_2$ ... $t_n$ starting at the bottom.
- For each interaction connecting a line labelled $a$ to a line labelled $b$ we have a factor $<a|\mu|b>$.
- For each interval $t_i$ we have a factor $e^{i(E_a - E_b)t_i}$ where $a$ is the label of the right line during this interval and $b$ the label of the left line. $E_a$ and $E_b$ are the corresponding energies.
- For each interaction on the right there is a factor $-1$.
- Add a Boltzmann factor $P(a) = \frac{1}{Z}e^{-E_a/kT}$ for the starting level $a$ at the very bottom.
- Finally sum over all labels and sum the contributions of all diagrams.
- The $n^{th}$ order response function has an overall phase $i^n$ from (44).

In Figure 2 we draw all possible 2$^{nd}$ order diagrams, while in Figure 3 all 3$^{rd}$ order diagrams are enumerated.

*Exercise*

Write down the algebraic expressions corresponding to the four 2$^{nd}$ order diagrams.

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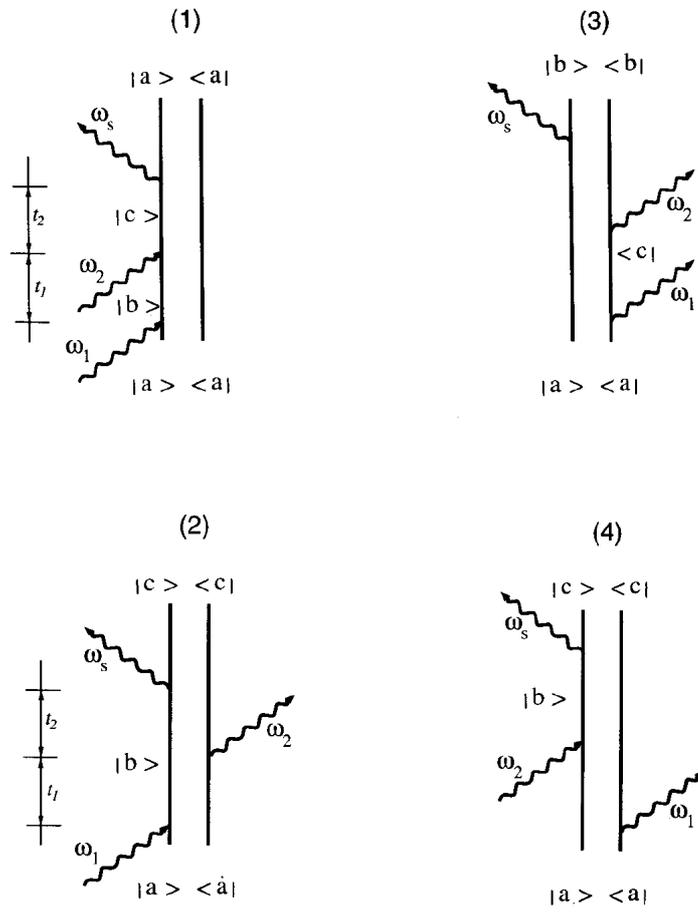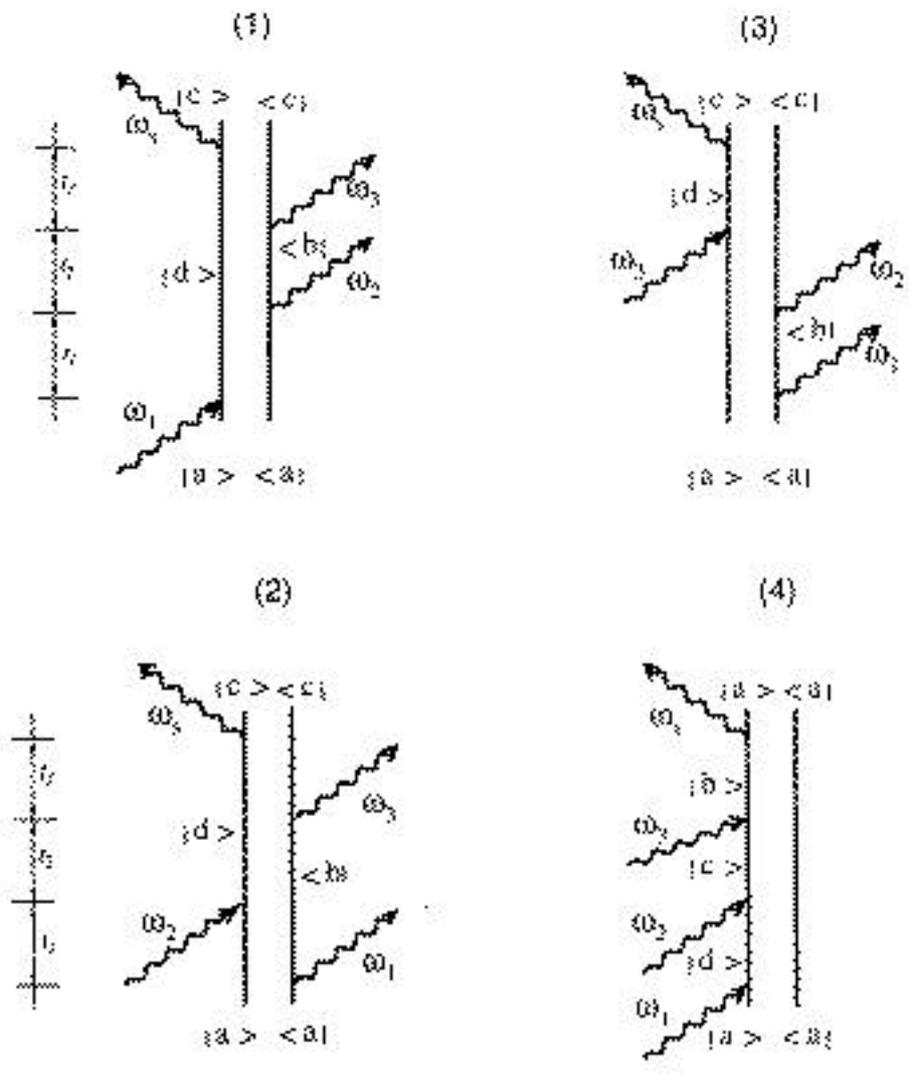
**Figure 2**

