CHM 504 – Module 13 – Linear & Nonlinear Spectroscopy

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In this last lecture on spectroscopy and light-matter interactions, we will try to provide some final intuition to wrap up everything we've discussed so far, and motivate how one could use the infrastructure we've built up to discuss higher-order nonlinear and multidimensional spectroscopies.

1 Linear and nonlinear spectroscopy

Up to this point we have considered traditional *linear* spectroscopies, where molecules interact with a single, weak, monochromatic beam of light. We can use a few observables to extract information about our sample from its linear spectrum: (a) the resonance frequencies of absorption or emission features, (b) the spectral intensities of these features, and (c) the lineshapes of these features.

However, linear absorption spectroscopy faces challenges in the analysis of complex systems. For instance:

(a) Two peaks appear in an absorption spectrum. Do these resonances arise from two different species present in a mixture, or are these transitions between different quantum states of the same molecule?

(b) A peak in an absorption spectrum features a broad lineshape. Is this a homogeneous lineshape broadened by a fast relaxation process? Or is it an inhomogeneous lineshape arising from a distribution of static absorption frequencies in our ensemble?

In nonlinear spectroscopy, the sample interacts with multiple pulses of light at different frequencies, arriving at different times. These higher-order light-matter processes can be used to correlate different spectral features: e.g. we can see how pumping of one spectral feature influences the appearance of other features as a function of time. The two examples above can be disentangled by double-resonance experiments that reveal how pumping at frequency ω_1 impacts absorption at ω_2.

Nonlinear spectroscopy encompasses processes like Raman spectroscopy, second harmonic generation, two-photon absorption, transient absorption, and a plethora of higher-order multidimensional processes. While we barely scratch the surface of these topics here, you should now have the tools to delve into them yourself. I highly recommend Zanni and Hamm's "Concepts and Methods of 2D Infrared Spectroscopy" textbook and Peter Hamm's pamphlet "Mukamel for Dummies" for those of you who are doing research in this field and want to know more.

2 Macroscopic polarization

Imagine that we prepare a two level system in its ground state at time $t = -\infty$. We excite the system with a weak laser pulse at $t = 0$ oscillating resonantly with $\omega = \omega_{12}$, and then let the system propagate field-free for time t:

$$|\psi(-\infty)\rangle = |1\rangle \xrightarrow[\text{pump}]{} |\psi(0)\rangle = c_1 |1\rangle + c_2 |2\rangle \xrightarrow[\text{evolve}]{} |\psi(t)\rangle = c_1 e^{-iE_1 t/\hbar} |1\rangle + c_2 e^{-iE_2 t/\hbar} |2\rangle$$

where we assume $c_1 \approx 1 \gg c_2$ for a weak pulse.

By pumping the system, we have created a coherent superposition of the $|1\rangle$ and $|2\rangle$ states. To make this happen, the oscillating applied electromagnetic field polarized the material: it pushed and pulled on charges in the molecule at their resonant frequencies and got them vibrating. As a result, the motion of the molecular dipole becomes synchronized to the field. This process creates a non-equilibrium distribution of charges in the system, which we can refer to as the *macroscopic polarization* of the sample: $P(t)$.

We define $P(t)$ as the expectation value of the molecular dipole operator:

$$P(t) \equiv \langle \hat{\mu} \rangle = \langle \psi(t) | \hat{\mu} | \psi(t) \rangle = \text{Tr}\left[\hat{\rho}(t)\, \hat{\mu}\right] \tag{1}$$

$$= |c_1|^2 \langle 1|\hat{\mu}|1\rangle + \cancelto{0}{|c_2|^2} \langle 2|\hat{\mu}|2\rangle + c_1^* c_2 e^{+i\omega_{12}t} \langle 1|\hat{\mu}|2\rangle + c_1 c_2^* e^{-i\omega_{12}t} \langle 2|\hat{\mu}|1\rangle \tag{2}$$

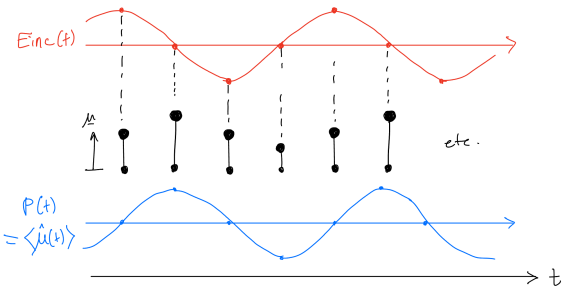
$$\approx |c_1|^2 \mu_{11} + 2 c_1 c_2 \mu_{12} \cos(\omega_{12} t) \tag{3}$$

where μ_{11} is the permanent dipole in the ground state; since this first term is time-independent and not field-induced, it's not of great interest here. We neglect the μ_{22} term since $|c_2|^2$ is assumed to be small. For simplicity, we take c_1 and c_2 to be real, and $\mu_{12} = \mu_{21}$.

