

CHM 504 - Linear & Nonlinear Spectroscopy

Prof. Marissa Weichman

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 Putting some pieces together

What are we actually doing when we perform a spectroscopic experiment? Let's imagine that we prepare a two level system in its ground state at time $t = -\infty$. We weakly excite the system with a laser pulse at $t = 0$ oscillating resonantly with $\omega = \omega_{12}$, and then we 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.

Importantly, by pumping the system, we have created a coherent superposition of the $|1\rangle$ and $|2\rangle$ states. To make this happen, the oscillating electromagnetic field pushed and pulled on the charge distribution of the molecule in order to get the molecule to vibrate. As a result, the phase of the molecular vibration 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: $P(t)$. The goal of much of time-resolved and nonlinear spectroscopy is to recover this quantity.

Practically, we define this macroscopic polarization as the expectation value of the transition dipole:

$$P(t) \equiv \langle \mu \rangle = \langle \psi(t) | \hat{\mu} | \psi(t) \rangle \quad (1)$$

$$= |c_1|^2 \langle 1 | \hat{\mu} | 1 \rangle + |c_2|^2 \langle 2 | \hat{\mu} | 2 \rangle + c_1^* c_2 e^{+i\omega_{12}t} \langle 1 | \hat{\mu} | 2 \rangle + c_1 c_2^* e^{-i\omega_{12}t} \langle 2 | \hat{\mu} | 1 \rangle \quad (2)$$

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

where μ_{11} is the static dipole of the molecule in its ground state; since this first term is time-independent and not field-induced, it's not of great interest here. We can also neglect the μ_{22} term since the $|c_2|^2$ coefficient that multiplies it is assumed to be small. We have also assumed here (in service of making a point) that c_1 and c_2 are real, and that $\mu_{12} = \mu_{21}$.

Moreover, 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 state in the first place. Therefore, the field-induced part of the macroscopic polarization is just:

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

If you go back to the Module 10 notes, you can see that this quantity is also proportional to the $\langle B_y \rangle$ component of the Bloch vector, which oscillates sinusoidally in time when the state is coherent.

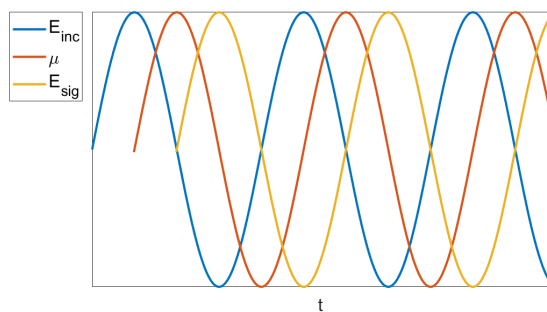
For an ensemble, we can use the same description of the macroscopic polarization, making use of mixed-state density matrices:

$$P(t) = \langle \hat{\mu} \rangle = \text{Tr}[\rho \mu] = \sum_{n,m} \rho_{nm} \mu_{mn} = \sum_{n,m} \langle c_n c_m^* \rangle \mu_{mn} \quad (5)$$

where again we can see that it is the off-diagonal elements of ρ which couple to μ_{mn} , allowing the system to absorb or emit light.

Aside: This is a good point to emphasize the classical description of light-matter interactions, which provides some useful intuition. Just as an oscillating field drives the dipole of our molecule to vibrate, the oscillating dipole of our molecule acts as an antenna, and will radiate light itself.

The molecular dipole oscillates with a 90° ($\pi/2$) phase shift with respect to the incident driving field $E_{inc}(t)$. This phase shift arises conceptually because $\frac{d\mu}{dt}$ is maximized when the field amplitude is maximized. The radiated field, $E_{sig}(t)$, experiences the same phase shift with respect to the dipole's oscillations for the same reason.



For continuous wave illumination, the radiated field oscillates 180° out of phase with the incident field, leading to destructive interference of the two fields when we experimentally detect $E_{inc} + E_{sig}$ in an experiment. We think of this phenomenon as light being *absorbed* by the molecule.

In a pulsed experiment, where E_{inc} is shut off after some period of time, then E_{sig} can be detected directly with no interference from E_{inc} . In reality, E_{sig} will decay in time due to dephasing and population decay effects. You might be familiar with this idea from NMR, where this signal is known as the free induction decay.