**Figure 3A**

Figure 3B

19
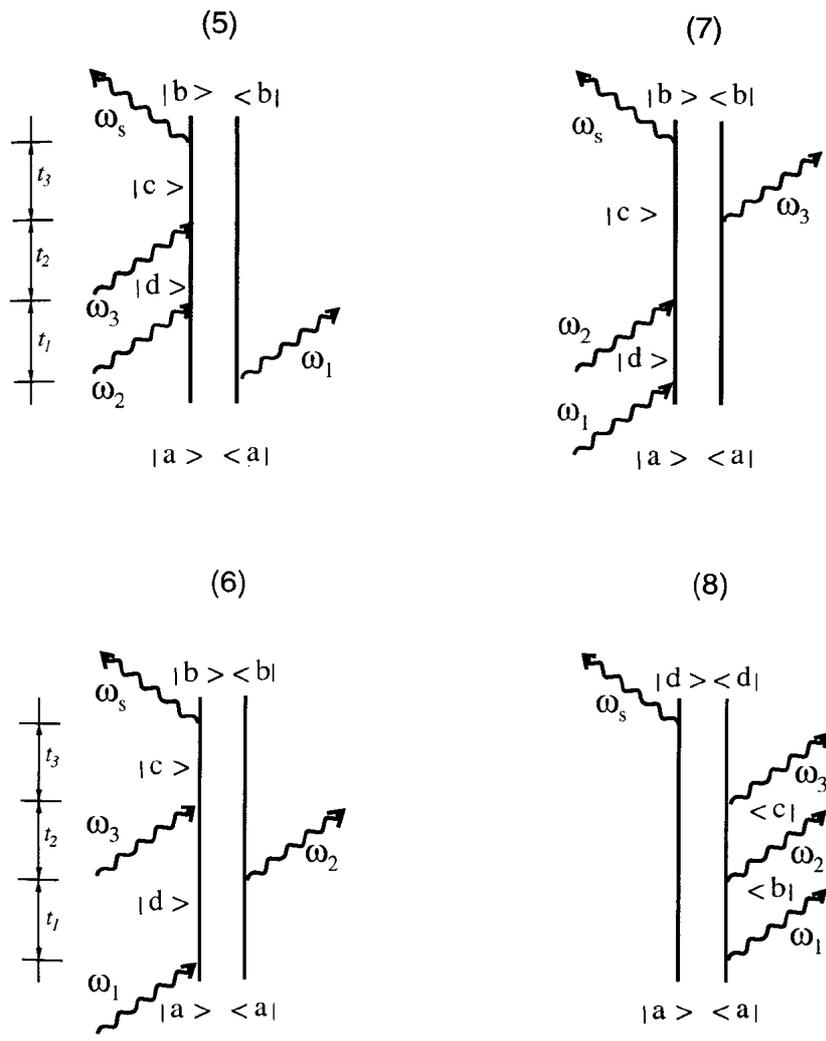
*Experimental Determination of Response Functions*

In the previous section we discussed how we can calculate the time development of the average dipole moment of a system under the influence of an external time dependent electric field. In real experiments of course, we have to consider a macroscopic sample and at any instant in time the electric field and consequently the induced dipole moment will depend on the position within the sample. However, in many cases it is a reasonably good approximation to assume that the local response only depends on the local field. We can then consider a volume element of our macroscopic system that is small compared to the wavelength of light and calculate the local dipole moment per unit volume (called the *polarisation P(r)*) just as in the previous section. Since we saw that the susceptibility only depends on the relative times defined in equation (48), we can write (44) at a particular point *r* in space in terms of these relative coordinates as:

$$P_i^{(n)}(t) = \sum_{i_n i_{n-1} \ldots i_1} \int_0^{} dt_n \int_0^{} dt_{n-1} \ldots \int_0^{} dt_1 \; \chi_{ii_n i_{n-1} \ldots i_1}(t_n, t_{n-1}, \ldots, t_1) \; E_{i_n}(t - t_n) E_{i_{n-1}}(t - t_n - t_{n-1}) \ldots E_{i_1}(t - t_n - t_{n-1} \ldots - t_1)$$

(49)

The time varying polarisation *P(t)* is in fact directly measurable, since from classical electrodynamics its generates a signal wave whose intensity is proportional to its square.