We know from perturbation theory that $c_2 \propto \mu_{12}$, since the transition dipole coupling to the field of light is what created the coherent superposition in the first place. Therefore, the time-dependent field-induced part of the macroscopic polarization is just:

$$P(t) \propto \mu_{12}^2 \cos(\omega_{12} t) \tag{4}$$

A classical description of light-matter interactions provides some additional useful intuition here. If we drive a molecular transition with a weak sinusoidal field $E_{inc}(t)$, then the molecular dipole will oscillate with a 90° (or $\pi/2$) phase shift with respect to the incident driving field, e.g. $P(t) \propto e^{-i\pi/2} E_{inc}(t) = -iE_{inc}(t)$. This phase shift arises intuitively because $\frac{d\mu}{dt}$ is maximized when the field amplitude is maximized.



Once oscillating, this molecular dipole acts as an antenna and radiates light itself. The radiated field, $E_{rad}(t)$, experiences the same 90° phase shift with respect to the dipole's oscillations, so $E_{rad}(t) \propto -iP(t) \propto -E_{inc}(t)$.

The radiated field therefore oscillates 180° out of phase with the incident field, leading to *destructive interference*. In a Beer's law absorption experiment, we detect the intensity of the field transmitted through the molecular sample, which is essentially a heterodyne measurement of $|E_{inc}(t) + E_{rad}(t)|^2$. The destructive interference of the two field amplitudes leads to less light hitting the detector; this is another way to understand how light is lost due to molecular absorption!

In a pulsed experiment, where $E_{inc}(t)$ is shut off after some period of time, $E_{rad}(t)$ can be detected directly with no interference from $E_{inc}(t)$. $E_{rad}(t)$ will usually decay in time due to dephasing and population decay effects. In NMR or multi-dimensional spectroscopy experiments this radiated signal is known as the *free induction decay*.

The goal of much of time-resolved and nonlinear spectroscopy is to recover $P(t)$. In linear optics, we think of the macroscopic polarization of the material as depending linearly on the electric field amplitude E:

$$P(t) = \epsilon_0 \cdot \chi^{(1)} \cdot E(t) \tag{5}$$

where $\chi^{(1)}$ is the linear susceptibility of the material. To describe nonlinear behavior, the polarization is instead expanded in powers of the electric field amplitude:

$$P(t) = \epsilon_0 \left[\chi^{(1)} \cdot E(t) + \chi^{(2)} \cdot E(t) \cdot E(t) + \chi^{(3)} \cdot E(t) \cdot E(t) \cdot E(t) + \dots \right] \tag{6}$$

$$= P^{(1)}(t) + P^{(2)}(t) + P^{(3)}(t) \dots \tag{7}$$

where $\chi^{(n)}$ is the nonlinear susceptibility of order n.

Aside: In isotropic media with inversion symmetry, we expect that if the sign of the electric field is reversed the sign of the polarization must change as well. However, even powers of $E(t)$ will always have positive magnitude. As a result, the even-order *susceptibilities* $\chi^{(2n)}$ must therefore vanish in isotropic media, and $\chi^{(3)}$ gives rise to the lowest-order nonlinear processes. Note, however, that $\chi^{(2n)}$ may be non-vanishing in situations lacking inversion symmetry, such as at interfaces, where second-order processes like second harmonic generation and sum frequency generation can indeed occur.

We've already motivated that the macroscopic polarization of the sample is given by the expectation value of the dipole operator $\hat{\mu}$:

$$P(t) = \langle \hat{\mu}(t) \rangle = \mathrm{Tr}\left[\hat{\mu}\,\hat{\rho}(t)\right] \tag{8}$$

If both the macroscopic polarization and the density matrix can be expanded in powers of the driving field $E(t)$, we can equate:

$$P^{(n)}(t) = \mathrm{Tr}\left[\hat{\mu} \cdot \hat{\rho}^{(n)}(t)\right] \tag{9}$$

Our goal in the following sections is to find an expression for $\hat{\rho}(t)$ evolving under a time-varying light-matter Hamiltonian. If we use a perturbative approach, we can find an expansion of $\hat{\rho}(t)$ in powers of the perturbing field amplitude, and directly relate terms in this expansion to the orders of the macroscopic polarization $P^{(n)}(t)$.

