

A Summer Short Course on Quantum Dynamics & Spectroscopy (2019)

2019/9/3, 9/6

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 ~~or~~ research field ~~and~~ 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) ^{timeless}.

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} ~~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:

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

← pure state.

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

By expanding $U(t)$ in the interaction picture,

one can show that $\rho^{(0)}(t) = U_0(t) \cdot \rho(0) \cdot U_0^\dagger(t)$ without $V(t)$, i.e.

$$\rho(t) = \rho^{(0)}(t) + \sum_{n=1}^{\infty} \left(\frac{-i}{\hbar}\right)^n \int_0^t dt_n \int_0^{t_n} dt_{n-1} \dots \int_0^{t_2} dt_1$$

$$U_0(t) \cdot [V_I(t_n), [V_I(t_{n-1}), \dots [V_I(t_1), \rho(0)]]] \cdot U_0^\dagger(t).$$

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

~~timeless~~

timeless

(5)

Let's assume $\rho^{(0)}$ is the equilibrium

density matrix $\rightarrow \rho^{(0)}(t) = U_0(t) \cdot \rho^{(0)} \cdot U_0^\dagger(t) = \rho^{(0)}$.

Since the system does not evolve before

$t = -\infty \dots 0$, we turn on the first pulse @ $t=0$.
we can push time $0 \rightarrow \infty$,
and use $\rho^{(0)} = \rho^{(-\infty)}$ to emphasize this.
Furthermore, we plug in

$$V(t) = E(t) \cdot \mu, \quad M_2(t) = U_0^\dagger(t) \cdot \mu \cdot U_0(t).$$

$$\therefore \rho(t) = \rho^{(0)} + \sum_{n=1}^{\infty} \left(\frac{-i}{\hbar}\right)^n \int_{-\infty}^t dt_n \dots \int_{-\infty}^{t_2} dt_1 \cdot E(t_n) E(t_{n-1}) \dots E(t_1) \\ \times U_0(t) \cdot [M_2(t_n), \dots [M_2(t_1), \rho^{(-\infty)}] \dots] \cdot U_0^\dagger(t).$$

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

If we define the n -th order polarization.

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

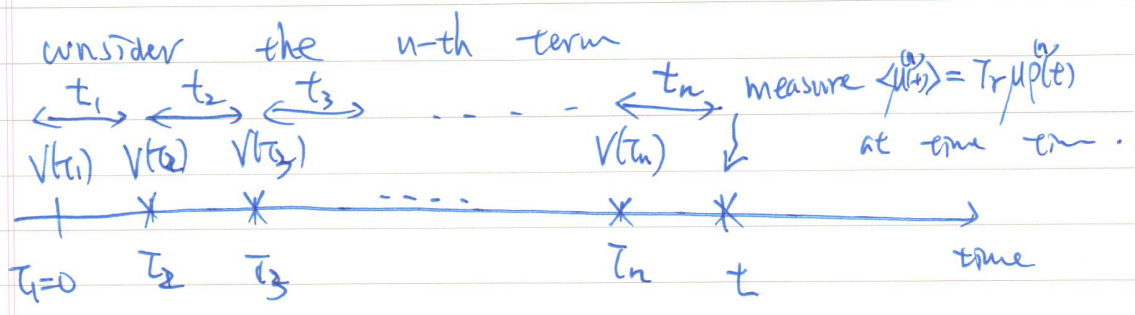
We obtain the total polarization as:

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

timeless

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



note the time ordering :

\Rightarrow 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 :

$$\begin{aligned}
 \tau_1 &= 0 \\
 \tau_1 &= T_2 - T_1 \\
 \tau_2 &= T_3 - T_2 \\
 &\vdots \\
 \tau_n &= t - T_n
 \end{aligned}$$

and use $\mu(t) = U^\dagger(t) \mu U(t)$

By change of variables, we reach (exercise):

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

system property
n-th order

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

not in commutator

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

$$S^{(n)}(t_n, \dots, t_1) = \left(\frac{-i}{\hbar}\right)^n \text{Tr} \left\{ \mu(t_n + \dots + t_1) [\dots] \right\}$$