The are two idealised ways to set up the experiment. In the first type of experiment, called *time domain spectroscopy,* the perturbation consists of a series of short pulses of radiation, that is short compared to the time scale of evolution of the system studied, but nevertheless containing several periods of oscillation in the electric field in order to still be able to assign definite frequencies to the beams. One then studies the response (the signal generated by the polarisation) as a function of the delays between the pulses.

In the second type of experiment, called *frequency domain spectroscopy,* one uses a set of continuous beams of various frequencies, and one studies the intensity of the continuous signal generated by the polarisation as a function of these frequencies.

*Time Domain Spectroscopy*

The perturbation in this case can be written as the sum of a series of pulses at times $\tau_1, \ldots \tau_{n-1}, \tau_n$ with frequencies $\omega_1, \ldots \omega_{n-1}, \omega_n$. We can write this as a sum of delta function contributions:

$$E(\tau) = \sum_{j=1}^{n} E_j \delta(\tau - \tau_j) e^{-i\omega_j \tau_j}$$

(50)

Substituting into (49) and using the transformation to relative coordinates (48) we find after performing all the trivial time integrations

$$P^{(n)}(t) = \chi(t_n, t_{n-1}, \ldots, t_1) \; E_n E_{n-1} \ldots E_1 e^{\left[i(\omega_1 + \omega_2 + \ldots \omega_n)t_n + \ldots + i(\omega_1 + \omega_{2n})t_2 + i\omega_1 t_1\right]} \times$$
$$e^{-i(\omega_1 + \omega_2 + \ldots \omega_n)t}$$

(51)

where we have suppressed the obvious spatial tensor indices on the vector fields and the response function. We see that in this case the signal intensity (which is proportional to the squared polarisation) is directly proportional to the absolute value of the response function.

$$I_s(t) \sim \left| \chi(t_n, t_{n-1}, \ldots, t_1) \right|^2 \tag{52}$$

In fact one can show that with a different detection technique (so called heterodyne detection, which we will not treat here), the phase can also be measured.

*Frequency Domain Spectroscopy*

In this case the perturbation consists of a number on continuous monochromatic beams, so we can write for the time dependent electric field:

$$E(\tau) = \sum_{j=1}^{n} E_j e^{-i\omega_j \tau} \tag{53}$$

Substituting into (49) we find

$$P^{(n)}(t) = \chi(\omega_1 + \omega_2 + \ldots \omega_n, \ldots, \omega_1 + \omega_2, \omega_1) \, E_n E_{n-1} \ldots E_1 e^{-i(\omega_1 + \omega_2 + \ldots \omega_n)t}$$

$$\chi(\omega_n, \omega_{n-1}, \ldots, \omega_1) \quad \int_0^{\infty} dt_n \int_0^{\infty} dt_{n-1} \ldots \int_0^{\infty} dt_1 \, \chi(t_n, t_{n-1}, \ldots, t_1) \, e^{i\omega_n t_n + \ldots + i\omega_2 t_2 + i\omega_1 t_1} \tag{54}$$

So the signal is now proportional to the (one sided) Fourier Transform of the response function and therefore provides essentially the same information.

$$I_s(t) \sim \left| \chi(\omega_1 + \omega_2 + \ldots \omega_n, \ldots, \omega_1 + \omega_2, \omega_1) \right|^2 \tag{55}$$

The Fourier Transform in (54) can easily be carried out on the expressions given by the rules for Double Sided Feynman Diagrams above. The (one sided) Fourier Transform of the time factors given there for each time interval are found to be

$$\int_0^{\infty} dt_i \, e^{i(\omega_i + i\eta)t_1} e^{i(E_a - E_b)t_1} = \frac{-i}{E_a - E_b + \omega_i + i\eta} \tag{56}$$

where we have added a small imaginary part $i\eta$ to make the Fourier Transform converge. So to write down the frequency dependent response functions from the diagrams we can use the same Feynman rules as above with two exceptions:

- For each interval $n$ we have instead of the time dependent factor a frequency dependent factor $\dfrac{1}{E_a - E_b + \omega_i + i\eta}$

- There are no factors of $-i$ (the original factors cancel with those in (56))

The Fourier frequencies $_i$ can be directly replaced by the frequencies $_i$ of the radiation beams to calculate the response (54) and (55) with

$$_i = \sum_{j=1}^{i} \omega_j \tag{57}$$

In Figures 1 to 3 the frequencies of the participating beams are used as labels for each interaction, thus facilitating the transcription to algebraic expressions.
For example the contribution to the frequency response of the diagram in Figure 1 is given according to these rules by

$$-\sum_{abc} P(a) \frac{\langle c|\mu_i|b\rangle\langle b|\mu_j|a\rangle\langle a|\mu_k|c\rangle}{(E_c - E_b + \omega_1 + \omega_2 + i\eta)(E_a - E_b + \omega_1 + i\eta)} \tag{58}$$

Note that the response can be very large if the frequencies of the beams are close to making one of the denominators in (58) vanish. In such a case the experiment is said to be *resonant* or *near resonant* and we can then usually neglect all contributions from other diagrams that are not resonant (this is known as the *Rotating Wave Approximation*). In this way a particular experiment can sometimes be described by one or only a few diagrams.