3 Perturbative expansion of $\hat{\rho}(t)$ in the interaction picture

Examining what happens when molecules interact with several laser pulses in a nonlinear experiment comes down to solving the Schrödinger equation for a time-varying Hamiltonian. We will take the usual setup:

$$\hat{H}(t) = \hat{H}_0 + \hat{H}'(t) \tag{10}$$

$$\hat{H}_0 \left|\psi_n\right\rangle = E_n \left|\psi_n\right\rangle \tag{11}$$

Instead of solving for $|\psi(t)\rangle$ using time-dependent perturbation theory, we will instead find $\hat{\rho}(t)$. Again, $\hat{\rho}(t)$ is more useful to understand the dynamics of the system than $|\psi(t)\rangle$, because

(a) it can be used to treat dephasing, population decay, and statistical mixtures of states

(b) we can extract the diagonal elements ρ_{nn} to examine the likelihood of finding the system in state n at time t

(c) we can compute the expectation value of any operator $\hat{A}$ at time t by taking $\mathrm{Tr}[\hat{A}\,\hat{\rho}(t)]$

It is easiest to find $\hat{\rho}(t)$ within the interaction picture, to separate out the field-induced dynamics from the intrinsic evolution of the reference Hamiltonian. Recall that we defined (way back in Module 2) the interaction picture wavefunction:

$$\left|\psi(t)\right\rangle \equiv e^{-i\hat{H}_0(t-t_0)/\hbar}\,\left|\psi_I(t)\right\rangle = \hat{U}_0(t,t_0)\left|\psi_I(t)\right\rangle \tag{12}$$

where t_0 is some reference time point, which we will later take, by convention, as $t_0 \to -\infty$.

By introducing this definition for the interaction picture wavefunction into the Schrödinger equation, one can prove that:

$$\frac{d}{dt}\left|\psi(t)\right\rangle = -\frac{i}{\hbar}\hat{H}\left|\psi(t)\right\rangle \qquad \rightarrow \qquad \frac{d}{dt}\left|\psi_I(t)\right\rangle = -\frac{i}{\hbar}\hat{H}'_I(t)\left|\psi_I(t)\right\rangle \tag{13}$$

where we have defined a new time-dependent perturbing Hamiltonian in the interaction picture:

$$\hat{H}'_I(t) \equiv e^{+i\hat{H}_0(t-t_0)/\hbar}\;\hat{H}'(t)\;e^{-i\hat{H}_0(t-t_0)/\hbar} \tag{14}$$

$$= \hat{U}_0^\dagger(t,t_0)\;\hat{H}'(t)\;\hat{U}_0(t,t_0) \tag{15}$$

We can now define the interaction picture density matrix, $\hat{\rho}_I(t)$, and inspect what happens to the Liouville-von Neumann equation:

$$\hat{\rho}_I(t) \equiv \left|\psi_I(t)\right\rangle\left\langle\psi_I(t)\right| = \hat{U}_0^\dagger(t,t_0)\;\left|\psi(t)\right\rangle\left\langle\psi(t)\right|\;\hat{U}_0(t,t_0) \tag{16}$$

$$= \hat{U}_0^\dagger(t,t_0)\;\hat{\rho}(t)\;\hat{U}_0(t,t_0) \tag{17}$$

Note that this definition is linear in $\hat{\rho}(t)$, and is therefore applicable to both pure and mixed states.

Following in the footsteps of Eqn. 13, it turns out that one can simply write the Liouville-von Neumann equation in terms of $\hat{\rho}_I(t)$ as:

$$\frac{d}{dt}\hat{\rho}(t) = -\frac{i}{\hbar}\big[\hat{H}(t),\hat{\rho}(t)\big] \qquad \rightarrow \qquad \frac{d}{dt}\hat{\rho}_I(t) = -\frac{i}{\hbar}\big[\hat{H}'_I(t),\hat{\rho}_I(t)\big] \tag{18}$$

One can integrate the above with respect to time to find:

$$\hat{\rho}_I(t) = \hat{\rho}_I(t_0) - \left(\frac{i}{\hbar}\right)\int_{t_0}^{t} d\tau \left[\hat{H}'_I(\tau), \hat{\rho}_I(\tau)\right] \tag{19}$$

The above can be iteratively solved to give:

$$\hat{\rho}_I(t) = \hat{\rho}_I(t_0) - \left(\frac{i}{\hbar}\right)\int_{t_0}^{t} d\tau_1 \left[\hat{H}'_I(\tau_1), \hat{\rho}_I(t_0)\right] \tag{20}$$

$$+ \left(-\frac{i}{\hbar}\right)^2 \int_{t_0}^{t} d\tau_2 \int_{t_0}^{\tau_2} d\tau_1 \left[\hat{H}'_I(\tau_2), [\hat{H}'_I(\tau_1), \hat{\rho}_I(t_0)\right] \quad + \quad \cdots \tag{21}$$

$$= \hat{\rho}_I(t_0) + \sum_{n=1}^{\infty}\left(-\frac{i}{\hbar}\right)^n \int_{t_0}^{t} d\tau_n \int_{t_0}^{\tau_n} d\tau_{n-1} \cdots \int_{t_0}^{\tau_2} d\tau_1 \left[\hat{H}'_I(\tau_n), \left[\hat{H}'_I(\tau_{n-1}), \cdots \left[\hat{H}'_I(\tau_1), \hat{\rho}_I(t_0)\right]\right]\right] \tag{22}$$

