5.74 Introductory Quantum Mechanics II
Spring 2009

10. <u>NONLINEAR SPECTROSCOPY</u>

10.1. <u>Introduction</u>

Spectroscopy comes from the Latin "spectron" for *spirit* or *ghost* and the Greek "σκοπιεν" for *to see*. These roots are very telling, because in molecular spectroscopy you use light to interrogate matter, but you actually never see the molecules, only their influence on the light. Different spectroscopies give you different perspectives. This indirect contact with the microscopic targets means that the interpretation of spectroscopy in some manner requires a model, whether it is stated or not. Modeling and laboratory practice of spectroscopy are dependent on one another, and therefore a spectroscopy is only as useful as its ability to distinguish different models. The observables that we have to extract microscopic information in traditional spectroscopy are resonance frequencies, spectral amplitudes, and lineshapes. We can imagine studying these spectral features as a function of control variables for the light field (amplitude, frequency, polarization, phase, etc.) or for the sample (for instance a systematic variation of the physical properties of the sample).

In complex systems, those in which there are many interacting degrees of freedom and in which spectra become congested or featureless, the interpretation of traditional spectra is plagued by a number of ambiguities. This is particularly the case for spectroscopy of disordered condensed phases, where spectroscopy is the primary tool for describing molecular structure, interactions and relaxation, kinetics and dynamics, and tremendous challenges exist on understanding the variation and dynamics of molecular structures. This is the reason for using nonlinear spectroscopy, in which multiple light-matter interactions can be used to correlate different spectral features and dissect complex spectra. We can resonantly drive one spectroscopic feature and see how another is influenced, or we can introduce time delays to see how properties change with time.

Absorption or emission spectroscopies are referred to as linear spectroscopy, because they involve a weak light-matter interaction with one primary incident radiation field, and are typically presented through a single frequency axis. The ambiguities that arise when interpreting linear spectroscopy can be illustrated through two examples:

1)   Absorption spectrum with two peaks.

Do these resonance arise from different, non-interacting molecules, or are these coupled quantum states of the same molecule? (One cannot resolve couplings or spectral correlations directly).
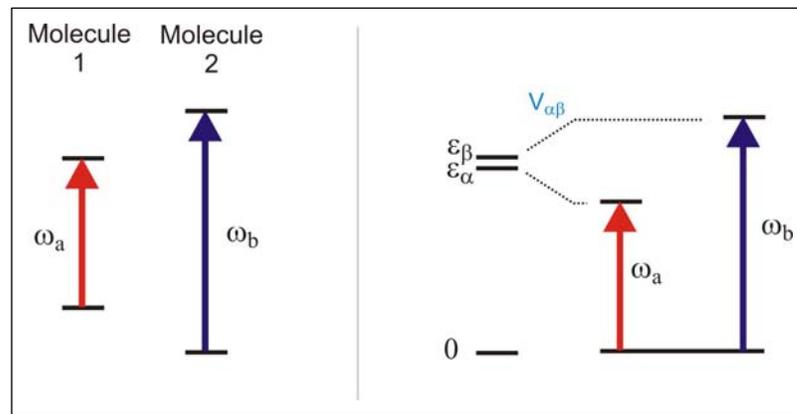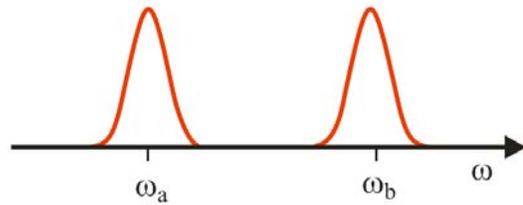
2)   Broad lineshapes. Can you distinguish whether it is a homogeneous lineshape broadened by fast irreversible relaxation or an inhomogeneous lineshape arising from a static distribution of different frequencies? (Linear spectra cannot uniquely interpret line-broadening mechanism, or decompose heterogeneous behavior in the sample).
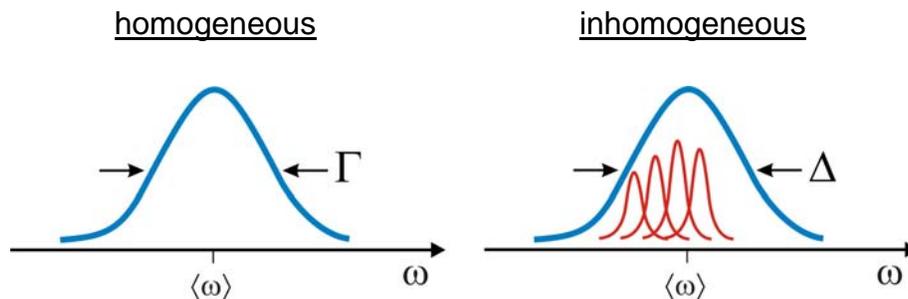
In the end effect linear spectroscopy does not offer systematic ways of attacking these types of problems. It also has little ability to interpret dynamics and relaxation. These issues take on more urgency in the condensed phase, when lineshapes become broad and spectra are congested.