*Exercise*

Calculate the contributions in the frequency domain for all the diagrams in Figure 2.

## 5.   Quantum Description of Relaxation Processes

*System-Bath Interaction*

As discussed in the introduction, experiments are rarely performed on single molecules in total isolation. Rather the systems studied interact with their environment during the course of the experiment and we have to take this interaction into account in some way in order to get a meaningful description of the response functions of the system. In order to do so we conceptually split the whole macroscopic system under consideration into the system proper, which we try to describe completely, and the rest which we will consider as a heat bath that can exchange energy with the system, but which we describe only in an average statistical way. The total Hamiltonian can then be written as the sum of the system Hamiltonian $\mathbf{H}_S$, the bath Hamiltonian $\mathbf{H}_B$ and their mutual interaction $\mathbf{H}_{SB}$. We can write these Hamiltonians in terms of their eigenstates and eigenenergies according to (6) as:

$$\mathbf{H}(q_S, q_B) = \mathbf{H}_S(q_S) + \mathbf{H}_B(q_B) + \mathbf{H}_{SB}(q_S, q_B)$$

$$\mathbf{H}_S = \sum_a E_a |a\rangle\langle a| \qquad \mathbf{H}_B = \sum_\alpha \varepsilon_\alpha |\alpha\rangle\langle\alpha| \tag{59}$$

$$\mathbf{H}_{SB} = \sum_{ab} F_{ab}(q_B)|a\rangle\langle b| = \sum_{a\alpha\, b\beta} F_{a\alpha b\beta}|a\alpha\rangle\langle b\beta|$$

*Reduced Density Operator*

Before the system and bath interact we can write the density operator for the total system as the product of the density operators of the system and the bath respectively

$$\rho = \rho_B \sigma \qquad \rho_B = \frac{1}{Z} e^{-H_B/kT} \tag{60}$$

where we assume the bath to be in thermodynamic equilibrium, but allow the system to be in a general state. However, once the system and the bath interact the density operator will evolve according to the Liouville equation under the influence of the total Hamiltonian and will loose the simple product form (60). On the other hand we are usually only interested in the properties of the system and not in those of the bath. If we consider the average value of an operator that only acts on the system coordinates we have according to (20)

$$\langle \mathbf{A}\rangle = Tr\rho\mathbf{A} = \sum_{a\alpha} \langle a\alpha|\rho\mathbf{A}|a\alpha\rangle = \sum_a \langle a| \sum_\alpha \langle\alpha|\rho|\alpha\rangle \, \mathbf{A}|a\rangle = Tr_S\sigma\mathbf{A}$$

$$\sigma \quad Tr_B\rho \tag{61}$$

where we have defined the *reduced density operator* $\sigma$ as the trace of the total density operator with respect to the bath coordinates. Note that this definition is consistent with (but more general than) equation (60) since the trace of the bath density operator in (60) is unity. In order to describe the dynamics of the system with this reduced density operator we need an equation of motion for it, which we can derive from the

equation of motion (27) for the total density operator. Just like in (39) we will describe the evolution in the Interaction Picture, but now the unperturbed Hamiltonian is the sum of system and bath Hamiltonian, while the perturbation is the system-bath interaction. We therefore have:

$$\frac{\partial \rho_I(t)}{\partial t} = -i\big[\mathbf{H}_{SB}(t), \rho_I(t)\big]$$

$$\rho_I(t) = \rho_I(0) - i \int_0^t d\tau \big[\mathbf{H}_{SB}(\tau_1), \rho_I(\tau)\big] \tag{62}$$

$$\frac{\partial \rho_I(t)}{\partial t} = -i\big[\mathbf{H}_{SB}(t), \rho_I(0)\big] - \int_0^t d\tau \big[\mathbf{H}_{SB}(t), \big[\mathbf{H}_{SB}(\tau), \rho_I(\tau)\big]\big]$$

where we have iterated the differential equation once in order to get it into a form which turns out to be more convenient for the purpose of eliminating the bath coordinates. Since we expect the (large) bath to be hardly affected by the presence of the evolving system, we can to second order in the interaction write the density operator on the right in its unperturbed product form (60) after which we can take the trace on both sides with respect to the bath coordinates:

$$\frac{\partial \sigma_I(t)}{\partial t} = \frac{\partial Tr_B \rho_I(t)}{\partial t} = -i Tr_B\big[\mathbf{H}_{SB}(t), \rho_B \sigma_I(0)\big] - \int_0^t d\tau \, Tr_B\big[\mathbf{H}_{SB}(t), \big[\mathbf{H}_{SB}(\tau), \rho_B \sigma_I(\tau)\big]\big]$$

$$\tag{63}$$

This equation is an integro-differential equation for time evolution of the system density operator. The first term involves the system-bath interaction averaged over the bath coordinates:

$$Tr_B \mathbf{H}_{SB} \rho_B = \sum_{ab\alpha} P(\alpha) F_{a\alpha b\alpha} |a\rangle\langle b| = \sum_{ab} \langle F_{ab}\rangle |a\rangle\langle b| \qquad (q_S) \tag{64}$$

This is simply an additional term in the system Hamiltonian and we can therefore add it to the unperturbed Hamiltonian. Without loss of generality we can therefore assume that the system-bath interaction is defined in such a way that the first term on the right of (63) vanishes.