2 Linear and nonlinear spectroscopy

Up to this point we have considered *linear* spectroscopies, where an ensemble of molecules interacts with a single, weak, monochromatic beam of light. We now turn to a treatment of *nonlinear* spectroscopies, where higher-order processes are possible. A sample can interact with several pulses of light of different frequencies, potentially arriving at different times.

In traditional linear spectroscopy, we use a few observables to extract information about our sample from its spectrum: the resonance frequencies of absorption or emission features, the spectral intensities of these features, and the lineshapes of these features. In complex systems, there are

many absorbing species present, and various interacting degrees of freedom can lead to congested or featureless spectra, making interpretation challenging and ambiguous.

Two representative examples of challenges faced in linear absorption spectroscopy include:

- (a) Two peaks appear in an absorption spectrum. Do these resonances arise from two different non-interacting species present in a mixture, or are these transitions between different quantum states of the same molecule? Linear spectroscopy can be compared to simulations to try to resolve these kinds of questions, but cannot directly interrogate spectral correlations between features.
- (b) An absorption spectrum features an extremely 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? Linear spectroscopy cannot distinguish between these broadening mechanisms.

In nonlinear spectroscopy, multiple light-matter interactions can be used to correlate different spectral features, see how pumping of one spectral feature influences the appearance of other features, and introduce time-delays between pulses to pick out relevant time scales of different processes. The two examples above can be disentangled by double-resonance experiments that reveal how pumping at frequency ω_1 impacts absorption at ω_2 .

We can also describe nonlinear 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” and Peter Hamm’s “Principles of Nonlinear Optical Spectroscopy: A Practical Approach” for those of you who are doing research in this field and want to know more.

3 Perturbative expansion of the density matrix

Examining what happens when we interact an ensemble of molecules with several ultrafast laser pulses comes down to (surprise, surprise!) solving the Schrödinger equation for a time-varying Hamiltonian.

We will take the usual setup:

$$\hat{H}(t) = \hat{H}_0 + \hat{H}'(t) \tag{6}$$

$$\hat{H}_0 |\psi_n\rangle = E_n |\psi_n\rangle \tag{7}$$

Except now instead of solving for $|\psi(t)\rangle$ using time-dependent perturbation, we will instead look for $\rho(t)$. Again, the density matrix will be more useful to understand the dynamics of the system than the wavefunction, because (a) it can account for dephasing and statistical mixtures of states, (b) we can still simply extract its diagonal terms ρ_{nn} to examine the likelihood of the system being in state n at time t , and (c) we can compute the expectation value of any operator A at time t by taking $\text{Tr}[A\rho(t)]$.

So, we will try to solve the Liouville-von Neumann equation, including a phenomenological

description of dephasing. For each element of $\rho(t)$ we have:

$$\frac{d}{dt}[\rho_{nm}(t)] = -\frac{i}{\hbar} [\hat{H}_0, \rho(t)]_{nm} - \frac{i}{\hbar} [\hat{H}'(t), \rho(t)]_{nm} - \rho_{nm}/T_2 \quad (8)$$

$$= -\left[i\omega_{mn} + \frac{1}{T_2}\right] \rho_{nm}(t) - \frac{i}{\hbar} [\hat{H}'(t), \rho(t)]_{nm} \quad (9)$$

The first term in Eqn. 8 is the trivial bit, which can be handled by expanding ρ in the basis of eigenstates of \hat{H}_0 :

$$\left[\hat{H}_0, |n\rangle \langle m|\right]_{nm} = \hat{H}_0 |n\rangle \langle m| - |n\rangle \langle m| \hat{H}_0 \quad (10)$$

$$= (E_n - E_m) |n\rangle \langle m| = \hbar\omega_{nm} |n\rangle \langle m| \quad (11)$$

$$\rightarrow -\frac{i}{\hbar} [\hat{H}_0, \rho(t)]_{nm} = -i\omega_{nm}\rho_{nm}(t) \quad (12)$$

We can begin to solve Eqn. 9 by defining our zeroth order density matrix as the static system before interaction with the laser, so there are no off-diagonal coherences: $\rho_{nm}^{(0)} = 0$ for $n \neq m$. We can plug in this zeroth order solution and solve for the first order solution:

$$\frac{d}{dt}[\rho_{nm}^{(1)}(t)] = -\left[i\omega_{mn} + \frac{1}{T_2}\right] \rho_{nm}^{(1)}(t) - \frac{i}{\hbar} [\hat{H}'(t), \rho^{(0)}]_{nm} \quad (13)$$