Nonlinear spectroscopy provides a way of resolving these scenarios because it uses multiple light fields with independent control over frequency or time-ordering in order to probe correlations between different spectral features. For instance, the above examples could be interpreted with the use of a double-resonance experiment that reveals how excitation at one frequency ω_1 influences absorption at another frequency ω_2.

What is nonlinear spectroscopy?

Linear spectroscopy commonly refers to light-matter interaction with one primary incident radiation field which is weak, and can be treated as a linear response between the incident light and the matter. From a quantum mechanical view of the light field, it is often conceived as a "one photon in/one photon out" measurement. Nonlinear spectroscopy is used to refer to cases that fall outside this view, including: (1) Watching the response of matter subjected to interactions with two or more independent incident fields, and (2) the case where linear response theory is inadequate for treating how the material behaves, as in the case of very intense incident radiation. If we work within the electric dipole Hamiltonian, nonlinear experiments can be expressed in terms of three or more transition matrix elements. The response of the matter in linear experiments will scale as $\left|\mu_{ab}\right|^2$ or $\mu_{ab}\mu_{ba}$, whereas in nonlinear experiments will take a form such as $\mu_{ab}\mu_{bc}\mu_{ca}$. Our approach to describing nonlinear spectroscopy will use the electric dipole Hamiltonian and a perturbation theory expansion of the dipole operator.

10.2. COHERENT SPECTROSCOPY AND THE NONLINEAR POLARIZATION

We will specifically be dealing with the description of coherent nonlinear spectroscopy. If you cross three intense light fields in a sample, you can observe an array of spots behind the sample, which may be the same or different colors. These are nonlinear signals that arise when one or more input fields coherently act on the dipoles of the sample to generate a macroscopic oscillating polarization. This polarization acts as a source to radiate a
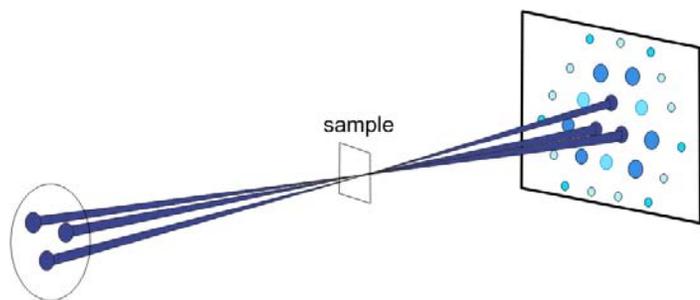
signal that we detect in a well-defined direction. This class includes experiments such as pump-probes, transient gratings, photon echoes, and coherent Raman methods. However understanding these experiments allows one to rather quickly generalize to other techniques.

Detection:	**Coherent**	**Spontaneous**
	$$I_{coherent} \propto \left| \sum_i \mu_i \right|^2$$ Dipoles are driven coherently, and radiate with constructive interference in direction $\overline{k}_{sig}$	$$I_{spont.} \propto \sum_i \left| \mu_i \right|^2$$ Dipoles radiate independently $$\overline{E}_{sig} \propto \sin\theta$$
Linear:	Absorption	Fluorescence, phosphorescence, Raman, and light scattering
Nonlinear:	Pump-probe transient absorption, photon echoes, transient gratings, CARS, impulsive Raman scattering	Fluorescence-detected nonlinear spectroscopy, i.e. stimulated emission pumping, time-dependent Stokes shift
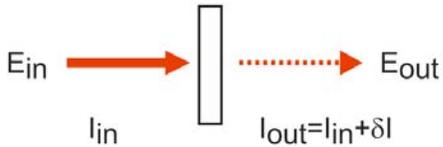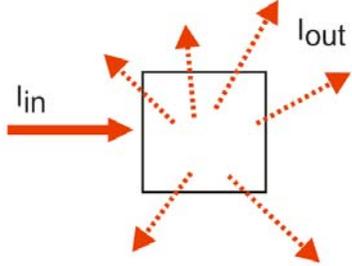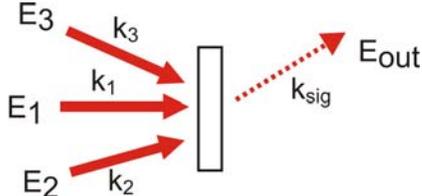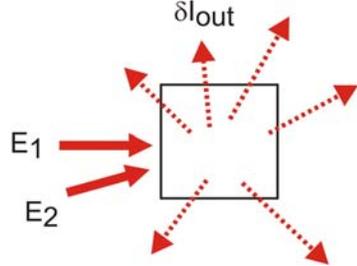
Spontaneous and coherent signals are both emitted from all samples, however, the relative amplitude of the two depend on the time-scale of dephasing within the sample. For electronic transitions in which dephasing is typically much faster than the radiative lifetime, spontaneous emission is the dominant emission process. For the case of vibrational transitions