In order to reveal the content of (63) more clearly we take its matrix elements in the basis of the system energy eigenstates

$$\tilde{\sigma}_{ab}(t) = \langle a|\sigma_I(t)|b\rangle \qquad\qquad \sigma_I(t) = \sum_{cd} |c\rangle \tilde{\sigma}_{cd}(t)\langle d|$$

$$\tag{65}$$

$$\frac{\partial \tilde{\sigma}_{ab}(t)}{\partial t} = - \sum_{cd} \int_0^t d\tau \, \Gamma_{abcd}(t,\tau) \tilde{\sigma}_{cd}(\tau)$$

with $\Gamma$ defined as

$$\Gamma_{abcd}(t,\tau) = Tr_B\langle a|\big[\mathbf{H}_{SB}(t), \big[\mathbf{H}_{SB}(\tau), \rho_B |c\rangle\langle d|\big]\big]|b\rangle \tag{66}$$

Substituting (59) we find for $\Gamma$ the slightly complicated expression

$$\Gamma_{abcd}(t,\tau) = \sum_j \left\langle F_{aj}(t)F_{jc}(\tau)\right\rangle \delta_{bd} + \sum_j \left\langle F_{dj}(\tau)F_{jb}(t)\right\rangle \delta_{ac}$$
$$-\left\langle F_{db}(t)F_{ac}(\tau)\right\rangle - \left\langle F_{db}(\tau)F_{ac}(t)\right\rangle \tag{67}$$

where the brackets signify the average of a (bath) operator over the bath variables

$$\left\langle A(t_2)B(t_1)\right\rangle = Tr A(t_2)B(t_1)\rho_B = \left\langle A(t_2 - t_1)B(0)\right\rangle \tag{68}$$

Since the bath is supposed to be unaffected by the system and remains in (time independent) equilibrium, the average in (68) can only depend on the difference of the two times involved. Expectation values such as in (68) are known as *correlation functions* (of the bath in this case) and they describe to what extent the value of A at $t_2$ depends on the value of *B* at $t_1$. Because of the rapid random motion in the bath we expect that after a sufficiently long time $\tau_c$, called the *correlation time*, the bath will have lost all memory of the situation at times longer ago than $\tau_c$. The average values of *A* and *B* will then be independent of each other and we simply have

$$\left\langle A(t_2)B(t_1)\right\rangle = \left\langle A(t_2)\right\rangle\left\langle B(t_1)\right\rangle \qquad t_2 - t_1 >> \tau_c \tag{69}$$

In the case of $\Gamma$ the average values of the *F* operators in (67) vanish (their average value was absorbed into the unperturbed Hamiltonian (see (64)). Therefore the $\Gamma$ functions will vanish if the difference of their time arguments is larger than the correlation time of the bath and moreover (68) tells us that they only depend on the difference of their arguments

$$\Gamma(t,\tau) = \Gamma(t - \tau)$$
$$\Gamma(t - \tau) = 0 \qquad t - \tau >> \tau_c \tag{70}$$

The equation of motion for the reduced density matrix (65) is difficult to solve in general even if the $\Gamma$ functions are known, but one can make progress in special circumstances. Let us assume that the random motions in the bath are so fast and consequently the correlation time so short, that our system does not evolve appreciably during a time interval equal to this correlation time. In this case, called the *homogeneous limit,* we can take the density matrix outside the integral in (65) and we can take the limits on the integration to infinity since $\Gamma$ vanishes anyway in this added integration range. We then find a differential equation with constant coefficients equation for the reduced density matrix, which can be solved:

$$\frac{\partial \tilde{\sigma}_{ab}(t)}{\partial t} = -\sum_{cd} \Gamma_{abcd}\, \tilde{\sigma}_{cd}(t)$$

$$\Gamma_{abcd} = \int_0^\infty d\tau\, \Gamma_{abcd}(\tau) \tag{71}$$

*Population Relaxation*

Let us study these equations a little closer in the simple case of a system with only two energy levels *a* and *b*. We first concentrate on the evolution of the populations (the diagonal elements). From (67) we have for the relevant matrix elements

$$\Gamma_{aaaa} = -\Gamma_{bbaa} = \int_0^\infty d\tau \langle F_{ab}(\tau)F_{ba}(0)\rangle e^{i\omega_{ab}\tau} + c.c \equiv \gamma_a$$

$$\Gamma_{bbbb} = -\Gamma_{aabb} = \int_0^\infty d\tau \langle F_{ba}(\tau)F_{ab}(0)\rangle e^{i\omega_{ab}\tau} + c.c \equiv \gamma_b \tag{72}$$