Let's check,

$$\begin{aligned} S^{(1)}(t) &= \left(\frac{-i}{\hbar}\right)^1 \text{Tr} \left\{ \mu(t) \cdot [\mu(0), \rho(-\infty)] \right\} \\ &= \left(\frac{-i}{\hbar}\right)^1 \text{Tr} \left\{ \mu(t) [\mu(0) \rho(-\infty) - \rho(-\infty) \mu(0)] \right\} \\ &= \left(\frac{-i}{\hbar}\right) \cdot \text{Tr} \left\{ \mu(t) \mu(0) \rho - \underbrace{\mu(t) \rho}_{\text{eq}} \underbrace{\rho \mu(0)}_{\text{eq}} \right\} \\ &= \left(\frac{-i}{\hbar}\right) \left[\langle \mu(t) \mu(0) \rangle - \langle \mu(0) \mu(t) \rangle \right] \\ &= \frac{2}{\hbar} \cdot \text{Im} \cdot \langle \mu(t) \mu(0) \rangle \quad \neq \end{aligned}$$

timeless

* Liouville pathways

For resonance interactions, these response functions have simple interpretations,

In this case the dipole operators are

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

↓ absorption
↑ emission

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

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

$$= \text{Tr} \{ \mu \cdot U_0(t_2) \cdot \mu \cdot \rho_{eq} \cdot U_0^\dagger(t_1) \}$$

$$\equiv \text{Tr} \{ \mu \cdot G(t) \cdot \mu \cdot |g\rangle\langle g| \}$$

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

elec. ground
state only,
ignore bath
now

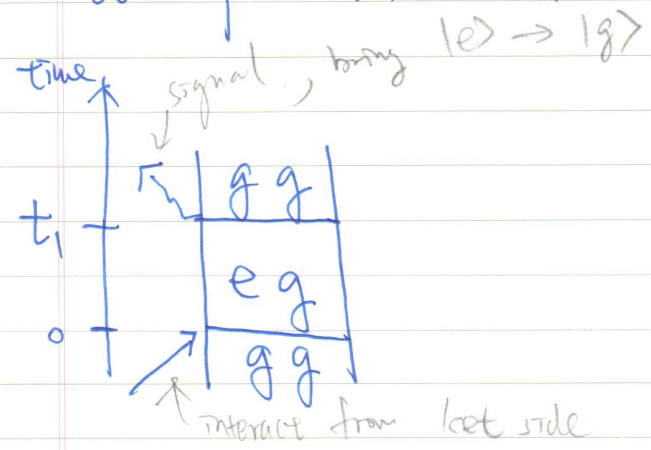
initially in g.s.
interact with pulse from "ket"
side, absorption, generate
many superpositions (coherences)
e.g. $|g\rangle\langle g| \rightarrow |e\rangle\langle g|$
propagate the coherence
for time t

measurement !!

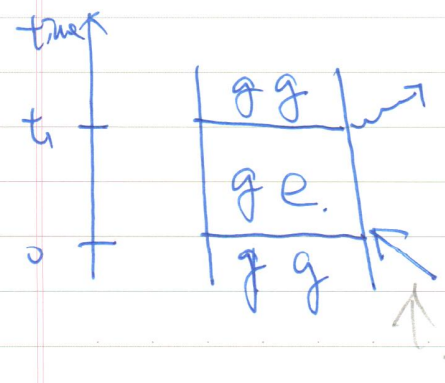
timeless

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)

↑ from the bra side

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

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

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

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

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

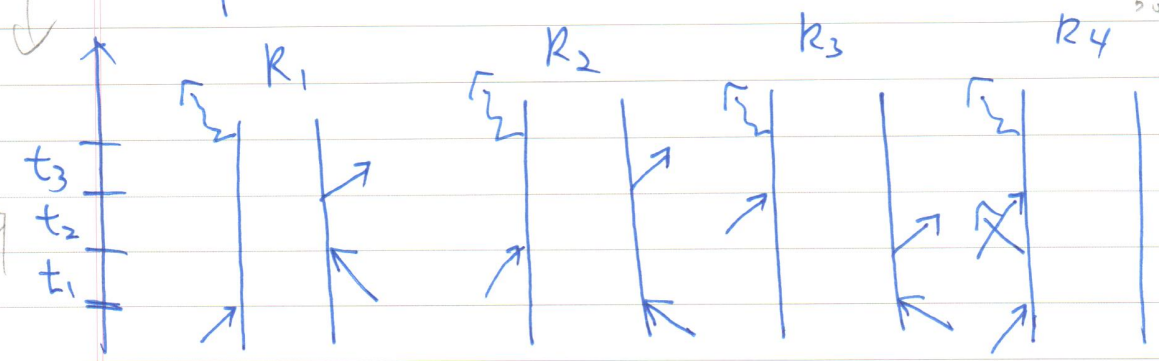
$$R_2 = \text{Tr} \left\{ \mu(t_3+t_2+t_1) \cdot \mu(t_1) \cdot \rho(-\infty) \mu(0) \mu(t_2+t_1) \right\}$$