where non-radiative relaxation is typically a picoseconds process and radiative relaxation is a μs or longer process, spontaneous emission is not observed.

The description of coherent nonlinear spectroscopies is rooted in the calculation of the polarization, $\bar{P}$. The polarization is a macroscopic collective dipole moment per unit volume, and for a molecular system is expressed as a sum over the displacement of all charges for all molecules being interrogated by the light

Sum over molecules:
$$\bar{P}(\bar{r}) = \sum_m \bar{\mu}_m \, \delta(\bar{r} - \bar{R}_m) \tag{10.1}$$

Sum over charges on molecules:
$$\bar{\mu}_m \equiv \sum_\alpha q_{m\alpha}(\bar{r}_{m\alpha} - \bar{R}_m) \tag{10.2}$$

In coherent spectroscopies, the input fields $\bar{E}$ act to create a macroscopic, coherently oscillating charge distribution

$$\bar{P}(\omega) = \chi \bar{E}(\omega) \tag{10.3}$$

as dictated by the susceptibility of the sample. The polarization acts as a source to radiate a new electromagnetic field, which we term the signal $\bar{E}_{sig}$. (Remember that an accelerated charge radiates an electric field.) In the electric dipole approximation, the polarization is one term in the current and charge densities that you put into Maxwell's equations.

From our earlier description of freely propagating electromagnetic waves, the wave equation for a transverse, plane wave was

$$\bar{\nabla}^2 \bar{E}(\bar{r},t) - \frac{1}{c^2}\frac{\partial^2 \bar{E}(\bar{r},t)}{\partial t^2} = 0 \,, \tag{10.4}$$

which gave a solution for a sinusoidal oscillating field with frequency ω propagating in the direction of the wavevector k. In the present case, the polarization acts as a source –an accelerated charge– and we can write

$$\bar{\nabla}^2 \bar{E}(\bar{r},t) - \frac{1}{c^2}\frac{\partial^2 \bar{E}(\bar{r},t)}{\partial t^2} = \frac{4\pi}{c^2}\frac{\partial^2 \bar{P}(\bar{r},t)}{\partial t^2} \tag{10.5}$$

The polarization can be described by solutions of the form

$$\bar{P}(\bar{r},t) = P(t)\exp\left(i\bar{k}'_{sig}\cdot\bar{r} - i\omega_{sig}t\right) + c.c. \tag{10.6}$$

As we will discuss further later, the wavevector and frequency of the polarization depend on the frequency and wave vector of incident fields.

$$\overline{k}_{sig} = \sum_n \pm \overline{k}_n \tag{10.7}$$

$$\omega_{sig} = \sum_n \pm \omega_n \; . \tag{10.8}$$

These relationships enforce momentum and energy conservation for the problem. The oscillating polarization radiates a coherent signal field, $\overline{E}_{sig}$, in a wave vector matched direction $\overline{k}_{sig}$. Although a single dipole radiates as a *sin* θ field distribution relative to the displacement of the charge,[1] for an ensemble of dipoles that have been coherently driven by external fields, P is given by (10.6) and the radiation of the ensemble only constructively adds along $\overline{k}_{sig}$. For the radiated field we obtain

$$\overline{E}_{sig}(\overline{r},t) = E_{sig}(\overline{r},t)\exp\left(i\overline{k}_{sig}\cdot\overline{r} - i\omega_{sig}t\right) + c.c. \tag{10.9}$$

This solution comes from solving (10.5) for a thin sample of length l, for which the radiated signal amplitude grows and becomes directional as it propagates through the sample. The emitted signal

$$\overline{E}_{sig}(t) = i\frac{2\pi\omega_s}{nc}l\overline{P}(t)\mathrm{sinc}\left(\frac{\Delta kl}{2}\right)e^{i\Delta kl/2} \tag{10.10}$$

Here we note the oscillating polarization is proportional to the signal field, although there is a $\pi/2$ phase shift between the two, $\overline{E}_{sig} \propto i\overline{P}$, because in the sample the polarization is related to the gradient of the field. Δk is the wave-vector mismatch between the wavevector of the polarization $\overline{k}'_{sig}$ and the radiated field $\overline{k}_{sig}$, which we will discuss more later.

