A Summer Short Course 2016

Lecture 7 : Nonlinear spectroscopy
Lecture 8 : Photon-echo & Two-dimensional electronic spectroscopy.

Lecture 7:
* nonlinear polarization
* nonlinear response function
* Liouville pathways & double-sided Feynman diagrams.

Lecture 8:
* Impulsive response function formalism.
* photon-echo spectroscopy.
* two-dimensional electronic spectroscopy

Now we are ready to turn to the more complex theoretical frameworks that describe laser experiments involving multiple pulses and time delays. Of course this is a vast research field ~~area~~ too complicated to fully covered in this short course. So we will focus on the very basic formalism & approximations and focus on photon-echo spectroscopy. (PE)

To properly introduce the PE spectroscopy, which is a four-wave mixing, third-order technique, we first provide a formal introduction to principles of nonlinear spectroscopy, here we aim to explain the following concepts:

* nonlinear polarization.
* double-sided Feynman diagram (Liouville pathways)
* time-ordering & the impulsive limit.
* rotating-wave approximation. (RWA).
* phase matching
* photon-echo.

These materials are based on Peter Hamm's lecture notes.

* nonlinear response function.

Let's recall the problem at hand is described by the Hamiltonian:

$$H = H_0 + V(t) = H_0 - \hat{\mu} \cdot E(t).$$

In the ~~interaction picture~~ quantum mechanics, an observable is generally calculated from:

$$\langle A(t) \rangle = \langle \psi(t) | A | \psi(t) \rangle = \mathrm{Tr}\, A \cdot \rho(t).$$

where $\rho(t) = U(t) \cdot \rho(0) \cdot U^{\dagger}(t)$.

By expanding $U(t)$ in the interaction picture, one can show that without $V(t)$, i.e. $\rho^{(0)}(t) = U_0(t) \cdot \rho(0) \cdot U_0^{\dagger}(t)$

$$\rho(t) = \rho^{(0)}(t) + \sum_{n=1}^{\infty} \left(\frac{-i}{\hbar}\right)^n \int_0^t d\tau_n \int_0^{\tau_n} d\tau_{n-1} \cdots \int_0^{\tau_2} d\tau_1 \cdot$$

$$U_0(t) \cdot [V_I(\tau_n), [V_I(\tau_{n-1}), \cdots [V_I(\tau_1), \rho(0)]]] \cdot U_0^{\dagger}(t).$$

$V_I(t) = U_0^{\dagger}(t) \cdot V(t) \cdot U_0(t)$

Let's assume $\rho(0)$ is the equilibrium density matrix $\longrightarrow$ $\rho^{(0)}(t) = U_0(t) \cdot \rho(0) \cdot U_0(t) = \rho(0)$.

Since the system does not evolve before we turn on the first pulse @ $t=0$
$t = -\infty \ldots 0$, we can push the $0 \to \infty$, and use $\rho(0) = \rho(-\infty)$ to emphasize this. Furthermore, we plug in

$$V(t) = E(t) \cdot \mu, \quad , \quad \mu_I(t) = U_0^\dagger(t) \cdot \mu \cdot U_0(t).$$

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

$$\times U_0(t) \cdot [\mu_I(\tau_n), \ldots\ldots [\mu_I(\tau_1), \rho(-\infty)] \ldots] \cdot U_0^\dagger(t).$$

$$\equiv \rho^{(0)}(-\infty) + \sum_{n=1}^{\infty} \rho^{(n)}(t).$$

If we define the n-th order polarization.

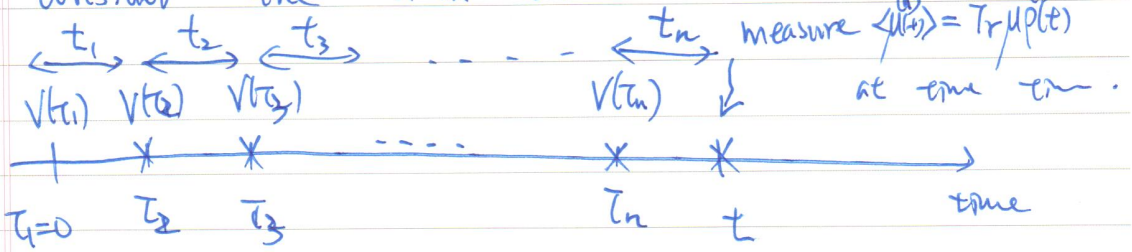
$$P^{(n)}(t) = \text{Tr}\, \mu \cdot \rho^{(n)}(t).$$