We can return to the Schrödinger picture density matrix using Eqn. 17, though note that the pertubation $\hat{H}'_I(t)$ still appears in the interaction picture:

$$\hat{\rho}(t) = \hat{\rho}^{(0)}(t) + \sum_{n=1}^{\infty}\left(-\frac{i}{\hbar}\right)^n \int_{t_0}^{t} d\tau_n \int_{t_0}^{\tau_n} d\tau_{n-1} \cdots \int_{t_0}^{\tau_2} d\tau_1 \tag{23}$$

$$\hat{U}_0(t,t_0)\left[\hat{H}'_I(\tau_n), \left[\hat{H}'_I(\tau_{n-1}), \cdots \left[\hat{H}'_I(\tau_1), \hat{\rho}(t_0)\right]\right]\right] \hat{U}_0^{\dagger}(t,t_0)$$

$$\equiv \hat{\rho}^{(0)}(t) + \sum_{n=1}^{\infty} \hat{\rho}^{(n)}(t) \tag{24}$$

Eqn. 23 is complicated to evaluate! Because it contains a nested set of commutators, the integral will contain a sum of 2^n terms with the various $\hat{H}'_I(\tau_k)$ operators acting on $\hat{\rho}(t_0)$ from both the ket and bra sides.

We can go a little further to make Eqn. 23 easier to work with. Let's use our typical expression for $\hat{H}'(t)$ for light-matter interactions:

$$\hat{H}'(t) = E(t)\,\hat{\mu} \tag{25}$$

$$\rightarrow \hat{H}'_I(t) = \hat{U}_0^{\dagger}(t,t_0)\; E(t)\; \hat{\mu}\; \hat{U}_0(t,t_0) \tag{26}$$

$$= E(t)\; \hat{U}_0^{\dagger}(t,t_0)\; \hat{\mu}\; \hat{U}_0(t,t_0) \tag{27}$$

$$\equiv E(t)\; \hat{\mu}_I(t) \tag{28}$$

where we define $\hat{\mu}_I(t) \equiv \hat{U}_0^{\dagger}(t,t_0)\; \hat{\mu}\; \hat{U}_0(t,t_0)$ as the interaction picture dipole operator.

Let's now consider the n^{th} term in our iterative definition of $\hat{\rho}(t)$ in Eqn. 24:

$$\hat{\rho}^{(n)}(t) \equiv \left(-\frac{i}{\hbar}\right)^n \int_{t_0}^{t} d\tau_n \int_{t_0}^{\tau_n} d\tau_{n-1} \cdots \int_{t_0}^{\tau_2} d\tau_1\, E(\tau_n)\, E(\tau_{n-1}) \cdots E(\tau_1) \tag{29}$$

$$\hat{U}_0(t,t_0)\left[\hat{\mu}_I(\tau_n), [\hat{\mu}_I(\tau_{n-1}), \cdots [\hat{\mu}_I(\tau_1), \hat{\rho}(t_0)]]\right] \hat{U}_0^{\dagger}(t,t_0)$$

There are two conventions to note here:

- By convention, the reference time is often taken in the limit $t_0 \to -\infty$, so you often see Eqn. 29 involving $\rho(-\infty)$. $\rho(-\infty)$ is considered to be the density matrix at equilibrium well before any perturbation occurs, which evolves only under the static reference Hamiltonian $\hat{H}_0$.
- While the dipole operator $\hat{\mu}$ is time-independent, in the interaction picture we have a time-dependent $\hat{\mu}_I(t)$ that evolves under $\hat{H}_0$. You will often see the I subscript dropped, and the interaction picture implied with the explicit time dependence $\hat{\mu}(t)$.

4 Connecting $\hat{\rho}(t)$ to the macroscopic polarization

We've already motivated that the macroscopic polarization of the sample is given by the expectation value of the dipole operator $\hat{\mu}$:

$$P(t) = \langle \hat{\mu}(t) \rangle = \mathrm{Tr}\left[\hat{\mu}\hat{\rho}(t)\right] \tag{30}$$

By inspecting Eqns. 7 and 29, we see that macroscopic polarization and the density matrix are now expanded in powers of $E(t)$. We can therefore equate:

$$P^{(n)}(t) = \mathrm{Tr}\left[\hat{\mu} \cdot \hat{\rho}^{(n)}(t)\right] \equiv \left\langle \hat{\mu} \cdot \hat{\rho}^{(n)}(t) \right\rangle \tag{31}$$

where we now use $\langle \dots \rangle$ as a compact notation for the trace.

