MIT Department of Chemistry
5.74, Spring 2004: Introductory Quantum Mechanics II
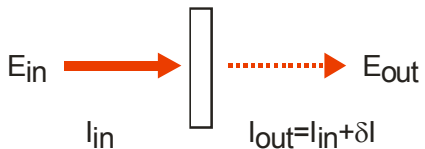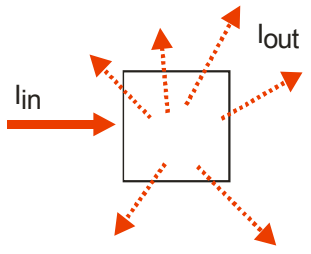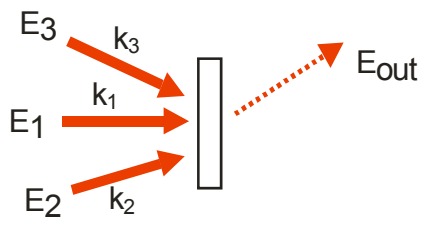Instructor: Prof. Andrei Tokmakoff

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COHERENT NONLINEAR SPECTROSCOPY

Use external fields to generate a signal field through interaction with your system. Measure generated field as a function of input fields (amplitude, phase, time, freq., polarization, $\bar{k}$).

Detection:	**Coherent**	**Spontaneous**
Linear:	Absorption (variation of input field)	Fluorescence Raman/Light scattering
Nonlinear:		Fluorescence-detected NLS, for instance, SEP, TDFSS
	$$I_{coherent} \propto \left| \sum_i E_i \right|^2$$	$$I_{incoherent} \propto \sum_i \left| E_i \right|^2$$ $$\propto \sum_i \left| \mu_i \right|^2$$

We'll discuss coherent nonlinear spectrosopies: One or more input fields generate a macroscopic oscillating polarization that radiates a signal, for instance pump probe; transient gratings; photon echoes; coherent simulated Raman . . .

The treatment is semi-classical: System: quantum; Field: classical. N^{th} order perturbation theory is used to describe the nonlinear signal (response) derived from a sequence of N fields.

We describe coherent spectroscopies by calculating the polarization, $\overline{P}$: the macroscopic collective dipole moment/unit volume.

$$\overline{P}(\overline{r}) = \sum_m \mu_m \, \delta(\overline{r} - \overline{R}_m) \qquad \text{\textit{sum over molecules}}$$

$$\mu_m \equiv \sum_\alpha q_{m\alpha}(\overline{r}_{m\alpha} - \overline{R}_m) \qquad \text{\textit{sum over displacement of charges}}$$

In coherent spectroscopies, the input fields act to create a macroscopic coherently oscillating charge distribution, which acts as a source to radiate a new electromagnetic field: the signal. Remember that an accelerated charge radiates an electric field. The polarization in the electric dipole approximation is one term in the current and charge densities that you put into Maxwell's equations.

The polarization and signal fields depend on the frequency and wave vector of incident fields.

(1) $$\overline{P}(\overline{r},t) = P(t) \exp(i\overline{k}_{sig} \cdot \overline{r} - i\omega_{sig}t) + c.c.$$

$$\overline{k}_{sig} = \sum_{in} \pm k_{in} \qquad \omega_{sig} = \sum_{in} \pm \omega_{in} \qquad \text{\textit{\underline{momentum and energy conservation}}}$$

The oscillating polarization radiates a coherent signal field, $\overline{E}_{sig}$, in a wave vector matched direction of constructive interference $\overline{k}_{sig}$.