For the populations we then have according to (71) a differential equation with simple solutions (check them):

$$\begin{pmatrix} \dot{\sigma}_{aa} \\ \dot{\sigma}_{bb} \end{pmatrix} = -\begin{pmatrix} \gamma_a & -\gamma_b \\ -\gamma_a & \gamma_b \end{pmatrix}\begin{pmatrix} \sigma_{aa} \\ \sigma_{bb} \end{pmatrix} \qquad \sigma_{aa} + \sigma_{bb} = 1$$

$$\sigma_{aa}(t) = \sigma_{aa}(\infty) + e^{-(\gamma_a + \gamma_b)t}\left(\sigma_{aa}(0) - \sigma_{aa}(\infty)\right) \qquad \sigma_{aa}(\infty) = \frac{\gamma_a}{\gamma_a + \gamma_b} \tag{73}$$

$$\sigma_{bb}(t) = \sigma_{bb}(\infty) + e^{-(\gamma_a + \gamma_b)_1 t}\left(\sigma_{bb}(0) - \sigma_{bb}(\infty)\right) \qquad \sigma_{bb}(\infty) = \frac{\gamma_b}{\gamma_a + \gamma_b}$$

We see that the populations decay exponentially due to the interaction with the bath and eventually reach constant values (they have relaxed). The inverse of the exponent in (73) is often denoted $T_1$ and is called the *longitudinal relaxation time*.

One can in fact show from (72) that there is a relation between the $\gamma$'s, called the *detailed balance condition* given by

$$\gamma_b = \gamma_a e^{-\omega_{ab}/kT} \tag{74}$$

Equation (73) tells us then that the final values for the populations are exactly given by the Boltzmann factor, i.e. our system has come into equilibrium at the temperature $T$ of the bath.

Note incidentally from (72) that the population relaxation is entirely due to the off-diagonal parts in the system-bath interaction, which is physically reasonable since these can cause transitions in the system which brings it to equilibrium. The diagonal parts do influence the system in a different way which we study next.

*Dephasing*

In a similar way as described above one can study the decay of the off-diagonal elements of the density matrix (the coherences). When left undisturbed the off-diagonal elements remain constant in the Interaction Picture and oscillate in the Schrödinger picture as

$$\sigma_{ab}(t) = \tilde{\sigma}_{ab} e^{i\omega_{ab}t} \tag{75}$$

When we take relaxation into account, the off-diagonal elements will decay to zero, i.e. they will loose their (time dependent) phase, a process which is therefore called *dephasing*. From equation (71) we have for the off-diagonal elements

$$\frac{\partial \tilde{\sigma}_{ab}(t)}{\partial t} = - \Gamma_{abab} \tilde{\sigma}_{ab} \qquad \tilde{\sigma}_{ab}(t) = \tilde{\sigma}_{ab}(0) e^{-\Gamma_{abab}t} \tag{76}$$

showing the decay of the coherences. Note that eventually the density matrix becomes diagonal with diagonal elements given by the Boltzmann factor (see above) as is required for thermodynamic equilibrium. The inverse of the exponent in (76) is often denoted $T_2$ and is called the *transverse relaxation rate* (the names longitudinal and transverse derive from applications in the theory of NMR spectroscopy and are not particularly descriptive in the general case).

We can calculate the $\Gamma$ coefficient in (76) again from (67) and it is then found to contain two terms, one from the off-diagonal system-bath interactions that also caused the population relaxation and a second one, called the *pure dephasing,* which arises from the diagonal elements of this interaction.

$$\Gamma_{abab} = \tfrac{1}{2}\left(\gamma_a + \gamma_b\right) + \hat{\Gamma}_{ab}$$

$$\hat{\Gamma}_{ab} = \tfrac{1}{2} \int_0^\infty \left\langle \left(F_{aa}(\tau) - F_{bb}(\tau)\right)\left(F_{aa}(0) - F_{bb}(0)\right)\right\rangle + c.c. \tag{77}$$

Note that the pure dephasing rate depends only on the difference of two bath operators that will modulate (through the random motion of the bath) the energy difference between the two levels. One can therefore interpret the decay of the coherences as the destructive interference of the frequencies in (75) that are randomly modulated by the interaction with the bath.