Let's go ahead and write down an expression for the n^{th}-order component of $P(t)$ in terms of our perturbative expansion of the $\hat{\rho}(t)$. Dropping the I subscripts for the dipole operators, we have:

$$\begin{aligned} P^{(n)}(t) = \Bigg\langle \hat{\mu} \cdot \left(-\frac{i}{\hbar}\right)^n \int_{t_0}^{t} d\tau_n \int_{t_0}^{\tau_n} d\tau_{n-1} \cdots \int_{t_0}^{\tau_2} d\tau_1 \, E(\tau_n)\, E(\tau_{n-1}) \cdots E(\tau_1) \\ \hat{U}_0(t,t_0)\left[\hat{\mu}(\tau_n), [\hat{\mu}(\tau_{n-1}), \cdots [\hat{\mu}(\tau_1), \hat{\rho}(t_0)]]\right] \hat{U}_0^\dagger(t,t_0) \Bigg\rangle \end{aligned} \tag{32}$$

$$\begin{aligned} = \left(-\frac{i}{\hbar}\right)^n \int_{0}^{t} d\tau_n \int_{0}^{\tau_n} d\tau_{n-1} \cdots \int_{0}^{\tau_2} d\tau_1 \, E(\tau_n)\, E(\tau_{n-1}) \cdots E(\tau_1) \\ \left\langle \hat{\mu} \cdot \hat{U}_0(t,t_0)\left[\hat{\mu}(\tau_n), [\hat{\mu}(\tau_{n-1}), \cdots [\hat{\mu}(\tau_1), \hat{\rho}(t_0)]]\right] \hat{U}_0^\dagger(t,t_0) \right\rangle \end{aligned} \tag{33}$$

The trace is invariant to cyclic permutation of multiplied terms within it (e.g. $\mathrm{Tr}[ABCD] = \mathrm{Tr}[BCDA] = \dots$). So therefore:

$$\begin{aligned} P^{(n)}(t) = \left(-\frac{i}{\hbar}\right)^n \int_{t_0}^{t} d\tau_n \int_{t_0}^{\tau_n} d\tau_{n-1} \cdots \int_{t_0}^{\tau_2} d\tau_1 \, E(\tau_n)\, E(\tau_{n-1}) \cdots E(\tau_1) \\ \left\langle \hat{U}_0^\dagger(t,t_0)\, \hat{\mu} \cdot \hat{U}_0(t,t_0)\left[\hat{\mu}(\tau_n), [\hat{\mu}(\tau_{n-1}), \cdots [\hat{\mu}(\tau_1), \hat{\rho}(t_0)]]\right] \right\rangle \end{aligned} \tag{34}$$

$$\begin{aligned} = \left(-\frac{i}{\hbar}\right)^n \int_{t_0}^{t} d\tau_n \int_{t_0}^{\tau_n} d\tau_{n-1} \cdots \int_{t_0}^{\tau_2} d\tau_1 \, E(\tau_n)\, E(\tau_{n-1}) \cdots E(\tau_1) \\ \left\langle \hat{\mu}(t)\left[\hat{\mu}(\tau_n), [\hat{\mu}(\tau_{n-1}), \cdots [\hat{\mu}(\tau_1), \hat{\rho}(t_0)]]\right] \right\rangle \end{aligned} \tag{35}$$

The n^{th}-order polarization is thus a convolution of n electric fields with the n^{th}-order nonlinear response function $S^{(n)}(t)$, defined as:

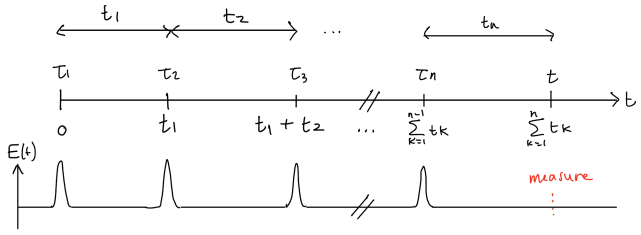
$$S^{(n)}(t) \equiv \left(-\frac{i}{\hbar}\right)^n \left\langle \hat{\mu}(t) \left[\hat{\mu}(\tau_n), [\hat{\mu}(\tau_{n-1}), \cdots [\hat{\mu}(\tau_1), \hat{\rho}(t_0)]]\right] \right\rangle \tag{36}$$

Or, without loss of generality, we can take

$$t_0 \to -\infty, \qquad \tau_1 = 0, \qquad t_1 = \tau_2 - \tau_1, \qquad t_2 = \tau_3 - \tau_2, \qquad \ldots \qquad t_n = t - \tau_n \tag{37}$$

and therefore

$$\tau_n = t - t_n, \qquad \tau_{n-1} = t - t_n - t_{n-1}, \qquad \ldots \qquad \tau_1 = t - t_n - t_{n-1} \cdots - t_1 \tag{38}$$