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

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

We don't give details of how to compare these here, (11)

They correspond to: consult Mukamel's book



The emergence of these diagrams are due to
 * response function
 * RWA * impulse limit
~~* phase match~~

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

$P^{(3)}$:

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

Note that in a 3-pulse experiment $E(t) = E_1(t) + E_2(t) + E_3(t) = 2E_1(t) \cdot \omega(\omega t) + 2E_2(t) \cdot \omega(\omega t) +$

$$E(t) = E_1(t) + E_2(t) + E_3(t) = 2E_1(t) \cdot \omega(\omega t) + 2E_2(t) \cdot \omega(\omega t) +$$

assume real

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

⇒ 6 terms

Therefore, don't underestimate the evaluation

timeless

(12)

of $p^{(n)}$, 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).

* Raman 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

timeless

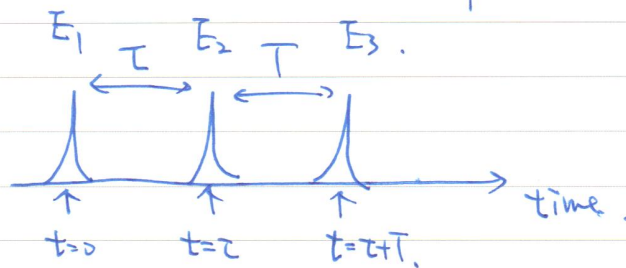
each field term,

$$E_1(t) = E_1 \cdot \delta(t) \cdot e^{\pm i\omega_1 t + i\mathbf{k}_1 \cdot \mathbf{r}}$$

$$E_2(t) = E_2 \cdot \delta(t - \tau) \cdot e^{\pm i\omega_2 t + i\mathbf{k}_2 \cdot \mathbf{r}}$$

$$E_3(t) = E_3 \cdot \delta(t - \tau - T) \cdot e^{\pm i\omega_3 t + i\mathbf{k}_3 \cdot \mathbf{r}}$$

↳ depicted by the pulse sequence



In this ~~case~~ ^{impulsive limit,} the number of terms

reduces to $2 \times 2 \times 2 \times 4 = 32$.

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

② rotating wave approximation.

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

~~Note that for the~~

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

We will use linear response as an

— $a.e.$

example:

— g

$$J(t) = \text{Tr} \left[\overset{|g\rangle\langle g| \otimes \rho_S}{\mu(t)} \rho(-\infty) \right] \propto |\mu_{01}|^2 \int_0^t e^{+i\omega g t_1} dt_1$$

$$\dot{b}^{(1)}(t) \propto \int_0^t dt_1 \cdot E(t-t_1) \cdot S^{(1)}(t_1)$$

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

↙ slow varying profile

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

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

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

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 $S^{(n)}(t_1, t_2, \dots, t_n)$

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 Rn term, Liouville pathway, gives rise to one term.

③ phase matching

Now we add wavevectors to the electric fields:

$$E(t) = \sum_{i=1}^3 E_i(t) \cdot [e^{-i\omega_i t + i\mathbf{k}_i \cdot \mathbf{r}} + e^{i\omega_i t - i\mathbf{k}_i \cdot \mathbf{r}}]$$

picking a particular rotating or

counter rotating term gives rise to different

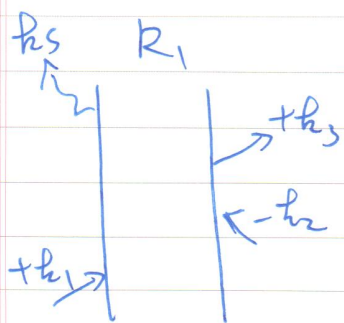
wavevectors of the field component and

$$\mathbf{k}_s = \pm \mathbf{k}_1 \pm \mathbf{k}_2 \pm \mathbf{k}_3$$

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

⇒ each R_n term will go out at a different direction !!