We obtain the total polarization as:

$$P(t) = \text{Tr}\, \mu \cdot \rho(t) = \sum_n P^{(n)}(t),$$

$\rho^{(n)}(t)$ has a simple physical interpretation,

consider the n-th term



note the time ordering :

⇒ it corresponds to a pulsed experiment with "n" input pulses !!

i.e. n system–field interactions.

Normally in a real experiment only duration between pulses is meaningful, so we choose another set of time variables :

$\tau_1 = 0$

$t_1 = \tau_2 - \tau_1$

$t_2 = \tau_3 - \tau_2$

$\vdots$

$t_n = t - \tau_n$.

and use $\mu(t) = U_0^\dagger(t)\,\mu\,U_0(t)$

By change of variables, we reach (practice): :

$$\rho^{(n)}(t) = \left(\frac{-i}{\hbar}\right)^n \cdot \int_0^\infty dt_n \int_0^\infty dt_{n-1} \cdots \int_0^\infty dt_1 \cdot E(t-t_n)\cdot E(t-t_n-t_{n-1})\cdot \ldots \cdot E(t-t_n-t_{n-1}-\ldots-t_1)\cdot$$

$$\times \mathrm{Tr}\left\{\mu(t_n+t_{n-1}+\ldots+t_1)\cdot\left[\mu(t_{n-1}+\ldots+t_1),\ldots\left[\mu(0),\rho(-\infty)\right]\ldots\right]\right\}$$

not in commutator

system property

~~n-th order~~

Thus we can define the n^{th}-order nonlinear response function.

$$S^{(n)}(t_n,\ldots,t_1) = \left(\frac{-i}{\hbar}\right)^n \cdot \mathrm{Tr}\left\{\mu(t_n+\ldots+t_1)\left[\ \ldots\ \right\}\right.$$

Let's check,

$$S^{(1)}(t_1) = \left(\frac{-i}{\hbar}\right)^1 \cdot \mathrm{Tr}\left\{\mu(t_1)\cdot\left[\mu(0),\rho(-\infty)\right]\right\}$$

$$= \left(\frac{-i}{\hbar}\right)^1 \cdot \mathrm{Tr}\left\{\mu(t_1)\left[\mu(0)\rho(-\infty) - \rho(-\infty)\mu(0)\right]\right\}$$

$$= \left(\frac{-i}{\hbar}\right) \cdot \mathrm{Tr}\left\{\mu(t_1)\mu(0)\cdot\rho_{eq} - \mu(t_1)\rho_{eq}\mu(0)\right\}.$$

$$= \left(\frac{-i}{\hbar}\right)\left[\langle\mu(t_1)\mu(0)\rangle - \langle\mu(0)\mu(t_1)\rangle\right].$$

$$= \frac{2}{\hbar}\cdot \mathrm{Im}\cdot\langle\mu(t_1)\mu(0)\rangle. \quad \#$$

* Liouville pathways

For resonance interactions, these response functions have simple interpretations,

In this case the dipole operators are.

absorption

$$\mu = \sum_i \left(\vec{\mu}_{e_i,g} \cdot |e_i\rangle\langle g| + \vec{\mu}_{g,e_i} \cdot |g\rangle\langle e_i| \right)$$

emission

The term $\mathrm{Tr}\{\mu(t_3)\mu(t_2)\mu(t_1)\rho_{eq}\}$

$$= \mathrm{Tr}\{U_0^\dagger(t_1) \cdot \mu \cdot U_0(t_1) \cdot \mu \cdot \rho_{eq}\}$$

$$= \mathrm{Tr}\{\mu \cdot U_0(t_2) \cdot \mu \cdot \rho_{eq} \cdot U_0^\dagger(t_1)\}$$ elec. ground state only, ignore both now

$$\equiv \mathrm{Tr}\{\mu \cdot G_{t_2}(t_3) \cdot \mu \cdot |g\rangle\langle g|\}$$

a superoperator, propagator that propagates a density matrix forward in time: $G(\tau)\rho(t) = \rho(t+\tau)$