Integrating this expression produces:

$$\rho_{nm}^{(1)}(t) = \frac{i}{\hbar} \int_0^\infty d\tau \left[\hat{H}'(t - t_1), \rho^{(0)}\right]_{nm} e^{-(i\omega_{mn} + 1/T_2)t_1} \quad (14)$$

Note: we've skipped some math here which involves using $\rho_{nm}^{(1)}(t) = S_{nm}^{(1)}(t) e^{-(i\omega_{mn} + 1/T_2)t_1}$ as a change of variables.

To proceed here, one would do the following:

- Expand the commutator in Eqn. 14 by substituting $H'(t) = \hat{\mu}E(t) \cos(\omega t)$ where $E(t)$ may encode the pulsed temporal structure of the driving field.
- Assume this driving field is resonant with $\omega = \omega_{mn}$.
- Take the rotating wave approximation.
- Inspect the matrix elements $\rho_{nn}^{(1)}(t)$ to determine how populations evolve in time, to first order.
- Evaluate the macroscopic polarization of the system, to first order: $P^{(1)}(t) = \langle \hat{\mu}\rho^{(1)}(t) \rangle$
- Iteratively plug $\rho^{(1)}(t)$ back into the integral in Eqn. 14 to find $\rho^{(2)}(t)$, etc.

Understandably, this becomes somewhat tedious. Things get a bit clearer if we use the interaction picture, to separate out the field-induced dynamics from the intrinsic evolution of the reference Hamiltonian.

4 Pertubative expansion of ρ in the interaction picture

Recall that we defined (way back in Module 2) the wavefunction in the interaction picture:

$$|\psi(t)\rangle \equiv e^{-i\hat{H}_0(t-t_0)/\hbar} |\psi_I(t)\rangle = \hat{U}_0(t, t_0) |\psi_I(t)\rangle \quad (15)$$

where t_0 is some reference time point. With this definition, if $\hat{H}'(t)$ is zero, then $|\psi_I(t)\rangle = |\psi(t_0)\rangle$ will just be a constant in time.

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

$$\frac{d}{dt} |\psi(t)\rangle = -\frac{i}{\hbar} \hat{H} |\psi(t)\rangle \quad \rightarrow \quad \frac{d}{dt} |\psi_I(t)\rangle = -\frac{i}{\hbar} \hat{H}'_I(t) |\psi_I(t)\rangle \quad (16)$$

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

$$\hat{H}'_I(t) \equiv e^{+i\hat{H}_0(t-t_0)/\hbar} \hat{H}'(t) e^{-i\hat{H}_0(t-t_0)/\hbar} \quad (17)$$

$$= \hat{U}_0^\dagger(t, t_0) \hat{H}'(t) \hat{U}_0(t, t_0) \quad (18)$$

We can now proceed to define the density matrix in the interaction picture, $\rho_I(t)$, and inspect what happens to the Liouville-von Neumann equation:

$$\rho(t) = |\psi(t)\rangle \langle \psi(t)| = \hat{U}_0(t, t_0) |\psi_I(t)\rangle \langle \psi_I(t)| \hat{U}_0^\dagger(t, t_0) \quad (19)$$

$$\equiv \hat{U}_0(t, t_0) \rho_I(t) \hat{U}_0^\dagger(t, t_0) \quad (20)$$

Note again that this expression is linear in ρ , and therefore holds for both pure and mixed states.

Following in the footsteps of Eqn. 16, it will turn out that we can simply write the Liouville-von Neumann equation in terms of the interaction picture density matrix as:

$$\frac{d}{dt} \rho(t) = -\frac{i}{\hbar} [\hat{H}(t), \rho(t)] \quad \rightarrow \quad \frac{d}{dt} \rho_I(t) = -\frac{i}{\hbar} [\hat{H}'_I(t), \rho_I(t)] \quad (21)$$

One can integrate the above to find:

$$\rho_I(t) = \rho_I(t_0) - \left(\frac{i}{\hbar}\right) \int_{t_0}^t d\tau [\hat{H}'_I(\tau), \rho_I(\tau)] \quad (22)$$

It's therefore much simpler to iteratively solve for the density matrix in the interaction picture:

$$\rho_I(t) = \rho_I(t_0) - \left(\frac{i}{\hbar}\right) \int_{t_0}^t d\tau_1 [\hat{H}'_I(\tau_1), \rho_I(t_0)] \quad (23)$$

$$+ \left(-\frac{i}{\hbar}\right)^2 \int_{t_0}^t d\tau_2 \int_{t_0}^{\tau_2} d\tau_1 [\hat{H}'_I(\tau_2), [\hat{H}'_I(\tau_1), \rho_I(t_0)]] \quad (24)$$

+ ...