For the purpose of our work, we obtain the polarization from the expectation value of the dipole operator

$$\overline{P}(t) \Rightarrow \overline{\mu(t)} \tag{10.11}$$

The treatment we will use for the spectroscopy is semi-classical, and follows the formalism that was popularized by Mukamel.[2] As before our Hamiltonian can generally be written as

$$H = H_0 + V(t) \tag{10.12}$$

where the material system is described by H_0 and treated quantum mechanically, and the electromagnetic fields $V(t)$ are treated classically and take the standard form

$$V(t) = -\overline{\mu}\cdot\overline{E} \tag{10.13}$$

The fields only act to drive transitions between quantum states of the system. We take the interaction with the fields to be sufficiently weak that we can treat the problem with perturbation theory. Thus, n^{th}-order perturbation theory will be used to describe the nonlinear signal derived from interacting with n electromagnetic fields.

Linear absorption spectroscopy

Absorption is the simplest example of a coherent spectroscopy. In the semi-classical picture, the polarization induced by the electromagnetic field radiates a signal field that is out-of-phase with the transmitted light. To describe this, all of the relevant information is in $R(t)$ or $\chi(\omega)$.

$$\bar{P}(t) = \int_0^\infty d\tau \, R(\tau) E(t-\tau) \tag{10.14}$$

$$\bar{P}(\omega) = \chi(\omega) \bar{E}(\omega) \tag{10.15}$$

Let's begin with a frequency-domain description of the absorption spectrum, which we previously found was proportional to the imaginary part of the susceptibility, χ''.[3] We consider one monochromatic field incident on the sample that resonantly drives dipoles in the sample to create a polarization, which subsequently re-radiate a signal field (free induction decay). For one input field, the energy and momentum conservation conditions dictate that $\omega_{in} = \omega_{sig}$ and $k_{in} = k_{sig}$, that is a signal field of the same frequency propagates in the direction of the transmitted excitation field.
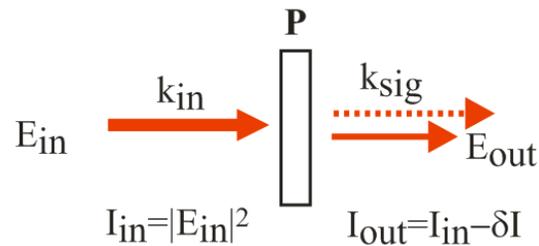
In practice, an absorption spectrum is measured by characterizing the frequency-dependent transmission decrease on adding the sample $A = -\log I_{out}/I_{in}$. For the perturbative case, let's take the change of intensity $\delta I = I_{in} - I_{out}$ to be small, so that $A \approx \delta I$ and $I_{in} \approx I_{out}$. Then we can write the measured intensity after the sample as

$$
\begin{aligned}
I_{out} &= \left| E_{out} + E_{sig} \right|^2 = \left| E_{out} + \left(iP \right) \right|^2 \\
&= \left| E_{out} + i\chi E_{in} \right|^2 \approx \left| E_{in} + i\chi E_{in} \right|^2 \\
&= \left| E_{in} \right|^2 \left| 1 + i \left(\chi' + i\chi'' \right) \right|^2 \\
&= I_{in} \left(1 - 2\chi'' + \dots \right) \qquad \Rightarrow \qquad I_{out} = I_{in} - \delta I
\end{aligned}
\tag{10.16}
$$

Here we have made use of the assumption that $\left| E_{in} \right| \gg \left| \chi \right|$. We see that as a result of the phase shift between the polarization and the radiated field that the absorbance is proportional to χ'': $\delta I = 2\chi'' I_{in}$.