*Incorporation of Relaxation into the Feynman Rules*

We have seen above that relaxation processes cause the density matrix elements to decay exponentially, but as (73) shows some populations, i.e. the ones at lower energy, also increase so as to preserve the trace. If we neglect this latter contribution we can make the approximation that all levels decay exponentially except the ground state level which remains constant. We can then write

$$\sigma_{ab}(t) = \sigma_{ab}(0) e^{i(\omega_{ab} + i\gamma_{ab})t} \qquad \gamma_{00} = 0 \tag{78}$$

This can easily be incorporated into the Feynman rules of the previous chapter.
In the time domain we have the modification
- For each interval $t_i$ we have a factor $e^{i(E_a - E_b + i\gamma_{ab})t_i}$ where $a$ is the label of the right line during this interval and $b$ the label of the left line. $E_a$ and $E_b$ are the corresponding energies

while in the frequency domain we obtain
- For each interval $n$ we have instead of the time dependent factor a frequency dependent factor $\dfrac{1}{E_a - E_b + \Omega_i + i\gamma_{ab}}$

As an example let us calculate the contribution to the frequency domain response of the diagram in Figure 1. Using the modified rules above we find instead of (58)

$$ - \sum_{abc} P(a) \frac{\langle c|\mu_i|b\rangle\langle b|\mu_j|a\rangle\langle a|\mu_k|c\rangle}{(E_c - E_b + \omega_1 + \omega_2 + i\gamma_{cb})(E_a - E_b + \omega_1 + i\gamma_{ab})} \tag{79}$$

Note that (79), unlike (58), can no longer become singular when we are at resonance. It might seem that (58) which was derived for an isolated system, without coupling to a bath that causes relaxation, would predict a singular (infinite) response when we would perform an experiment at resonance on an (almost) isolated system such as a molecule in a dilute gas. However, in reality there is always a relaxation process, even if we can neglect collisions in a dilute gas, namely the phenomenon of spontaneous emission, which can take place even in the absence of a radiation field. One can consider this process as a special case of the system-bath interaction described above, if one considers spontaneous emission as being caused by the interaction of the system with the zero point fluctuations of the quantized electro-magnetic field, which then plays the role of the bath. In practice the contribution of spontaneous emission is much smaller than the influence of molecular collisions and therefore only becomes important as a relaxation process in dilute gasses.

*Relaxation and Lineshape*

As a simple example of the theory above let us study the linear process of absorption of a beam of frequency    in a polarisable medium. In the presence of a polarisation P(r,t) the electromagnetic wave equation (which can be directly derived from the macroscopic Maxwell equations for a classical electromagnetic field) can be written as

$$ \nabla^2 E(r,t) + \frac{1}{c^2}\frac{\partial^2}{\partial t^2} E(r,t) = -\frac{4\pi}{c^2}\frac{\partial^2}{\partial t^2} P(r,t) \tag{80}$$

In the absence of the right hand side, (80) would simply be the well known wave equation for the electromagnetic field in vacuo, which has the simple wave solution (for a monochromatic wave travelling in the z-direction)

$$ E(z,t) = E_0 e^{ikz - i\omega t} = E_0 e^{i\frac{\omega}{c} z - i\omega t} \qquad \frac{kc}{\omega} = 1 \tag{81}$$

which shows that the wave travels with a speed c.
If we now include the influence of the medium on the right hand side and if we realise that in general the polarisation is related non-linearly to the electric field (see (49)) equation (80) becomes a complicated non-linear differential equation that essentially contains all the various effects on non-linear optics.
Here we will confine ourselves to the simple case of linear response and we then have according to (54), using only the linear susceptibility

$$ P(r,t) = \chi(\omega)E(r,t) \tag{82}$$

In this case we can incorporate the right hand side of (80) on the left and find a modified wave equation

$$\nabla^2 E(r,t) + \frac{\varepsilon(\omega)}{c^2}\frac{\partial^2}{\partial t^2}E(r,t) = 0 \qquad \varepsilon(\omega) = 1 + 4\pi\chi(\omega) \tag{83}$$

where we have defined the frequency dependent dielectric constant in terms of the susceptibility. This is again of the form of the wave equation in vacuum with a solution like (81), except that the relation between the wave vector k and the frequency $\omega$ has now become frequency dependent and consequently the velocity of light in the medium has been changed and is different for different frequencies (colours), a phenomenon known as dispersion. Moreover, one has to realise that the susceptibility is in general a complex quantity and we can write

$$\frac{kc}{\omega} = \sqrt{\varepsilon(\omega)} = \sqrt{1 + 4\pi\chi(\omega)} \equiv n(\omega) + i\kappa(\omega)$$

$$n(\omega) \approx \sqrt{1 + 4\pi\,\mathrm{Re}\,\chi(\omega)} \qquad \kappa(\omega) \approx \frac{2\pi}{n(\omega)}\,\mathrm{Im}\,\chi(\omega) \tag{84}$$

where we have defined the *index of refraction n(ω)* and the *extinction coefficient κ(ω)*. So in a medium the solution (81) now becomes

$$E(z,t) = E_0\,e^{ikz-i\omega t} = E_0\,e^{i\frac{\omega n(\omega)}{c}z - \frac{\omega\kappa(\omega)}{c}z - i\omega t} \tag{85}$$