With these new time definitions one can show that Eqns. 35 and 36 become:

$$P^{(n)}(t) = \int_0^\infty dt_n \int_0^\infty dt_{n-1} \cdots \int_0^\infty dt_1 \tag{39}$$
$$E(t - t_n) \cdot E(t - t_n - t_{n-1}) \cdots E(t - t_n - t_{n-1} - \cdots - t_1) \cdot S^{(n)}(t)$$

$$S^{(n)}(t) = \left(-\frac{i}{\hbar}\right)^n \left\langle \hat{\mu}(t) \left[\hat{\mu}(t_{n-1} + \cdots + t_1), \cdots \left[\hat{\mu}(0), \hat{\rho}(-\infty)\right] \cdots \right] \right\rangle \tag{40}$$

In the above, the n interactions of the dipole with the field at times $t = 0, t_1,\ t_1 + t_2,\ \cdots,\ \sum_{k=1}^{n-1} t_k$ act on the system's initial density matrix $\hat{\rho}(-\infty)$ to generate a non-equilibrium n^{th}-order density matrix $\hat{\rho}^{(n)}(t)$. The off-diagonal elements of $\hat{\rho}^{(n)}(t)$ generate the n^{th}-order macroscopic polarization of the sample.

Only the first n interactions with the dipole operator are part of the commutator. The final term $\hat{\mu}(t) = \hat{\mu}(t_n + \cdots + t_1)$ lies outside the commutator, and represents our measurement of the macroscopic polarization of the sample at time $t = \sum_{k=1}^{n} t_k$ after all interactions with the field have already transpired.

5 Higher-order spectroscopies

To provide some concrete, simple examples, let's consider the set of terms that arise from the nested set of commutators in Eqn. 40 for both the linear and the third-order responses. We will skip the second-order response – as noted earlier it is assumed to vanish in isotropic media.

5.1 The first order response & linear spectroscopy

The first-order response function evaluated at time t_1 is given by:

$$S^{(1)}(t_1) = -\frac{i}{\hbar} \langle\, \hat{\mu}(t_1)[\hat{\mu}(0), \hat{\rho}(-\infty)] \,\rangle \tag{41}$$

$$= -\frac{i}{\hbar}\Big[\langle \hat{\mu}(t_1)\hat{\mu}(0)\hat{\rho}(-\infty)\rangle - \langle \hat{\mu}(t_1)\hat{\rho}(-\infty)\hat{\mu}(0)\rangle \Big] \tag{42}$$

$$= -\frac{i}{\hbar}\Big[\langle \hat{\mu}(t_1)\hat{\mu}(0)\hat{\rho}(-\infty)\rangle - \langle \hat{\rho}(-\infty)\hat{\mu}(0)\hat{\mu}(t_1)\rangle \Big] \tag{43}$$

$$= -\frac{i}{\hbar}\Big[\langle \hat{\mu}(t_1)\hat{\mu}(0)\hat{\rho}(-\infty)\rangle - \langle \hat{\mu}(t_1)\hat{\mu}(0)\hat{\rho}(-\infty)\rangle^* \Big] \tag{44}$$

$$= -\frac{i}{\hbar}\Big[\langle \hat{\mu}(t_1)\hat{\mu}(0)\hat{\rho}(-\infty)\rangle - \text{C.C.} \Big] \tag{45}$$

where C.C. denotes the complex conjugate of the first term. In the above, we have made use of the invariance of the trace to cyclic permutation and the fact that:

$$\Big\langle [\hat{\mu}(t_1)\hat{\mu}(0)\hat{\rho}(-\infty)]^\dagger \Big\rangle = \Big\langle \hat{\rho}^\dagger(-\infty)\hat{\mu}^\dagger(0)\hat{\mu}^\dagger(t_1) \Big\rangle \tag{46}$$

$$= \langle \hat{\rho}(-\infty)\hat{\mu}(0)\hat{\mu}(t_1)\rangle \tag{47}$$

where the last step is possible as all operators are Hermitian and by definition self-adjoint.

What is actually happening here? At time $t = 0$, we act with $\hat{\mu}(0)$ to perturb $\hat{\rho}(-\infty)$, which we know creates non-zero off-diagonal matrix elements like ρ_{12}. We know from solving the optical Bloch equations that this off-diagonal density matrix element will evolve as:

$$\rho_{12}(t) \propto \mu_{12}\, e^{-i\omega_{12}t}\, e^{-\gamma t} \tag{48}$$

where γ is the dephasing rate.

These off-diagonal matrix elements of $\hat{\rho}$ represent a macroscopic polarization of the sample which will emit its own field with amplitude again proportional to the off-diagonal matrix elements of the dipole operator. At our measurement time t_1, we act again with $\hat{\mu}(t_1)$ to yield a response given by:

$$S^{(1)}(t_1) \propto -\frac{i}{\hbar}\mu_{12}^2\, e^{-i\omega_{12}t_1}\, e^{-\gamma t_1} \tag{49}$$

The above is our (somewhat handwavey) solution to Eqn. 40; we now want to plug this into Eqn. 35 to treat the specific interaction with the field.