Or considering the entire expansion:

$$\rho_I(t) = \rho_I(t_0) + \sum_{n=1}^{\infty} \left(-\frac{i}{\hbar}\right)^n \int_{t_0}^t d\tau_n \int_{t_0}^{\tau_n} d\tau_{n-1} \cdots \int_{t_0}^{\tau_2} d\tau_1 [\hat{H}'_I(\tau_n), [\hat{H}'_I(\tau_{n-1}), \cdots [\hat{H}'_I(\tau_1), \rho_I(t_0)]]] \quad (25)$$

We can finally return to the Schrödinger picture density matrix using Eqn. 20, though note that the interaction picture perturbation \hat{H}'_I that still appears:

$$\rho(t) = \rho^{(0)}(t) + \sum_{n=1}^{\infty} \left(-\frac{i}{\hbar}\right)^n \int_{t_0}^t d\tau_n \int_{t_0}^{\tau_n} d\tau_{n-1} \cdots \int_{t_0}^{\tau_2} d\tau_1 \quad (26)$$

$$\begin{aligned} & \hat{U}_0(t, t_0) \left[\hat{H}'_I(\tau_n), \left[\hat{H}'_I(\tau_{n-1}), \cdots \left[\hat{H}'_I(\tau_1), \rho(t_0) \right] \right] \right] \hat{U}_0^\dagger(t, t_0) \\ & \equiv \rho^{(0)}(t) + \sum_{n=1}^{\infty} \rho^{(n)}(t) \end{aligned} \quad (27)$$

Eqn. 27 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 $\rho(t_0)$ from both its ket and bra sides.

We can go a little further to make Eqn. 27 easier to work with. Let's use our explicit expression for $\hat{H}'(t)$ for light-matter interactions:

$$\hat{H}'(t) = E(t) \hat{\mu} \quad (28)$$

$$\rightarrow \hat{H}'_I(t) = \hat{U}_0^\dagger(t, t_0) E(t) \hat{\mu} \hat{U}_0(t, t_0) \quad (29)$$

$$= E(t) \hat{U}_0^\dagger(t, t_0) \hat{\mu} \hat{U}_0(t, t_0) \quad (30)$$

$$\equiv E(t) \hat{\mu}_I(t) \quad (31)$$

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 our iterative definition of $\rho(t)$ as an expansion of terms:

$$\rho(t) = \rho(t_0) + \sum_{n=1}^{\infty} \rho^{(n)}(t) \quad (32)$$

$$\begin{aligned} \rho^{(n)}(t) & \equiv \left(-\frac{i}{\hbar}\right)^n \int_{t_0}^t d\tau_n \int_{t_0}^{\tau_n} d\tau_{n-1} \cdots \int_{t_0}^{\tau_2} d\tau_1 E(\tau_n) E(\tau_{n-1}) \cdots E(\tau_1) \\ & \hat{U}_0(t, t_0) [\hat{\mu}_I(\tau_n), [\hat{\mu}_I(\tau_{n-1}), \cdots [\hat{\mu}_I(\tau_1), \rho(t_0)]]] \hat{U}_0^\dagger(t, t_0) \end{aligned} \quad (33)$$

There are two conventions to note here:

- By convention t_0 is taken in the limit $t_0 \rightarrow -\infty$, so you often see Eqn. ?? involving $\rho(-\infty)$ rather than $\rho(t_0)$. $\rho(-\infty)$ is considered to be the density matrix at equilibrium well before any perturbation occurs, which is static under the reference Hamiltonian \hat{H}_0 .
- The dipole operator $\hat{\mu}$ is time independent, while 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 $\hat{\mu}(t)$.