Remember from earlier: For a freely propagating E.M. wave, the wave equation for a transverse, plane wave was

$$\overline{\nabla}^2 \overline{E}(\overline{r}) - \frac{1}{c^2}\ddot{\overline{E}}(\overline{r}) = 0$$

which gave a solution for a sinusoidal oscillating field with frequency ω propagating along k. If instead, we have the polarization acting as a source – an accelerated charge, we can write

(2) $$\overline{\nabla}^2 \overline{E}(\overline{r}) - \frac{1}{c^2}\ddot{\overline{E}}(\overline{r}) = \frac{4\pi}{c^2}\ddot{\overline{P}}(\overline{r})$$

Although one dipole would radiate in a *sin θ* distribution relative to the displacement of the charge, when you have a ensemble of dipoles that have been coherently driven by external fields,

P is given by (1) and the radiation of the ensemble only constructively adds along $\bar{k}_{sig}$. For the radiated field we obtain

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

A further observation you can make is that the oscillating polarization is proportional to the signal field, although there is a $\pi/2$ phase shift between the two:
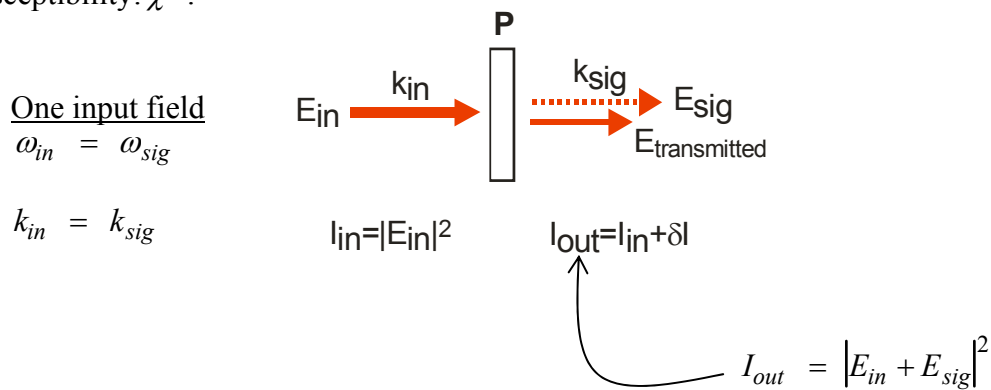
$$\bar{E}_{sig} \propto i\bar{P}.$$

Linear absorption spectroscopy. Absorption is a coherent spectroscopy in which an E.M. field induces a polarization that radiates a signal field that is out of phase with the transmitted light. To describe this, all of the relevant information is in $R^{(1)}(t)$ or $\chi^{(1)}(\omega)$.

$$\bar{P}(t) = \overline{\mu(t)} - \langle \mu \rangle = \int_0^\infty d\tau\, R^{(1)}(\tau)\, E(t-\tau)$$

$$\bar{P}(\omega) = \chi^{(1)}(\omega) \cdot \bar{E}(\omega)$$

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

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

$\varepsilon(\omega)$: dielectric constant
$n(\omega)$: Index of refraction
$\kappa(\omega)$: Absorption coefficient

For absorption, we found that the absorption lineshape was proportional to the imaginary part of the susceptibility: χ''.

P

One input field
$\omega_{in} = \omega_{sig}$

$k_{in} = k_{sig}$

E_{in} k_{in} →

k_{sig} ┄┄► E_{sig}
$E_{transmitted}$

$I_{in} = |E_{in}|^2$ $I_{out} = I_{in} + \delta I$

$$I_{out} = \left|E_{in} + E_{sig}\right|^2$$

$$I_{out} = \left| E_{in} + E_{sig} \right|^2$$

$$= \left| E_{in} + (iP) \right|^2 = \left| E_{in} + i\chi E_{in} \right|^2$$

$$= \left| E_{in} \right|^2 \left| 1 + i(\chi' + i\chi'') \right|^2$$

$$= I_{in}(1 - 2\chi'' \cdots) \qquad \Rightarrow \qquad I_{out} = I_{in} - \delta I$$

$$(\delta I) = 2\chi'' I_{in} \qquad \qquad \text{for } \left| E_{in} \right| \gg \left| \chi \right|$$

Nonlinear Polarization. For nonlinear spectroscopy, we will calculate the polarization P arising from interactions with multiple fields. For our purposes, $\overline{P}(t) = \overline{\mu(t)}$, and we expand P in powers of the incoming fields.