Let's assume we have a field with a carrier frequency that is resonant with our transition of interest, $\omega = \omega_{12}$, but which is only on for a very short duration near time 0:

$$E(t) \quad = \quad E_0(t) \cdot 2\cos(\omega t) \quad = \quad E_0(t)\left[e^{i\omega t} + e^{-i\omega t}\right] \quad = \quad E_0\,\delta(t)\left[e^{i\omega t} + e^{-i\omega t}\right] \tag{50}$$

For the first-order polarization of the sample evaluated at measurement time t_1, we find:

$$P^{(1)}(t) = \int_0^\infty dt_1\ E(t-t_1)\, S^{(1)}(t) \tag{51}$$

$$= -\frac{i}{\hbar}\int_0^\infty dt_1\ E_0\,\delta(t-t_1)\left[e^{i\omega(t-t_1)} + e^{-i\omega(t-t_1)}\right]\cdot \mu_{12}^2\, e^{-i\omega_{12}t}e^{-\gamma t} \tag{52}$$

$$= -\frac{i}{\hbar}E_0\,\mu_{12}^2\, e^{-i\omega_{12}t}e^{-\gamma t}\underbrace{\int_0^\infty dt_1\,\delta(t-t_1)\left[e^{i\omega(t-t_1)} + e^{-i\omega(t-t_1)}\right]}_{\delta(t-t_1)\text{ plucks out integrand with } t_1=t} \tag{53}$$

$$= -\frac{2i}{\hbar}E_0\,\mu_{12}^2\, e^{-i\omega_{12}t_1}e^{-\gamma t_1} \tag{54}$$

This macroscopic polarization will emit a field with a 90-degree phase lag, so $E^{(1)}(t) \propto -iP^{(1)}(t)$. This radiated field represents the free induction decay! If you were to resolve the spectrum of this field with a spectrometer, you would essentially be performing a Fourier transform from time into frequency space. In the resulting frequency-domain spectrum, you would see a Lorentzian line at the ω_{12} resonance frequency.

5.2 Third order response & nonlinear spectroscopy

The same exercise as above for the third-order response yields the following terms for $S^{(3)}(t)$ (plus their complex conjugates), now evaluated at measurement time $t \equiv t_1 + t_2 + t_3$:

$$\langle\mu(t_3+t_2+t_1)\hat{\mu}(0)\hat{\rho}(-\infty)\hat{\mu}(t_1)\hat{\mu}(t_2+t_1)\rangle - \text{C.C.} \tag{55}$$

$$\langle\mu(t_3+t_2+t_1)\hat{\mu}(t_1)\hat{\rho}(-\infty)\hat{\mu}(0)\hat{\mu}(t_2+t_1)\rangle - \text{C.C.} \tag{56}$$

$$\langle\mu(t_3+t_2+t_1)\hat{\mu}(t_2+t_1)\hat{\rho}(-\infty)\hat{\mu}(0)\hat{\mu}(t_1)\rangle - \text{C.C.} \tag{57}$$

$$\langle\mu(t_3+t_2+t_1)\hat{\mu}(t_2+t_1)\hat{\mu}(t_1)\hat{\rho}(-\infty)\hat{\mu}(0)\rangle - \text{C.C.} \tag{58}$$

There is some additional complication here because in addition to the 2^3 terms of $S^{(3)}(t)$, the electric field also has several terms, for example:

$$P^{(3)}(t) = \int_0^\infty dt_3 \int_0^\infty dt_2 \int_0^\infty dt_1\ E(t-t_3)E(t-t_3-t_2)E(t-t_3-t_2-t_1)\, S^{(3)}(t) \tag{59}$$

In practice in the laboratory, these fields will originate from a series of short laser pulses, e.g.

$$E(t) = E_1(t)\left[e^{i\omega_1 t} + e^{-i\omega_1 t}\right] + E_2(t)\left[e^{i\omega_2 t} + e^{-i\omega_2 t}\right] + E_3(t)\left[e^{i\omega_3 t} + e^{-i\omega_3 t}\right] \tag{60}$$

so each factor of $E(t)$ in Eqn. 59 adds 6-fold more terms to the calculation of $P^{(3)}(t)$.

To simplify this situation, we can make use of *time ordering* of pulses. We assume the width of the laser pulses in time are short compared to their separation times, but long compared to the oscillation period of the light ω. So, the first pertubation from $\hat{\mu}(0)$ originates solely from interaction with $E_1(t)$, $\hat{\mu}(t_1)$ comes solely from $E_2(t)$, and so forth. We can also approximate the pulse envelopes as δ functions, so, e.g. $E_1(t) = E_1\delta(t)e^{\pm i\omega_1 t}$, again simplifying the integrals.