4.1 Connecting ρ to macroscopic polarization

When matter interacts with light, it becomes *polarized*: its dipole moment changes in response to the applied electromagnetic field. In linear optics, the polarization of the material depends linearly

on the electric field E :

$$P = \epsilon_0 \cdot \chi^{(1)} \cdot E \quad (34)$$

where $\chi^{(1)}$ is the linear susceptibility of the material. For strong enough electric fields, this linear approximation is no longer true, and the polarization is instead expanded in powers of the electric field:

$$P = \epsilon_0 \left[\chi^{(1)} \cdot E + \chi^{(2)} \cdot E \cdot E + \chi^{(3)} \cdot E \cdot E \cdot E + \dots \right] \quad (35)$$

$$= P^{(1)} + P^{(2)} + P^{(3)} \dots \quad (36)$$

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

Aside: In media with inversion symmetry (such as isotropic media like a bulk liquid), 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 will always have positive magnitude. As a result, the even-order *susceptibilities* $\chi^{(2n)}$ must therefore vanish in isotropic media, and the 3rd order nonlinearity gives rise to the lowest-order nonlinear processes. (Note that this is not true 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 $\hat{\mu}$:

$$P(t) = \langle \hat{\mu}(t) \rangle = \text{Tr} [\hat{\mu} \rho(t)] \quad (37)$$

We can note now by inspecting Eqns. 33 and 36 that since both the macroscopic polarization and the density matrix are expanded in powers of E , we can equate:

$$P^{(n)}(t) = \text{Tr} [\hat{\mu} \cdot \rho^{(n)}(t)] \equiv \langle \hat{\mu} \cdot \rho^{(n)}(t) \rangle \quad (38)$$

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

So let's now write down an expression for the n^{th} -order component of the macroscopic polarization in terms of our perturbative expansion of the density matrix. Dropping the I subscripts for the transition dipoles:

$$P^{(n)}(t) = \left\langle \hat{\mu} \cdot \left(-\frac{i}{\hbar} \right)^n \int_{t_0}^t d\tau_n \int_{t_0}^{\tau_n} d\tau_{n-1} \dots \int_{t_0}^{\tau_2} d\tau_1 E(\tau_n) E(\tau_{n-1}) \dots E(\tau_1) \right. \\ \left. \hat{U}_0(t, t_0) [\hat{\mu}(\tau_n), [\hat{\mu}(\tau_{n-1}), \dots [\hat{\mu}(\tau_1), \rho(t_0)]]] \hat{U}_0^\dagger(t, t_0) \right\rangle \quad (39)$$

$$= \left(-\frac{i}{\hbar} \right)^n \int_{t_0}^t d\tau_n \int_{t_0}^{\tau_n} d\tau_{n-1} \dots \int_{t_0}^{\tau_2} d\tau_1 E(\tau_n) E(\tau_{n-1}) \dots E(\tau_1) \\ \left\langle \hat{\mu} \cdot \hat{U}_0(t, t_0) [\hat{\mu}(\tau_n), [\hat{\mu}(\tau_{n-1}), \dots [\hat{\mu}(\tau_1), \rho(t_0)]]] \hat{U}_0^\dagger(t, t_0) \right\rangle \quad (40)$$

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

$$P^{(n)}(t) = \left(-\frac{i}{\hbar}\right)^n \int_{t_0}^t d\tau_n \int_{t_0}^{\tau_n} d\tau_{n-1} \cdots \int_{t_0}^{\tau_2} d\tau_1 E(\tau_n) E(\tau_{n-1}) \cdots E(\tau_1) \quad (41)$$

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

$$= \left(-\frac{i}{\hbar}\right)^n \int_{t_0}^t d\tau_n \int_{t_0}^{\tau_n} d\tau_{n-1} \cdots \int_{t_0}^{\tau_2} d\tau_1 E(\tau_n) E(\tau_{n-1}) \cdots E(\tau_1) \quad (42)$$

$$\left\langle \hat{\mu}(t) [\hat{\mu}(\tau_n), [\hat{\mu}(\tau_{n-1}), \cdots [\hat{\mu}(\tau_1), \rho(t_0)]]] \right\rangle$$

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

$$S^{(n)}(t) \equiv \left(-\frac{i}{\hbar}\right)^n \left\langle \mu(t) [\mu(\tau_n), [\mu(\tau_{n-1}), \cdots [\mu(\tau_1), \rho(t_0)]]] \right\rangle \quad (43)$$