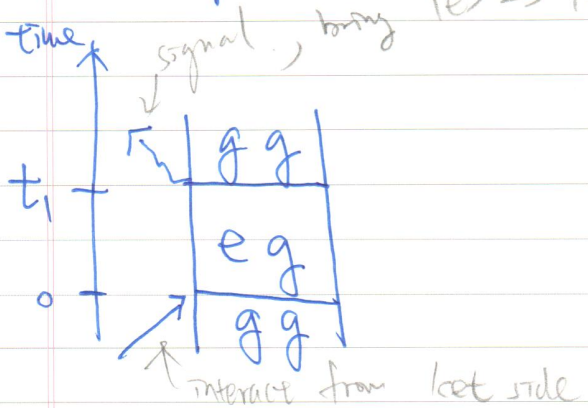
initially in g.s.

interact with pulse from "ket" side, absorption, generate many superpositions (coherences) e.g. $|g\rangle\langle g| \rightarrow |e\rangle\langle g|$,

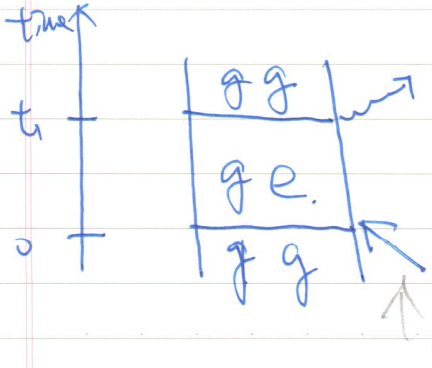
propagate the coherence for time t_2

measurement!!

This can be easily represented by a double-sided Feynman diagram that denotes the field-induced evolution of density matrix elements:



It is easy to verify that the other term is denoted as



(complex conjugate)

For a TSO-type system, the 2nd-order response is zero, and the lowest-order nonlinear response is the 3rd-order response, which is related to four-time correlation functions: $\left(\frac{-i}{\hbar}\right)^3$.

$$S^{(3)}(t_1,t_2,t_3) = \left(\frac{-i}{\hbar}\right)^3 Tr\left\{\mu(t_3+t_2+t_1)\left[\mu(t_2+t_1),\left[\mu(t_1),\left[\mu(0),\rho(-\infty)\right]\right]\right]\right\}$$

There are totally 8 terms, corresponse to four different contributions:

$$S^{(3)}(t_1,t_2,t_3) = \sum_{i=1}^{4}\left\{R_i(t_1,t_2,t_3) - R_i^*(t_1,t_2,t_3)\right\}$$

$$R_1 = Tr\left\{\mu(t_3+t_2+t_1)\,\mu(0)\,\rho(-\infty)\,\mu(t_1)\,\mu(t_2+t_1)\right\}$$

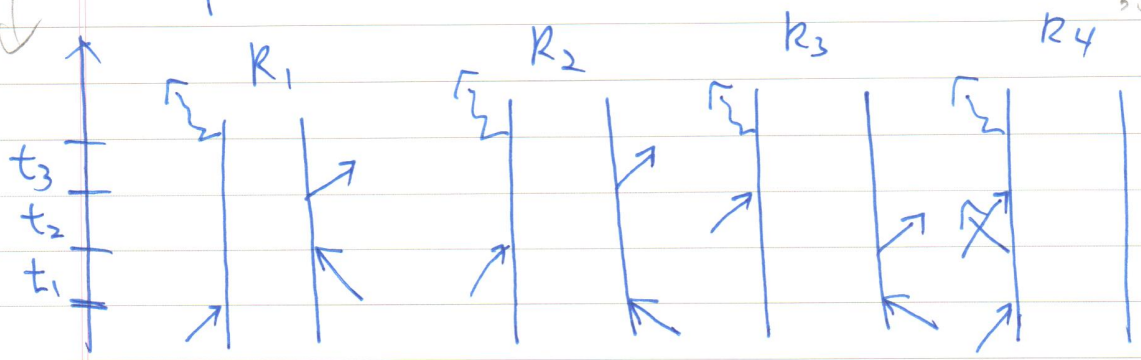
$$R_2 = Tr\left\{\mu(t_3+t_2+t_1)\cdot\mu(t_1)\cdot\rho(-\infty)\,\mu(0)\,\mu(t_2+t_1)\right\}$$