k_3
 $k_s = ?$



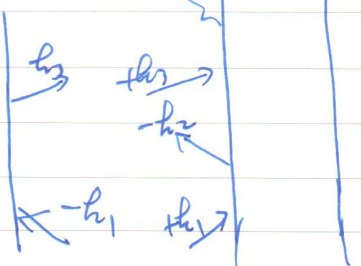
$$k_s = k_1 - k_2 + k_3$$



$$k_s = -k_1 + k_2 + k_3 \quad k_s = ?$$

timeless

R_4



* photon-echo

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* What a long journey !!

Now we can finally talk about

photon-echo signals. The first photon echo

→ $|e\rangle$ exp. was done using two different pulses,

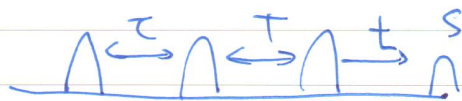
~~which~~ However, here we describe three-pulse

→ $|g\rangle$

photon-echo, which is the most general form

and can be reduced to other various

photon-echo techniques.



for simplicity, we consider a

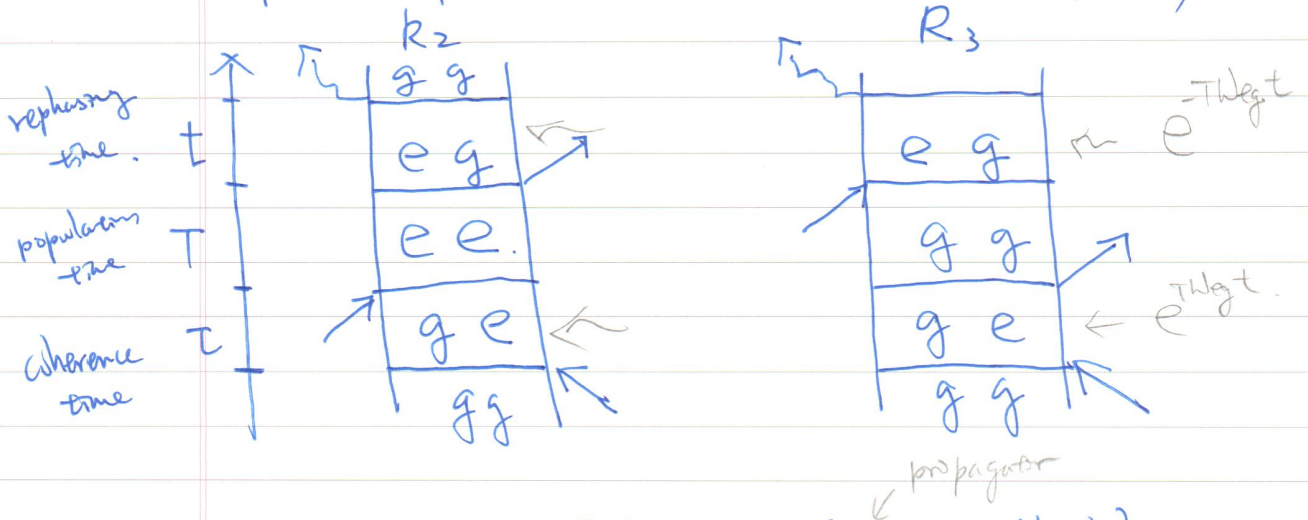
simple two-level chromophore. i.e.,

$|g\rangle$ & $|e\rangle$.

(A)

photon-echo signals are collected in the $k_s = -k_1 + k_2 + k_3$ direction, which

picks up the two Liouville pathways



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

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

Ignore both

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

$$\omega_{1,2} = \frac{E_1 - E_2}{\hbar}$$

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

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

timeless

phases early.