Or, without loss of generality, taking

$$t_0 \rightarrow -\infty \quad (44)$$

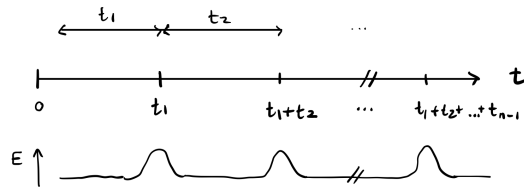
$$\tau_1 = 0 \quad (45)$$

$$t_1 = \tau_2 - \tau_1 \quad (46)$$

$$t_2 = \tau_3 - \tau_2 \dots \quad (47)$$

We can write

$$S^{(n)}(t_n, \dots, t_1) = \left(-\frac{i}{\hbar}\right)^n \left\langle \mu(t_n + \cdots + t_1) [\mu(t_{n-1} + \cdots + t_1), \cdots [\mu(0), \rho(-\infty)] \cdots] \right\rangle \quad (48)$$



This n^{th} response function is defined for n interactions of the molecular dipole with the field at positive times $\sum_k t_k$ that defined with respect to an arbitrary time 0.

The interactions of the dipole with the field at various times act on the initial density matrix $\rho(-\infty)$ to generate a non-equilibrium density matrix $\rho^{(n)}(t)$ whose off-diagonal elements generate a macroscopic polarization of the sample.

Only the first n interactions with the dipole operator are part of the commutator. The final term $\mu(t_n + \cdots + t_1)$ lies outside the commutator, and represents our final measurement of the macroscopic polarization of the sample as a function of time after all interactions with the field have already transpired.

5 Representing spectroscopy

When a laser pulse interacts with an ensemble of molecules, the transition dipole operator $\hat{\mu}$ perturbs the density operator ρ , and it does so from either the bra (left) or the ket (right) sides of ρ . Each set of commutators in our expressions above give us 2^n terms, within which there are pairs of terms that are just complex conjugates.

5.1 The first order response & linear spectroscopy

As a simple example, let's consider the set of terms that arise from the nested set of commutators for both the linear and the third-order responses. We skip the second-order response, as we said earlier that it is assumed to vanish in isotropic media.

The linear response function evaluated at time t_1 is

$$S^{(1)}(t_1) = -\frac{i}{\hbar} \langle \hat{\mu}(t_1) [\mu(0), \rho(-\infty)] \rangle \quad (49)$$

$$= -\frac{i}{\hbar} \left[\langle \hat{\mu}(t_1) \hat{\mu}(0) \rho(-\infty) \rangle - \langle \hat{\mu}(t_1) \rho(-\infty) \hat{\mu}(0) \rangle \right] \quad (50)$$

$$= -\frac{i}{\hbar} \left[\langle \hat{\mu}(t_1) \hat{\mu}(0) \rho(-\infty) \rangle - \langle \rho(-\infty) \hat{\mu}(0) \hat{\mu}(t_1) \rangle \right] \quad (51)$$

$$= -\frac{i}{\hbar} \left[\langle \hat{\mu}(t_1) \hat{\mu}(0) \rho(-\infty) \rangle - \langle \hat{\mu}(t_1) \hat{\mu}(0) \rho(-\infty) \rangle^* \right] \quad (52)$$

$$= -\frac{i}{\hbar} \left[\langle \hat{\mu}(t_1) \hat{\mu}(0) \rho(-\infty) \rangle - C.C. \right] \quad (53)$$

where we have made use of the invariance of the trace to cyclic permutation and the fact that:

$$\langle [\hat{\mu}(t_1) \hat{\mu}(0) \rho(-\infty)]^\dagger \rangle = \langle \rho^\dagger(-\infty) \hat{\mu}^\dagger(0) \hat{\mu}^\dagger(t_1) \rangle \quad (54)$$

$$= \langle \rho(-\infty) \hat{\mu}(0) \hat{\mu}(t_1) \rangle \quad (55)$$

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

What is actually happening here? At time $t = 0$, we apply a $\hat{\mu}(0)$ to $\rho(-\infty)$, which now creates off-diagonal matrix elements like ρ_{12} . The probability that this happens is proportional to μ_{12} . We know from solving the optical Bloch equations that the off-diagonal density matrix element evolves in time as:

$$\rho_{12}(t) \propto \mu_{12} e^{-i(\omega_{12})t} e^{-t/T_2} \quad (56)$$

where T_2 is the dephasing time.