$$R_3 = Tr\left\{\mu(t_3+t_2+t_1)\,\mu(t_2+t_1)\cdot\rho(-\infty)\,\mu(0)\,\mu(t_1)\right\}$$

$$R_4 = Tr\left\{\mu(t_3+t_2+t_1)\cdot\mu(t_2+t_1)\,\mu(t_1)\,\mu(0)\,\rho(-\infty)\right\}$$

We don't give details of how to compute these here, consult Mukamel's book.

They correspond to:



the convergence of these diagrams are due to * response function * RWA * impulse limit. * ~~phase matching~~

The third-order polarization that is directly related to experimental observable

T_3 :

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

Note that in a 3-pulse experiment

$$E(t) = E_1(t)\cdot\cos(\omega_1 t) + E_2(t)\cdot\cos(\omega_2 t) + E_3(t)\cdot\cos(\omega_3 t)$$

assume real

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

$\Rightarrow$ 6 terms

Therefore, don't underestimate the evaluation

of $p^{(3)}(t)$, it contains

$$6 \times 6 \times 6 \times 4 = 864 \text{ terms !!}$$

Fortunately, in a properly setup experiment, not all 864 terms will contribute, due to the following physics, the number of terms drops considerably:

* time-order (short pulse).
* Rotating wave approximation.
* phase matching

① Impulsive limit & time-ordering.

Now, if we first assume very short pulses are applied so that the pulses are perfectly time-ordered, we can use a single field to

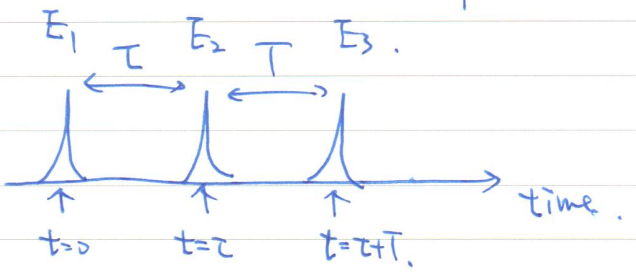
each field term.

$$E_1(t) = E_1 \cdot \delta(t) \cdot e^{\pm i\omega t \mp k_1 r}$$

$$E_2(t) = E_2 \cdot \delta(t-\tau) \cdot e^{\pm i\omega_2 t \mp k_2 r}$$

$$E_3(t) = E_3 \cdot \delta(t-\tau-T) \cdot e^{\pm i\omega_3 t \mp k_3 r}.$$

∴ depicted by the pulse sequence.



In this impulsive limit, the number of terms reduces to $2 \times 2 \times 2 \times 4 = 32$.

and $P^{(3)}(t) \propto E_1 \cdot E_2 \cdot E_3 \cdot S(t, T, \tau)$.

② rotating wave approximation.

Now each field contributes two terms, they are rotating & counter rotating terms, acturally means absorption (field $e^{+i\omega t}$) & emission (field $e^{-i\omega t}$) terms.

~~Note that~~

Rotating wave approximation can be further admitted to reduce these terms.

We will use linear response as an example:

$\mu(t_1) =$

$J(t) = \mathrm{Tr}\,[\mu(t_1)\,\mu(0)\,\rho(-\infty)] \propto |\mu_{01}|^2 \times e^{+i\omega_{eg} t_1}$

$|g\rangle\langle e|\,|e\rangle\langle g|\,|g\rangle\langle g|$

$\Rightarrow P^{(1)}(t) \propto \int_0^\infty dt_1 \cdot E(t-t_1) \cdot S^{(1)}(t_1)$

note $E(t) \propto E_0(t) \cdot [e^{-i\omega t} + e^{i\omega t}]$.