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Now we turn back to consider R_2 & R_{2y} for a real ensemble.

in general, we can use as the "lens ~~diagram~~ ^{analogy}" to

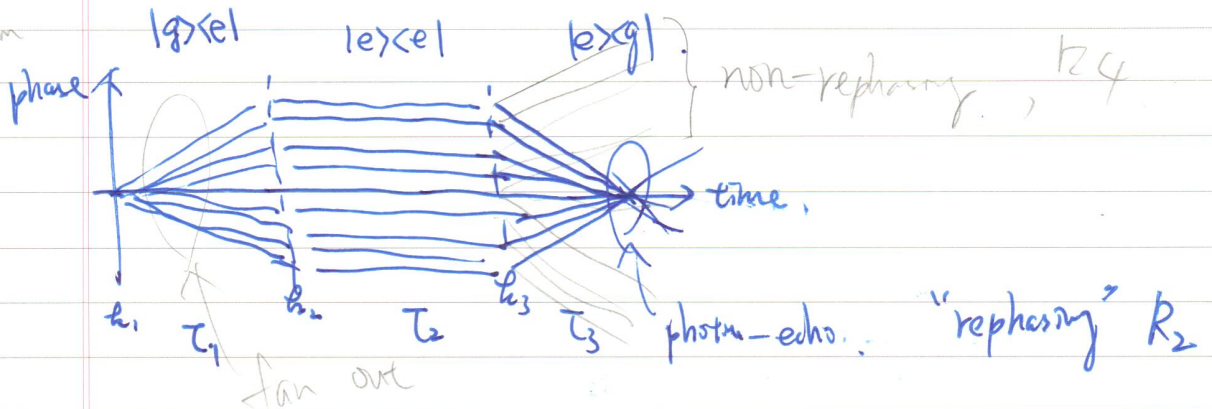
"picture" the phase evolution of ~~the system~~ ^{an ensemble of systems.}

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.

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

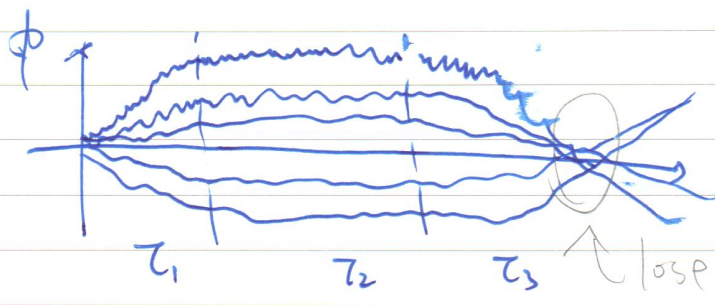
phase factors cancel out @ $T_3 = T_1 + T_2$
 \therefore rephasing

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

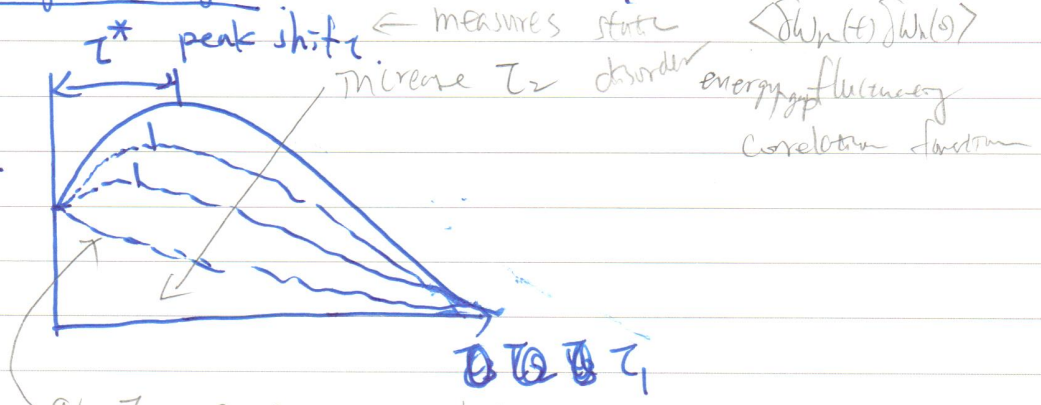


In general, ω_n depends on time
 "energy fluctuation"
 $\omega_n(t) = \omega_0 + \delta\omega_n + \delta\omega_n(t)$

↑ spectral diffusion
 dynamical disorder.
 comes dephasing



Integrated signal at a fixed τ_1 ← Capabstap, reflecting



Three-pulse photon-echo peak shift

Finite PS @ τ_2 indicates strong proton
 state disorder, $\langle \omega_n^2 \rangle \gg \langle \delta\omega_n(t) \rangle^2$

* 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.

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

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

and many-many recent research works —