A time-domain approach to absorption draws on eq. (10.14) and should recover the relationships to the dipole autocorrelation function that we discussed previously. Equating $\bar{P}(t)$ with $\overline{\mu(t)}$, we can calculate the polarization in the density matrix picture as

$$
\bar{P}(t) = Tr\left(\mu_I(t) \rho_I^{(1)}(t) \right)
\tag{10.17}
$$

where the first-order expansion of the density matrix is

$$
\rho_I^{(1)} = -\frac{i}{\hbar} \int_{-\infty}^{t} dt_1 \left[V_I(t_1), \rho_{eq} \right].
\tag{10.18}
$$

Substituting eq. (10.13) we find

$$
\begin{aligned}
\bar{P}(t) &= Tr\left(\mu_I(t) \frac{i}{\hbar} \int_{-\infty}^{t} dt' \left[-\mu_I(t') E(t'), \rho_{eq} \right] \right) \\
&= \frac{-i}{\hbar} \int_{-\infty}^{t} dt' \, E(t') \, Tr\left(\mu_I(t) \left[\mu_I(t'), \rho_{eq} \right] \right) \\
&= +\frac{i}{\hbar} \int_{0}^{\infty} d\tau \, E(t-\tau) \, Tr\left(\left[\mu_I(\tau), \mu_I(0) \right] \rho_{eq} \right)
\end{aligned}
\tag{10.19}
$$

In the last line, we switched variables to the time interval $\tau = t - t'$, and made use of the identity $\left[A, \left[B, C \right] \right] = \left[\left[A, B \right], C \right]$. Now comparing to eq. (10.14), we see, as expected

$$
R(\tau) = \frac{i}{\hbar} \theta(\tau) Tr\left(\left[\mu_I(\tau), \mu_I(0) \right] \rho_{eq} \right)
\tag{10.20}
$$

So the linear response function is the sum of two correlation functions, or more precisely, the imaginary part of the dipole correlation function.

$$
R(\tau) = \frac{i}{\hbar} \theta(\tau) \left(C(\tau) - C^*(\tau) \right)
\tag{10.21}
$$

$$C(\tau) = Tr\left(\mu_I(\tau)\mu_I(0)\rho_{eq}\right)$$
$$C^*(\tau) = Tr\left(\mu_I(\tau)\rho_{eq}\,\mu_I(0)\right)$$

(10.22)

Also, as we would expect, when we use an impulsive driving potential to induce a free induction decay, i.e., $E(t-\tau) = E_0\delta(t-\tau)$, the polarization is directly proportional to the response function, which can be Fourier transformed to obtain the absorption lineshape.

Nonlinear Polarization

For nonlinear spectroscopy, we will calculate the polarization arising from interactions with multiple fields. We will use a perturbative expansion of P in powers of the incoming fields

$$\bar{P}(t) = P^{(0)} + P^{(1)} + P^{(2)} + P^{(3)} + \cdots$$

(10.23)

where $P^{(n)}$ refers to the polarization arising from n incident light fields. So, $P^{(2)}$ and higher are the nonlinear terms. We calculate P from the density matrix

$$\bar{P}(t) = Tr\left(\bar{\mu}_I(t)\rho_I(t)\right)$$
$$= Tr\left(\bar{\mu}_I\rho_I^{(0)}\right) + Tr\left(\bar{\mu}_I\,\rho_I^{(1)}(t)\right) + Tr\left(\mu_I\rho_I^{(2)}(t)\right) + \ldots$$

(10.24)

As we wrote earlier, $\rho_I^{(n)}$ is the nth order expansion of the density matrix

$$\rho^{(0)} = \rho_{eq}$$

$$\rho_I^{(1)} = -\frac{i}{\hbar}\int_{-\infty}^{t} dt_1\left[V_I(t_1),\rho_{eq}\right]$$

(10.25)

$$\rho_I^{(2)} = \left(-\frac{i}{\hbar}\right)^2\int_{-\infty}^{t} dt_2\int_{-\infty}^{t_2} dt_1\left[V_I(t_2),\left[V_I(t_1),\rho_{eq}\right]\right]$$

$$\rho_I^{(n)} = \left(-\frac{i}{\hbar}\right)^n\int_{-\infty}^{t} dt_n\int_{-\infty}^{t_n} dt_{n-1}\ldots\int_{-\infty}^{t_2} dt_1\left[V_I(t_n),\left[V_I(t_{n-1}),\left[\ldots,\left[V_I(t_1),\rho_{eq}\right]\ldots\right]\right]\right].$$

(10.26)

Let's examine the second-order polarization in order to describe the nonlinear response function. Earlier we stated that we could write the second-order nonlinear response arise from two time-ordered interactions with external potentials in the form

$$\bar{P}^{(2)}(t) = \int_0^{\infty} d\tau_2\int_0^{\infty} d\tau_1\, R^{(2)}(\tau_2,\tau_1)\bar{E}_1(t-\tau_2-\tau_1)\bar{E}_2(t-\tau_2)$$

(10.27)