slow varying profile

$$P^{(1)}(t) \propto \int_0^\infty dt_1 \cdot E_0(t-t_1) \cdot \left[e^{-i\omega_0(t-t_1)} + e^{i\omega_0(t-t_1)} \right] \cdot e^{i\omega_{eg} t_1}$$

resonance condition $\omega_0 \approx \omega_{eg}$

$$= e^{+i\omega_0 t} \cdot \int_0^\infty dt_1 \, E_0(t-t_1) + e^{-i\omega_0 t} \cdot \int_0^\infty dt_1 \cdot E_0(t-t_1) \cdot e^{-i2\omega_0 t_1}$$

← signal emitted at $\omega_s \approx \omega_0$

→ ∞

rapidly oscillating term

If we F.T. $P^{(1)}(t)$, a peak will appear at $\omega \approx \omega_0 \approx \omega_{eg}$

$\Rightarrow$ this leads to signal emitted at $\omega_s \approx \omega_0$.

In general, applying RWA allows us to peak a single field combination for each term in the $S^{(n)}(t_1, t_2, \ldots, t_n)$

for 3rd-order experiments, this further

$\omega_s = \pm\omega_1 \pm\omega_2 \pm\omega_3$ reduces the terms contributing to $P^{(3)}(t)$

to $1 \times 1 \times 1 \times 4 = 4$ terms.

i.e. each Rα term, Liouville pathway, gives rise to one term.

(3) phase matching

Now we add wavevectors to the electric fields:

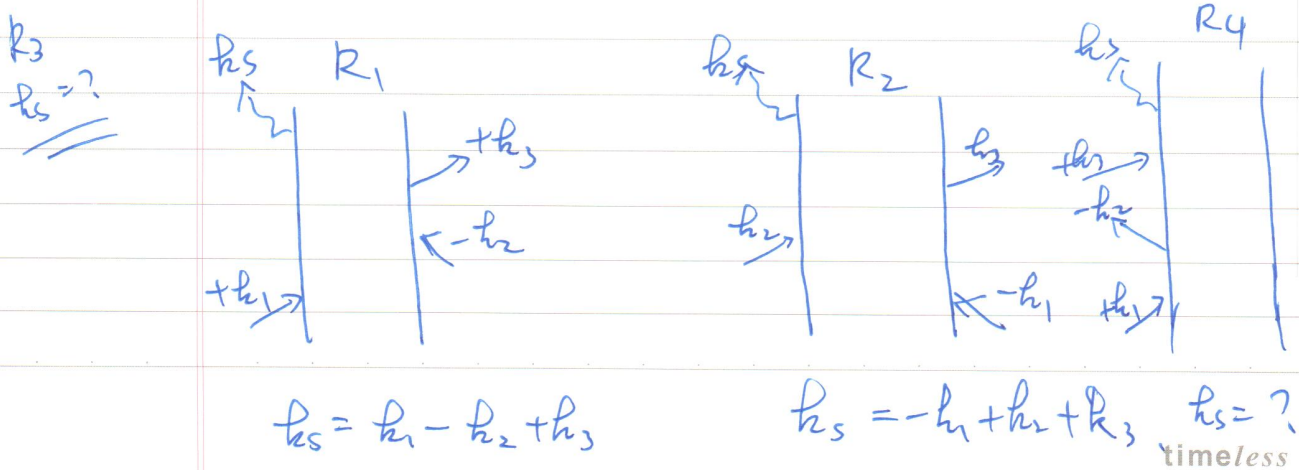
$$E(t) = \sum_{i=1}^{3} E_i(t) \cdot \left[e^{-i\omega_i t + i k_i r} + e^{i\omega_i t - i k_i r} \right] + \dots$$

picking a particular rotating or counter rotating term gives rise to different wavevectors of the field components and

$$k_s = \pm k_1 \pm k_2 \pm k_3$$

$$(\omega_s = \pm \omega_1 \pm \omega_2 \pm \omega_3)$$

$\Rightarrow$ each Rn term will go out at a different direction!!

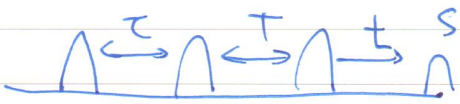


* photon-echo
* What a long journey !!