At time t_1 , the off-diagonal matrix element, representing a macroscopic polarization of the sample, emits a light field, which is again proportional to μ_{12} , so

$$S^{(1)}(t_1) \propto \mu_{12}^2 e^{-i(\omega_{12})t_1} e^{-t_1/T_2} \quad (57)$$

Let's now assume we have a very short pulsed field with a carrier frequency that is resonant with our transition of interest, so $\omega = \omega_{12}$:

$$E(t) = E_0(t) \cdot 2 \cos(\omega t) = E_0(t) [e^{-i\omega t} + e^{i\omega t}] = E_0 \delta(t) [e^{-i\omega t} + e^{i\omega t}] \quad (58)$$

For the first order-polarization of the sample, we therefore calculate:

$$P^{(1)}(t) = -\frac{i}{\hbar} \int_0^\infty dt_1 E(t-t_1) S^{(1)}(t_1) \quad (59)$$

$$= -\frac{i}{\hbar} \int_0^\infty dt_1 E_0 \delta(t-t_1) \left[e^{-i\omega(t-t_1)} + e^{i\omega(t-t_1)} \right] \cdot \mu_{12}^2 e^{-i\omega t_1} e^{-t_1/T_2} \quad (60)$$

$$= -\frac{i}{\hbar} E_0 \mu_{12}^2 \int_0^\infty dt_1 \delta(t-t_1) \left[e^{-i\omega t} + e^{i\omega t} \cancel{e^{-2i\omega t_1}} \right] e^{-t_1/T_2} \quad (61)$$

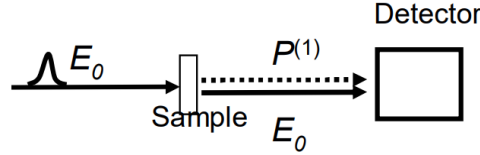
$$= -\frac{i}{\hbar} E_0 \mu_{12}^2 e^{-i\omega t} \int_0^\infty dt_1 \delta(t-t_1) e^{-t_1/T_2} \quad (62)$$

$$= -\frac{i}{\hbar} E_0 \mu_{12}^2 e^{-i\omega t} e^{-t/T_2} \quad (63)$$

This oscillating polarization will emit a field with a 90-degree phase lag, so $E^{(1)}(t) \propto -iP^{(1)}(t)$. This is the free induction decay, which interferes with the incident field $E_0(t)$. On a square law detector, you measure the intensity rather than the field amplitude:

$$|E_0(t) + E^{(1)}(t)|^2 = |E_0(t)|^2 + |E^{(1)}(t)|^2 + 2\Re[E_0(t)E^{(1)}(t)] \quad (64)$$

In a linear absorption measurement, the phase shift of the radiated field with respect to the incident field causes destructive interference, which leads to a lower intensity of light on the detector at the resonance frequency ω .



If you were to resolve the spectrum of this field with a spectrometer, which performs a Fourier transform of the fields from time into frequency space, and calculate an absorption spectrum, you would see a negative-going Lorentzian line at the $0 \rightarrow 1$ resonance frequency representing the absorption of light by the sample.

5.2 Third order response & nonlinear spectroscopy

The same exercise as above for the third-order response yields the following terms for $S^{(3)}$ (plus their complex conjugates):

$$\langle \mu(t_3 + t_2 + t_1) \hat{\mu}(0) \rho(-\infty) \hat{\mu}(t_1) \hat{\mu}(t_2 + t_1) \rangle - C.C. \quad (65)$$

$$\langle \mu(t_3 + t_2 + t_1) \hat{\mu}(t_1) \rho(-\infty) \hat{\mu}(0) \hat{\mu}(t_2 + t_1) \rangle - C.C. \quad (66)$$

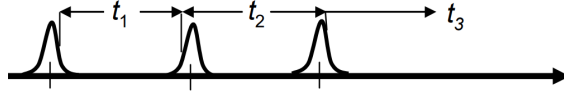
$$\langle \mu(t_3 + t_2 + t_1) \hat{\mu}(t_2 + t_1) \rho(-\infty) \hat{\mu}(0) \hat{\mu}(t_1) \rangle - C.C. \quad (67)$$

$$\langle \mu(t_3 + t_2 + t_1) \hat{\mu}(t_2 + t_1) \hat{\mu}(t_1) \rho(-\infty) \hat{\mu}(0) \rangle - C.C. \quad (68)$$