We can compare this result to what we obtain from $P^{(2)}(t) = Tr\left(\mu_I(t)\rho_I^{(2)}(t)\right)$. Substituting as we did in the linear case,

$$P^{(2)}(t) = Tr\left\{\mu_I(t)\left(-\frac{i}{\hbar}\right)^2 \int_{-\infty}^{t} dt_2 \int_{-\infty}^{t_2} dt_1 \left[V_I(t_2), \left[V_I(t_1), \rho_{eq}\right]\right]\right\}$$

$$= \left(\frac{i}{\hbar}\right)^2 \int_{-\infty}^{t} dt_2 \int_{-\infty}^{t_2} dt_1 \, E_2(t_2) E_1(t_1) Tr\left\{\left[\left[\mu_I(t), \mu_I(t_2)\right], \mu_I(t_1)\right]\rho_{eq}\right\} \tag{10.28}$$

$$= \left(\frac{i}{\hbar}\right)^2 \int_{0}^{\infty} d\tau_2 \int_{0}^{\infty} d\tau_1 \, E_2(t-\tau_2) E_1(t-\tau_2-\tau_1) Tr\left\{\left[\left[\mu_I(\tau_1+\tau_2), \mu_I(\tau_1)\right], \mu_I(0)\right]\rho_{eq}\right\}$$

In the last line we switched variables to the time-intervals $t_1 = t - \tau_1 - \tau_2$ and $t_2 = t - \tau_2$, and enforced the time-ordering $t_1 \leq t_2$. Comparison of eqs. (10.27) and (10.28) allows us to state that the second order nonlinear response function is

$$R^{(2)}(\tau_1, \tau_2) = \left(\frac{i}{\hbar}\right)^2 \theta(\tau_1)\theta(\tau_2) Tr\left\{\left[\left[\mu_I(\tau_1+\tau_2), \mu_I(\tau_1)\right], \mu_I(0)\right]\rho_{eq}\right\} \tag{10.29}$$

Again, for impulsive interactions, i.e. delta function light pulses, the nonlinear polarization is directly proportional to the response function.

Similar exercises to the linear and second order response can be used to show that the nonlinear response function to arbitrary order $R^{(n)}$ is

$$R^{(n)}(\tau_1, \tau_2, \ldots \tau_n) = \left(\frac{i}{\hbar}\right)^n \theta(\tau_1)\theta(\tau_2)\ldots\theta(\tau_n)$$

$$\times Tr\left\{\left[\left[\ldots\left[\mu_I(\tau_n+\tau_{n-1}+\ldots+\tau_1), \mu_I(\tau_{n-1}+\tau_n+\cdots\tau_1)\right],\ldots\right]\mu_I(0)\right]\rho_{eq}\right\} \tag{10.30}$$

We see that in general the nonlinear response functions are sums of correlation functions, and the nth order response has 2^n correlation functions contributing. These correlation functions differ by whether sequential operators act on the *bra* or *ket* side of ρ when enforcing the time-ordering. Since the *bra* and *ket* sides represent conjugate wavefunctions, these correlation functions will contain coherences with differing phase relationships during subsequent time-intervals.

To see more specifically what a specific term in these nested commutators refers to, let's look at $R^{(2)}$ and enforce the time-ordering:

Term 1 in eq. (10.29):

$$Q_1 = Tr\left(\mu_I\left(\tau_1+\tau_2\right)\mu_I\left(\tau_1\right)\mu_I\left(0\right)\rho_{eq}\right)$$

$$= Tr\left(\underline{U_0^\dagger\left(\tau_1+\tau_2\right)}\mu\ \underline{U_0\left(\tau_1+\tau_2\right)U_0^\dagger\left(\tau_1\right)}\ \mu\ U_0\left(\tau_1\right)\mu\ \rho_{eq}\right)$$

$$\quad\quad U_0^\dagger\left(\tau_1\right)U_0^\dagger\left(\tau_2\right)\quad\quad U_0\left(\tau_2\right)$$

$$= Tr\left(\mu\ U_0\left(\tau_2\right)\mu\ U_0\left(\tau_1\right)\mu\ \rho_{eq}U_0^\dagger\left(\tau_1\right)U_0^\dagger\left(\tau_2\right)\right)$$
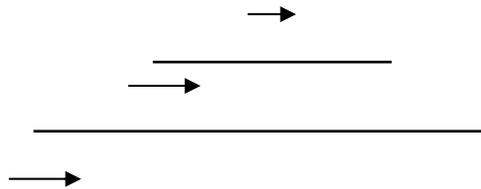
(1) dipole acts on **ket** of ρ_{eq}
(2) evolve under H_0 during τ_1.
(3) dipole acts on **ket**.
(4) Evolve during τ_2.
(5) Multiply by μ and take trace.