Now we can finally talk about photon-echo signals. The first photon echo exp. was done using two different pulses, However, here we describe three-pulse photon-echo, which is the most general form and can be reduced to other various photon-echo techniques.

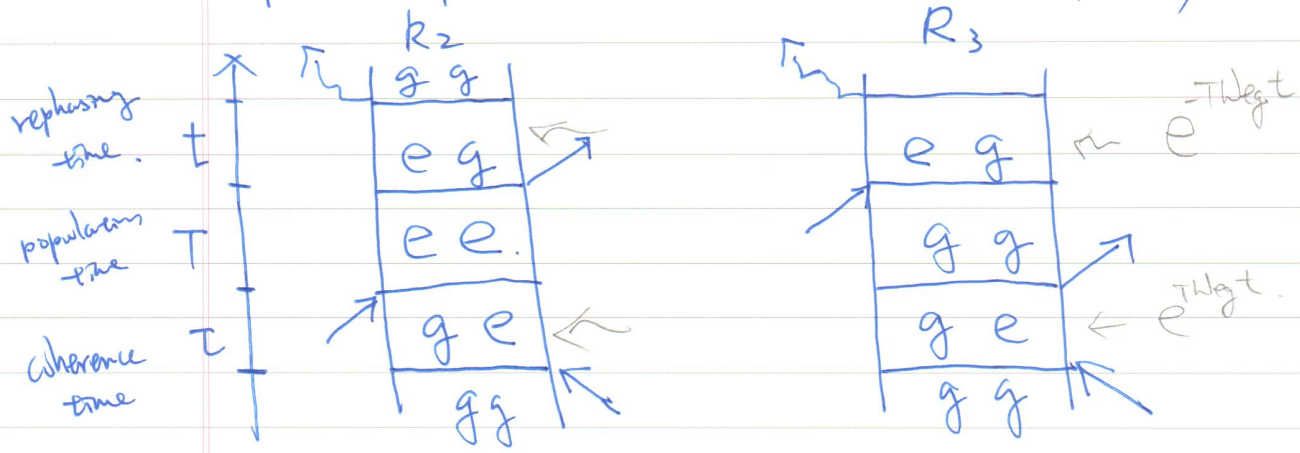
|e⟩

|g⟩



for simplicity, we consider a simple two-level chromophore. i.e. |g⟩ & |e⟩.

photon-echo signals are collected in the $k_s = -k_1 + k_2 + k_3$ direction, which picks up the two Liouville pathways



$$R_2(\tau, T, t) = Tr\{\mu(G(t)(G(t)\mu(G(\tau)\rho(-\infty)\mu))\mu)\}$$

$$R_3(\tau, T, t) = Tr\{\mu(G(t)\mu(G(T)(G(\tau)\rho(-\infty)\mu)\mu))\}$$

Ignore both

Note: $G(t)\cdot|g\rangle\langle e| = e^{-\frac{iHt}{\hbar}}\cdot|g\rangle\langle e|\, e^{\frac{iHt}{\hbar}}$

$$= e^{-i\omega_{ge}t}\cdot|g\rangle\langle e|$$

$$= e^{i\omega_{eg}t}$$

$$G(t)\,|e\rangle\langle e| = |e\rangle\langle e|, \quad G(t)\,|g\rangle\langle g| = |g\rangle\langle g|$$

$$G(t)\cdot|e\rangle\langle g| = e^{-i\omega_{eg}t}\cdot|e\rangle\langle g|$$

$$\omega_{12} = \frac{E_1 - E_2}{\hbar}$$

phase cycle.

for a real ensemble.