$$\overline{P}(t) = P^{(0)} + P^{(1)} + \underbrace{P^{(2)} + P^{(3)} + \cdots}_{\text{nonlinear terms}}$$

$$\overline{\mu(t)} = \langle \mu \rangle + \chi E_1 + \cdots$$

Earlier we wrote

$$\overline{P}^{(2)}(t) = \int_0^\infty d\tau_2 \int_0^\infty d\tau_1 \, R^{(2)}(\tau_2, \tau_1) \overline{E}_3(t - \tau_2 - \tau_1) \overline{E}_2(t - \tau_2)$$

$$\overline{P}^{(2)}(\omega) = \chi^{(2)}(\omega; \omega_1, \omega_2) \overline{E}_1(\omega_1) \overline{E}_2(\omega_2)$$

We will calculate P from the density matrix:

$$\overline{P}(t) \;=\; Tr\left(\overline{\mu}_I(t) \rho_I(t) \right)$$

$$=\; P^{(0)} + P^{(1)} + P^{(2)} + \ldots$$

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

Here $\rho_I^{(i)}$ is the ith order expansion of the density matrix from the solution to the Liouville equation:

$$\rho_I(t) = \rho_I(t_0) - \frac{i}{\hbar}\int_{t_0}^{t} dt' \left[V_I(t'), \rho_I(t')\right].$$

Which we evaluate through iterative substitution:

$$\rho^{(0)} = \rho_I(t_0) = \rho_{eq}$$

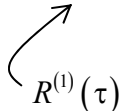$$\rho_I^{(1)} = -\frac{i}{\hbar}\int_{-\infty}^{t} dt_1 \left[V_I(t_1), \rho_{eq}\right]$$

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

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

Remember that the variables τ_i are defined as time intervals. Since the initial state of the system is equilibrium, we have set $t_0 = -\infty$.

<u>Linear polarization</u>:

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

$$= Tr\left(\mu_I(t)\frac{i}{\hbar}\int_{-\infty}^{t} dt' \left[-\mu_I(t')E(t'), \rho_{eq}\right]\right)$$

$$= \frac{-i}{\hbar}\int_{-\infty}^{t} dt' \, E(t') \, Tr\left(\mu_I(t)\left[\mu_I(t'), \rho_{eq}\right]\right)$$

$$= +\frac{i}{\hbar}\int_{0}^{\infty} d\tau \, E(t-\tau) \, Tr\left(\left[\mu_I(\tau), \mu_I(0)\right]\rho_{eq}\right)$$

$$R^{(1)}(\tau)$$

$$R^{(1)}(\tau) = \frac{i}{\hbar}\theta(\tau)Tr\left(\left[\mu_I(\tau),\mu_I(0)\right]\rho_{eq}\right)$$

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

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

Note, for $E(t-\tau) = E_0\delta(t-\tau)$ the polarization is described by the response function. What about the nonlinear polarization?

$$P^{(2)}(t) = Tr\left(\mu_I(t)\rho_I^{(2)}(t)\right)$$

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

Using $A\left[B,[C,D]\right] = \left[[A,B],C\right],D$

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

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

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

Again, for delta function pulses, the nonlinear polarization is given by the response function. To arbitrary order the nonlinear response function $R^{(n)}$ is

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

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

The nonlinear response functions are sums of correlation functions $\left(R^n \to 2^n\right)$

- These correlation functions differ by whether operators act on the bra or ket side of ρ when enforcing the time-ordering.
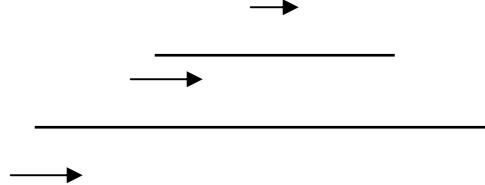
Let's look at $R^{(2)}$ and enforce the time-ordering:

Term 1:

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

$$\Rightarrow Tr\left(\underbrace{U_0^\dagger(\tau_1 + \tau_2)}_{U_0^\dagger(\tau_1)U_0^\dagger(\tau_2)}\mu\underbrace{U_0(\tau_1 + \tau_2)U_0^\dagger(\tau_1)}_{U_0(\tau_2)}\mu U_0(\tau_1)\mu\,\rho_{eq}\right)$$

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

(1) dipole acts on **ket** of ρ_{eq}
(2) evolve under H_0 during τ_1.
(3) dipole acts on **ket** τ_1.
(4) Evolve during τ_2.
(5) Multiply by μ and take trace.