KET/KET interaction

At each point of interaction with the external potential, the dipole operator acted on *ket* side of ρ. Different correlation functions are distinguished by the order that they act on *bra* or *ket*. We only count the interactions with the incident fields, and the convention is that the final operator that we use prior to the trace acts on the *ket* side. So the term Q_1 is a *ket/ket* interaction.

An alternate way of expressing this correlation function is in terms of the time-propagator for the density matrix, a superoperator defined through: $\hat{G}(t)\rho_{ab} = U_0|a\rangle\langle b|U_0^\dagger$. Remembering the time-ordering, this allows Q_1 to be written as

$$Q_1 = Tr\left(\mu\hat{G}(\tau_2)\mu\hat{G}(\tau_1)\mu\rho_{eq}\right). \tag{10.31}$$

Term 2:

$$Q_2 = Tr\left(\mu_I\left(0\right)\mu_I\left(\tau_1+\tau_2\right)\mu_I\left(\tau_1\right)\rho_{eq}\right)$$

$$= Tr\left(\mu_I\left(\tau_1+\tau_2\right)\mu_I\left(\tau_1\right)\rho_{eq}\ \mu_I\left(0\right)\right)$$

BRA/KET interaction

For the remaining terms we note that the *bra* side interaction is the complex conjugate of *ket* side, so of the four terms in eq. (10.29), we can identify only two independent terms:

$$Q_1 \Rightarrow ket/ket \qquad Q_1^* \Rightarrow bra/bra \qquad Q_2 \Rightarrow ket/bra \qquad Q_2^* = bra/ket .$$

This is a general observation. For $R^{(n)}$, you really only need to calculate 2^{n-1} correlation functions. So for $R^{(2)}$ we write

$$R^{(2)} = \left(\frac{i}{\hbar}\right)^2 \theta(\tau_1)\theta(\tau_2) \sum_{\alpha=1}^{2} \left[Q_\alpha(\tau_1,\tau_2) - Q_\alpha^*(\tau_1,\tau_2) \right] \tag{10.32}$$

where

$$Q_1 = Tr\left[\mu_I(\tau_1+\tau_2)\mu_I(\tau_1)\mu_I(0)\rho_{eq} \right] \tag{10.33}$$

$$Q_2 = Tr\left[\mu_I(\tau_1)\mu_I(\tau_1+\tau_2)\mu_I(0)\rho_{eq} \right] . \tag{10.34}$$

So what is the difference in these correlation functions? Once there is more than one excitation field, and more than one time period during which coherences can evolve, then one must start to carefully watch the relative phase that coherences acquire during different consecutive time-periods, $\phi(\tau) = \omega_{ab}\tau$. To illustrate, consider wavepacket evolution: light interaction can impart positive or negative momentum ($\pm \bar{k}_{in}$) to the evolution of the wavepacket, which influences the direction of propagation and the phase of motion relative to other states. Any subsequent field that acts on this state must account for time-dependent overlap of these wavepackets with other target states. The different terms in the nonlinear response function account for all of the permutations of interactions and the phase acquired by these coherences involved. The sum describes the evolution including possible interference effects between different interaction pathways.

Third-Order Response

Since $R^{(2)}$ orientationally averages to zero for isotropic systems, the third-order nonlinear response described the most widely used class of nonlinear spectroscopies.

$$R^{(3)}(\tau_1,\tau_2,\tau_3) = \left(\frac{i}{\hbar}\right)^3 \theta(\tau_3)\theta(\tau_2)\theta(\tau_1) Tr\left\{ \left[\left[\left[\mu_I(\tau_1+\tau_2+\tau_3), \mu_I(\tau_1+\tau_2) \right], \mu_I(\tau_1) \right], \mu_I(0) \right] \rho_{eq} \right\} \tag{10.35}$$

$$R^{(3)}(\tau_1,\tau_2,\tau_3) = \left(\frac{i}{\hbar}\right)^3 \theta(\tau_3)\theta(\tau_2)\theta(\tau_1) \sum_{\alpha=1}^{4} \left[R_\alpha(\tau_3,\tau_2,\tau_1) - R_\alpha^*(\tau_3,\tau_2,\tau_1) \right] \tag{10.36}$$