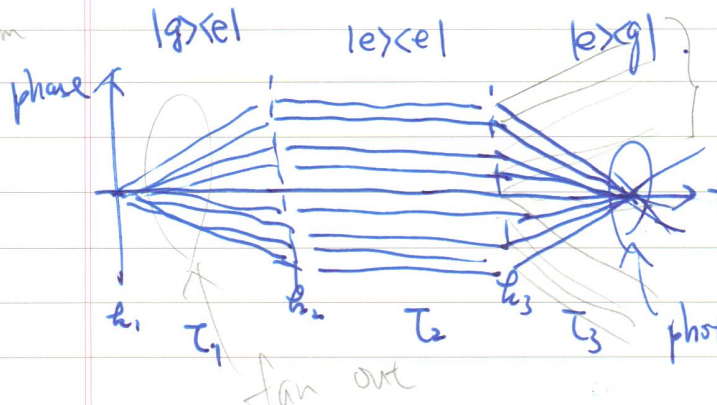
Now we turn back to consider R_2 & k_{sig}

in general, we can use the "lens analogy" to "picture" the phase evolution of an ensemble of systems.

first $\Rightarrow$ $e^{i\omega t} \sim 1 + i\omega t$ at small t.

we consider "phase" accumulation in the duration of the experiment:

lens diagram



In reality; for an ensemble of disordered systems.

static

$\omega_n = \omega_0 + \delta\omega_n$

phase factors cancel out @ $\tau_3 = \tau_1$; τ_2

$\Rightarrow$ rephasing

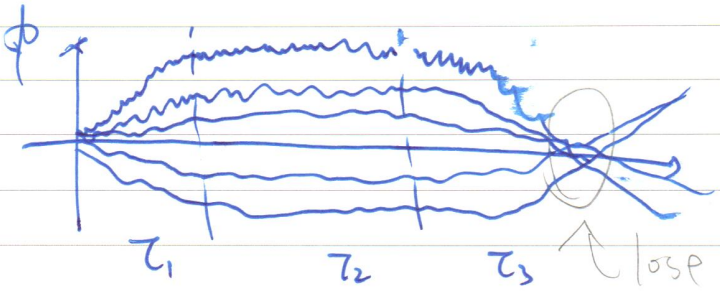
for R_4, does not occur. $\Rightarrow$ non-rephasing timeless

In general, ω_n depends on time
"energy fluctuation"

$$\omega_n(t) = \omega_0 + \Delta\omega_n + \delta\omega_n(t)$$

($\delta\omega_n(t)$: dynamical)

↑ spectral diffusion
dynamical disorder.
causes dephasing



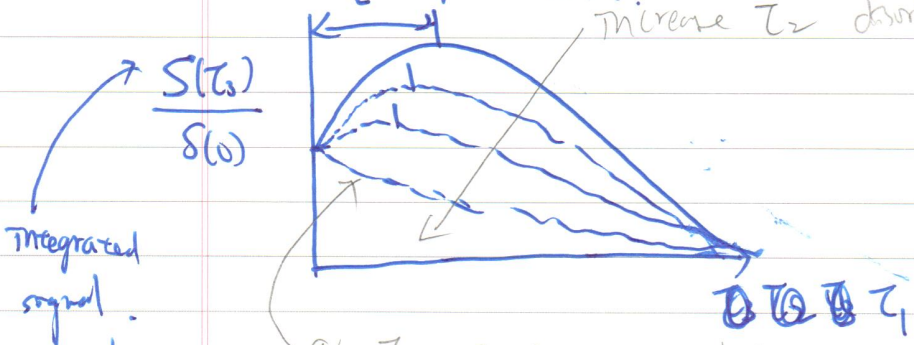
↑ loss of rephasing capability, relaxing

Integrated signal at a fixed τ_1

τ^* peak shift ← measures static

Increase τ_2 disorder

$\langle \delta\omega_n(t)\,\delta\omega_n(0)\rangle$
energy gap fluctuation
correlation function



At $\tau_2 \to \infty$, no memory, $\tau^* = 0$.

Three-pulse photon-echo peak shift.

finite PS @ $\tau_2 \approx \infty$ indicates strong static disorder, $\langle \Delta\omega_n^2 \rangle >> \langle \delta\omega_n(0)^2 \rangle$ proteins

* Two-dimensional electronic spectroscopy.

The photon-echo technique can be extended to produce 2D correlation spectrum of electronic transitions in the optical range.

This part of the lecture will be given in powerpoint slides. and for details the readers are referred to the following papers.

* Ginsberg et al., Acc. Chem. Res., 42, 1352 (2009).

* Cheng & Fleming, J. Chem. Phys. A, 112, 4254 (2008).

and many-many recent research works ——