KET/KET interaction

Each time the operator acted on ket side of ρ. Different correlation functions are distinguished by the order that they act on bra or ket.

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

Convention: Final operator acts on ket side.

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

BRA/KET interaction

- Notice that bra side interaction is complex conjugate of ket side.

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

- For $R^{(n)}$, you really only need 2^{n-1} correlation functions.

So for $R^{(2)}$ we write

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

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

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

ket/bra $\quad Q_2 = Tr\left[\mu_I(\tau_1)\mu_I(\tau_1+\tau_2)\mu_I(0)\rho_{eq}\right] = Tr\left[\mu_I(\tau_1+\tau_2)\mu_I(0)\rho_{eq}\mu_I(\tau_1)\right]$

Third Order Response

Since $R^{(2)}$ orientationally averages to zero for isotropic systems, the third order response describes most experiments.

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

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

$R_1 \Rightarrow ket/ket/ket \quad R_2 \Rightarrow bra/ket/bra \quad R_3 \Rightarrow bra/bra/ket \quad R_4 \Rightarrow ket/bra/bra$

The individual correlation function can be explicitly written in terms of a sum over all possible intermediate states. For a third-order experiment, this means up to four states involves in the process. (Third-order nonlinear experiments can also be referred to a four-wave mixing).

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

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

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

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

General Expressions for n^{th} Order Nonlinearity

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

$$R^{(n)}\left(\tau_1,\tau_2,\ldots\tau_n\right) = \left(\frac{i}{\hbar}\right)^n \theta\left(\tau_1\right)\theta\left(\tau_2\right)\ldots\theta\left(\tau_n\right)$$
$$\times Tr\left\{\left[\left[\ldots\left[\mu_I\left(\tau_n+\tau_{n-1}+\ldots+\tau_1\right),\mu_I\left(\tau_{n-1}+\tau_n+\cdots\tau_1\right)\right],\ldots\right]\mu_I\left(0\right)\right]\rho_{eq}\right\}$$

For delta function pulses: $\bar{E}_1\left(t-t_0\right) = \bar{E}_1\delta\left(t-t_0\right)$ the polarization and response function are directly proportional $P^{(n)}(t) = R^{(n)}\left(\tau_1,\tau_2,\ldots\tau_{n-1},t\right)\bar{E}_1\cdots\bar{E}_n$.

Propagating the density matrix

Our nonlinear response functions for the nonlinear polarization are sequences of interaction with the field (dipole operator) followed by propagation of the system under the equilibrium Hamiltonian. We can represent the evolution with a time-propagator G (super operator).

$$\dot{\rho}_I = \frac{-i}{\hbar}[V_I, \rho_I] \quad \Leftrightarrow \quad \dot{\rho}_I = \frac{-i}{\hbar}\mathscr{L}\,\rho_I$$

Liouvillian super-operator

Time propagator

$$\rho_I(t) = U_0\,\rho_I U_0^\dagger \quad \Leftrightarrow \quad \rho_I(t) = G(t)\rho_I$$

for a particular element of density matrix

$$G(t)\rho_{ab} = U_0|a\rangle\langle b|U_0^\dagger$$

$$= e^{-iH_0 t/t}|a\rangle\langle b|e^{+iH_0 t/\hbar}$$

$$= e^{-i\omega_{ab}t}|a\rangle\langle b| \qquad \textit{for eigenstates (no bath / damping)}$$

To include propagation of the system with phenomenological relaxation, we can write

$$G(t)\rho_{ab} = exp\left[-i\omega_{ab}t - \Gamma_{ab}t\right]\rho_{ab} \qquad\qquad \Gamma_{ab} = \Gamma_{ba} \qquad G_{ab}^* = G_{ba}$$

$$\Gamma_{ii} \rightarrow \textit{ population relaxation } \left(\frac{1}{T_1}\right) \qquad \Gamma_{ij} \rightarrow \textit{ dephasing (coherence) } \left(\frac{1}{T_2}\right)$$