Here the convention for the time-ordered interactions with the density matrix is $R_1 = ket/ket/ket$; $R_2 = bra/ket/bra$; $R_3 = bra/bra/ket$; and $R_4 \Rightarrow ket/bra/bra$. In the

eigenstate representation, the individual correlation functions can be explicitly written in terms of a sum over all possible intermediate states (a,b,c,d):

$$R_1 = \sum_{a,b,c,d} p_a \left\langle \mu_{ad}(\tau_1 + \tau_2 + \tau_3)\mu_{dc}(\tau_1 + \tau_2)\mu_{cb}(\tau_1)\mu_{ba}(0)\right\rangle$$

$$R_2 = \sum_{a,b,c,d} p_a \left\langle \mu_{ad}(0)\mu_{dc}(\tau_1 + \tau_2)\mu_{cb}(\tau_1 + \tau_2 + \tau_3)\mu_{ba}(\tau_1)\right\rangle$$

(10.37)

$$R_3 = \sum_{a,b,c,d} p_a \left\langle \mu_{ad}(0)\mu_{dc}(\tau_1)\mu_{cb}(\tau_1 + \tau_2 + \tau_3)\mu_{ba}(\tau_1 + \tau_2)\right\rangle$$

$$R_4 = \sum_{a,b,c,d} p_a \left\langle \mu_{ad}(\tau_1)\mu_{dc}(\tau_1 + \tau_2)\mu_{cb}(\tau_1 + \tau_2 + \tau_3)\mu_{ba}(0)\right\rangle$$

Summary: General Expressions for n^{th} Order Nonlinearity

For an nth-order nonlinear signal, there are n interactions with the incident electric field or fields that give rise to the radiated signal. Counting the radiated signal there are $n+1$ fields involved ($n+1$ light-matter interactions), so that n^{th} order spectroscopy is also at times referred to as $(n+1)$-wave mixing.

The radiated nonlinear signal field is proportional to the nonlinear polarization:

$$P^{(n)}(t) = \int_0^\infty d\tau_n \cdots \int_0^\infty d\tau_1 R^{(n)}(\tau_1, \tau_2, \ldots \tau_n)\bar{E}_1(t - \tau_n - \cdots - \tau_1)\cdots \bar{E}_n(t - \tau_n) \quad (10.38)$$

$$R^{(n)}(\tau_1, \tau_2, \ldots \tau_n) = \left(\frac{i}{\hbar}\right)^n \theta(\tau_1)\theta(\tau_2)\ldots\theta(\tau_n)$$

$$\times Tr\left\{ \left[\left[\ldots\left[\mu_I(\tau_n + \tau_{n-1} + \ldots + \tau_1), \mu_I(\tau_{n-1} + \tau_n + \cdots \tau_1)\right], \ldots\right]\mu_I(0)\right]\rho_{eq}\right\}$$

(10.39)

Here the interactions of the light and matter are expressed in terms of a sequence of consecutive time-intervals $\tau_1 \ldots \tau_n$ prior to observing the system. For delta-function interactions, $\bar{E}_i(t - t_0) = |\bar{E}_i|\delta(t - t_0)$, the polarization and response function are directly proportional

$$P^{(n)}(t) = R^{(n)}(\tau_1, \tau_2, \ldots \tau_{n-1}, t)|\bar{E}_1|\cdots|\bar{E}_n| \ . \quad (10.40)$$
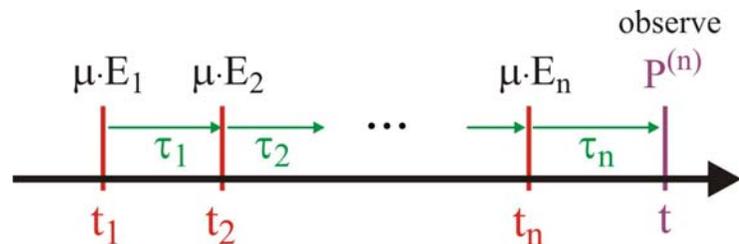
1. The radiation pattern in the far field for the electric field emitted by a dipole aligned along the z axis is

$$E\left(r,\theta,\phi,t\right)=-\frac{p_0 k^2}{4\pi\varepsilon_0}\frac{\sin\theta}{r}\sin\left(k\cdot r-\omega t\right).$$

(written in spherical coordinates). See Jackson, *Classical Electrodynamics*.

2. S. Mukamel, *Principles of Nonlinear Optical Spectroscopy*. (Oxford University Press, New York, 1995).

3. Remember the following relationships of the susceptibility with the complex dielectric constant $\varepsilon\left(\omega\right)$, the index of refraction $n\left(\omega\right)$, and the absorption coefficient $\kappa\left(\omega\right)$:

$$\varepsilon\left(\omega\right)=1+4\pi\chi\left(\omega\right)$$

$$\sqrt{\varepsilon\left(\omega\right)}=\tilde{n}\left(\omega\right)=n\left(\omega\right)+i\kappa\left(\omega\right)$$