which clearly shows that the velocity of the beam has been changed by a factor equal to the index of refraction. In addition the extinction coefficient contributes a term which exponentially extinguishes the beam, i.e. the beam is being *absorbed*. From (84) we see that the strength of the absorption is directly proportional to the *imaginary* part of the linear susceptibility. The absorption of course depends on the frequency and will in general exhibit a more or less sharp peak near a resonance of the system. The behaviour of the absorption around the resonance, called the *line form,* is therefore directly determined by the imaginary part of $\chi$. Let us calculate this line form with the tools developed in the previous sections. First we write down the Double Sided Feynman Diagrams for the linear susceptibility of which there are only two:
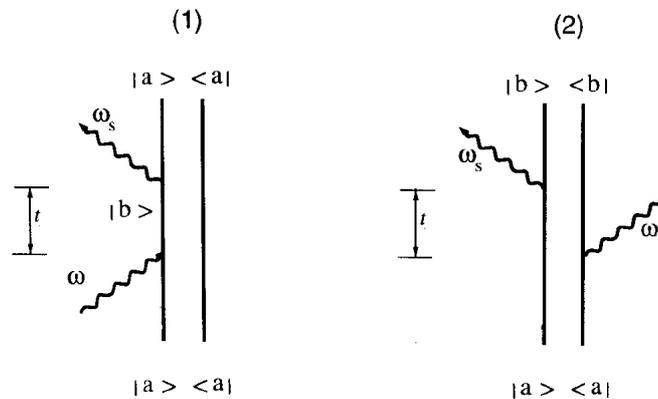


**Figure 4**

We can immediately write down the linear susceptibility in the frequency domain using our rules and we find

$$\chi(\omega) = \sum_{ab} P(a)\frac{\langle a|\mu|b\rangle\langle b|\mu|a\rangle}{E_a - E_b + \omega + i\gamma_{ab}} - \sum_{ab} P(a)\frac{\langle a|\mu|b\rangle\langle b|\mu|a\rangle}{E_b - E_a + \omega + i\gamma_{ba}} \tag{86}$$

If we assume that we are near the resonance $\omega \approx E_b - E_a$ only the first term becomes large, while the second (said to be anti-resonant) can be neglected (Rotating Wave Approximation). Also in the sum we can neglect all non-resonant terms and we can then find the imaginary part of the susceptibility, which directly gives us the absorption line form as

$$\text{Im}\,\chi(\omega) = \text{Im}\,P(a)\frac{\langle a|\mu|b\rangle\langle b|\mu|a\rangle}{E_a - E_b + \omega + i\gamma_{ab}} = P(a)|\langle a|\mu|b\rangle|^2\frac{\gamma_{ab}}{\left(E_a - E_b + \omega\right)^2 + \gamma_{ab}^2} \tag{87}$$

The line shape has the characteristic *Lorentzian Form* in this homogeneous (see above) limit. If the relaxation was totally absent (which as discussed above is never realistic) we would obtain an infinitely sharp delta function form

$$\text{Im}\,\chi(\omega) = \lim_{\eta \to 0}\text{Im}\,P(a)\frac{\langle a|\mu|b\rangle\langle b|\mu|a\rangle}{E_a - E_b + \omega + i\eta} = P(a)|\langle a|\mu|b\rangle|^2 \pi\delta(E_a - E_b + \omega) \tag{88}$$

and therefore the relaxation is said to be responsible for *line broadening* (in the limit (87) *homogeneous line broadening*). If the only relaxation process is spontaneous emission, we again find (87) with the 's (the inverse lifetimes) determined by the interaction with the quantised electromagnetic field. The line shape is then called the *Natural Line Shape*, which usually has a much smaller width than any broadening caused by other relaxation mechanisms if present.

We can also consider the opposite limit to the homogeneous relaxation process. We assume that the motions in the bath are so slow that our system (say a molecule in a liquid or a glass) only sees a static environment during the course of the experiment. We can then calculate the response function for each environment, all with slightly different energy differences and we subsequently average the response over all environments. If we assume that the energy differences $_{ba}$ have a Gaussian distribution around the average $E_b$-$E_a$ with a width $\Delta$ we find using (88) weighted with this distribution

$$\langle\text{Im}\,\chi(\omega)\rangle = \int_{-}^{} e^{-\frac{(\omega_{ba} - (E_b - E_a))^2}{\Delta^2}}\left(P(a)|\langle a|\mu|b\rangle|^2 \pi\delta(\omega - \omega_{ba})\right)d\omega_{ba}$$

$$= P(a)|\langle a|\mu|b\rangle|^2 \pi e^{-\frac{(\omega - (E_b - E_a))^2}{\Delta^2}} \tag{89}$$

So in this case, called the *inhomogeneous limit* (the system is inhomogeneous in the sense that each molecule sees a different environment), we find a *Gaussian Line Form* and we speak of *inhomogeneous line broadening*.

*Outlook*

In general at least some bath motions are neither fast nor slow on the time scale of the experiment and neither of the above limits is then reached.

In this general case it is impossible to calculate the response functions or find the line forms without a detailed modelling of the bath itself, which we will not consider in this short course. Two ways of tackling this problem have been widely used. In the first approach the bath is modelled by a large collection of random (Brownian) harmonic oscillators of various frequencies that interact in a simple way with the system studied, which leads to models that can at least be approximately solved. The second approach, used e.g. in the description of response in liquids, is to describe the intermolecular motions of the molecules (which constitute the bath from the point of view of a single molecule) by classical mechanics using molecular dynamics simulations.

## 6. General References

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