In practice, *phase matching* is also used to distinguish between the various terms in $S^{(n)}$ that contribute to the experimental signal. If we think about the spatial geometry of the fields, the laser pulses can travel along different wavevectors, e.g. $E_1(t) = E_1(t)\left[e^{-i\omega_1 t + ik_1 r} + e^{-i\omega_1 t - ik_1 r}\right]$. The product of $E_3(t-t_3)E_2(t-t_3-t_2)E_1(t-t_3-t_2-t_1)$ will carry a wavevector of $k = \pm k_1 \pm k_2 \pm k_3$. By setting up the geometry of the system, these can be distinguished spatially.

5.3 A more concrete example of nonlinear signals

Let's at last touch on a simple non-linear experiment for a two-level system. We will through the contribution of just Eqn. 55 above to the third-order signal.

- We begin with a density matrix initialized in the ground state, $|1\rangle$:

$$\hat{\rho}(-\infty) = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} \tag{61}$$

  and we will assume our light-matter perturbation takes the form

$$\hat{\mu} = \begin{pmatrix} 0 & \mu_{12} \\ \mu_{12} & 0 \end{pmatrix} \tag{62}$$

- At time $t = 0$, the first perturbation acts from the left to generate an off-diagonal matrix element of ρ proportional to μ_{12}:

$$\hat{\mu}(0) \cdot \hat{\rho}(-\infty) = \begin{pmatrix} 0 & \mu_{12} \\ \mu_{12} & 0 \end{pmatrix} \cdot \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} = \begin{pmatrix} 0 & 0 \\ \mu_{12} & 0 \end{pmatrix} \tag{63}$$

- We then let the density matrix evolve under the reference Hamiltonian $\hat{H}_0$ in the absence of interactions until time t_1. We know this evolution leaves the diagonal matrix elements of $\hat{\rho}(t)$ unchanged, but multiplies the off-diagonal elements by a complex exponential. Neglecting population relaxation and other dynamics for now, at time t_1 we have:

$$\begin{pmatrix} 0 & 0 \\ \mu_{12} e^{-i\omega_{12} t_1} & 0 \end{pmatrix} \tag{64}$$

- At time $t = t_1$ we are perturbed again, this time from the right:

$$\hat{\mu}(0) \cdot \hat{\rho}(-\infty) \cdot \hat{\mu}(t_1) = \begin{pmatrix} 0 & 0 \\ \mu_{12} e^{-i\omega_{12} t_1} & 0 \end{pmatrix} \cdot \begin{pmatrix} 0 & \mu_{12} \\ \mu_{12} & 0 \end{pmatrix} = \begin{pmatrix} 0 & 0 \\ 0 & \mu_{12}^2 e^{-i\omega_{12} t_1} \end{pmatrix} \tag{65}$$

- We now let the system evolve under $\hat{H}_0$ again until time $t_1 + t_2$. Note however that there is no temporal evolution of the diagonal elements of the density matrix during this period!

- Continuing on with two more interactions with the field at times $t_1 + t_2$ and $t_1 + t_3$, and evolution of the off-diagonal elements for time t_3 we finally have:

$$\mu(t_3 + t_2 + t_1)\hat{\mu}(0)\rho(-\infty)\hat{\mu}(t_1)\hat{\mu}(t_2 + t_1) = \begin{pmatrix} \mu_{12}^4 e^{-i\omega_{12}(t_1+t_3)} & 0 \\ 0 & 0 \end{pmatrix} \tag{66}$$

- We then take the trace of the above and subtract its own complex conjugate to find:

$$\left\langle \mu(t_3 + t_2 + t_1)\hat{\mu}(0)\rho(-\infty)\hat{\mu}(t_1)\hat{\mu}(t_2 + t_1) \right\rangle - C.C. \quad \propto \quad \mu_{12}^4 \sin[\omega_{12}(t_3 + t_1)] \tag{67}$$

Note that we've neglected dephasing and population decay here, but their effects are easily added into each step above.

Following this procedure, one can generate contributions to the molecular responses from all the relevant pathways in Eqns. 55 - 58. One would finally then integrate $S^{(3)}(t)$ against the electric field, as shown in Eqn. 59 to obtain the macroscopic polarization $P^{(3)}(t)$, from which the radiated field $E^{(3)}(t) \propto -iP^{(3)}(t)$ can be determined. The Fourier transform of $E^{(3)}(t)$ will then give the nonlinear absorption spectrum, which will change as the timing between the pulses is varied.

The sum of all the terms of $S^{(3)}(t)$ will contribute to this final signal, though again one can distinguish between these pathways using phase matching.