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

$$P^{(3)}(t) = \int_0^\infty dt_3 \int_0^\infty dt_2 \int_0^\infty dt_1 E(t-t_3) E(t-t_3-t_2) E(t-t_3-t_2-t_1) S^{(3)}(t_3, t_2, t_1) \quad (69)$$

In practice in the laboratory, the field will originate from a series of short laser pulses:



with

$$E(t) = E_1(t) [e^{i\omega t} + e^{-i\omega t}] + E_2(t) [e^{i\omega t} + e^{-i\omega t}] + E_3(t) [e^{i\omega t} + e^{-i\omega t}] \quad (70)$$

so each factor of $E(t)$ in Eqn. 69 adds 6-fold more terms to the calculation of $P(t)$.

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 perturbation from $\hat{\mu}(0)$ originates from $E_1(t)$, and so forth. We can also again approximate the envelopes as δ functions, so, e.g. $E_1(t) = E_1\delta(t)e^{\pm i\omega t}$, again simplifying the integral in Eqn. 69.

In practice, *phase matching* is also used to distinguish between the various terms in $S^{(n)}$ that contribute to experimental signal. If we think about the spatial geometry of the fields, the laser pulses can travel along different wavevectors, e.g. $E_1(t) = E_1(t) [e^{-i\omega_1 t + ik_1 r} + e^{-i\omega_1 t - ik_1 r}]$. 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.

5.3 A more concrete example of nonlinear signals

Let's at long last touch on a simple non-linear experiment. Let's work through the contribution of Eqn. 65 above to the signal for a two-level system.

- We'll initialize our density matrix in the ground state:

$$\rho(-\infty) = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} \quad (71)$$

and assume our light-matter perturbation takes the form

$$\hat{\mu} = \begin{pmatrix} 0 & \mu_{12} \\ \mu_{12} & 0 \end{pmatrix} \quad (72)$$

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

$$\hat{\mu}(0) \cdot \rho(-\infty) = \begin{pmatrix} 0 & \mu_{12} \\ \mu_{12} & 0 \end{pmatrix} \cdot \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} = \begin{pmatrix} 0 & 0 \\ \mu_{12} & 0 \end{pmatrix} \quad (73)$$

- We then let the system evolve in the absence of interactions until time t_1 . Let's neglect population relaxation or any other dynamics for now, so at time t_1 we have a density matrix given by:

$$\begin{pmatrix} 0 & 0 \\ \mu_{12}e^{-i\omega_{12}t_1} & 0 \end{pmatrix} \quad (74)$$

- At time $t = 1$ we are perturbed again, this time from the right:

$$\hat{\mu}(0) \cdot \rho(-\infty) \hat{\mu}(t_1) = \begin{pmatrix} 0 & 0 \\ \mu_{12} e^{-i\omega_{12} t_1} & 0 \end{pmatrix} \cdot \begin{pmatrix} 0 & \mu_{12} \\ \mu_{12} & 0 \end{pmatrix} = \begin{pmatrix} 0 & 0 \\ 0 & \mu_{12}^2 e^{-i\omega_{12} t_1} \end{pmatrix} \quad (75)$$

- We now let the system evolve until time $t_1 + t_2$, but note that there is no temporal evolution of the diagonal elements of the density matrix, which represent populations!
- 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:

$$\mu(t_3 + t_2 + t_1) \hat{\mu}(0) \rho(-\infty) \hat{\mu}(t_1) \hat{\mu}(t_2 + t_1) = \begin{pmatrix} \mu_{12}^4 e^{-i\omega_{12}(t_1+t_3)} & 0 \\ 0 & 0 \end{pmatrix} \quad (76)$$

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

$$\langle \mu(t_3 + t_2 + t_1) \hat{\mu}(0) \rho(-\infty) \hat{\mu}(t_1) \hat{\mu}(t_2 + t_1) \rangle - C.C. \quad \propto \quad \mu_{12}^4 \sin(\omega_{12}(t_3 + t_1)) \quad (77)$$

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. 65 - 68. One would finally then integrate $S^{(3)}(t)$ against the electric field, as shown in Eqn. 69 to obtain the macroscopic polarization $P^{(3)}(t)$, from which the radiated field $E^{(3)}(t)$ can be directly 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.