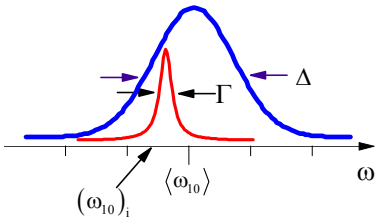
## Photon Echo

- Used to distinguish static and dynamic line-broadening, and time-scales for energy gap fluctuations. The rephasing character of $R_2$ and $R_3$ allows you to separate homogeneous and inhomogeneous broadening.

Remember linear spectroscopy can't distinguish the two:

$$R^{(1)}(\tau) = |\mu_{ab}|^2 \, e^{-i\omega_{ab}\tau - g(\tau)} + c.c.$$




For an inhomogeneous distribution, $R^{(1)} = \int d\omega_{ab} \, Z(\omega_{ab}) R^{(1)}(\omega_{ab})$

$$Z(\omega_{ba}) = exp\left( -\frac{\left(\omega_{ba} - \langle \omega_{ba} \rangle\right)^2}{2\Delta^2} \right)$$

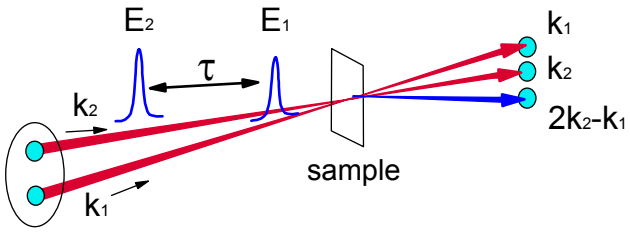
(or equivalently $g(t) = \Gamma_{ba} t + \frac{1}{2}\Delta^2 t^2$). If $\Delta > \Gamma$, we get a broad Gaussian line in our absorption spectrum.

Now look at the experiment in which two pulses are crossed to generate a signal:

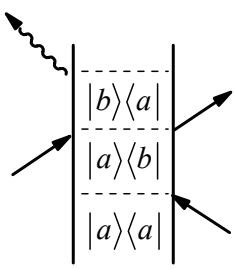
$$k_{sig} = 2k_2 - k_1$$

Special case of $(k_3 + k_2 - k_1)$

Two-pulse photon echo




The second and third interactions come from same pulse, so $\tau_2 = 0$ and $R_2 = R_3$.




$$R^{(3)} = \int d\omega_{ab} \, Z(\omega_{ab}) R^{(3)}(\omega_{ab})$$

Using our $R_2$ expression from p. 155:

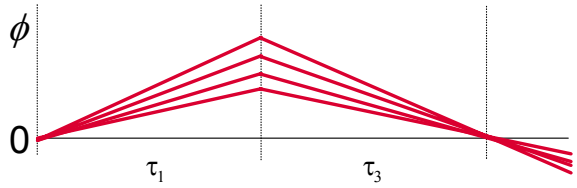
$$R^{(3)}(\omega_{ab}) = |\mu_{ab}|^4 \, p_a \, e^{-i\omega_{ab}(\tau_1 - \tau_3)} e^{-\Gamma_{ab}(\tau_1 + \tau_3)}$$

$$R^{(3)} = |\mu_{ab}|^4 \, p_a \, e^{-i\langle\omega_{ab}\rangle(\tau_1 - \tau_3)} \, e^{-\Gamma_{ab}(\tau_1 + \tau_3)} \, e^{-(\tau_1 - \tau_3)^2 \Delta^2 / 2}$$

Damps with homogeneous dephasing

Peaked at $\tau_3 = \tau_1$

For $\Delta >> \Gamma_{ab}$, $R^{(3)}$ is sharply peaked at $\tau_1 = \tau_3$, $e^{-(\tau_1-\tau_3)^2\Delta^2/2} \approx \delta(\tau_1 - \tau_3)$. The broad distribution of frequencies that rapidly dephased during $\tau_1$ is rephrased (or refocused) during $\tau_3$ leading to a large constructive enhancement of the polarization at $\tau_1=\tau_3$: an echo.




The observed signal for a pulse separation $\tau$ (setting $\tau_1=\tau$) is the integrated signal radiated from the sample during $\tau_3$:

$$I_{sig}(\tau) = \left|E_{sig}\right|^2 \propto \int_0^\infty d\tau_3 \left|P^{(3)}(\tau,\tau_3)\right|^2$$

In the inhomogeneous limit, we find

$$I_{sig}(\tau) \propto e^{-4\Gamma_{ab}\tau}$$

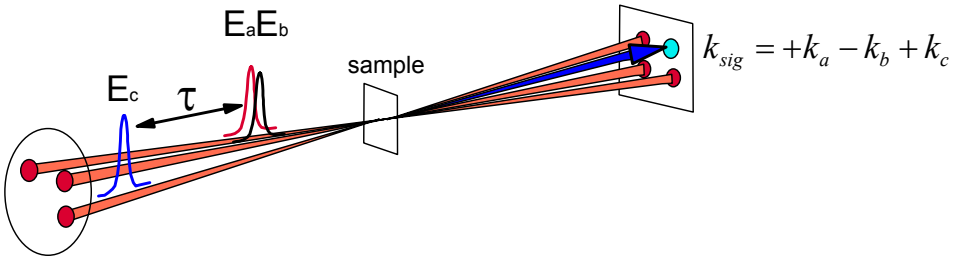
Inhomogeneity removed

## Transient Grating

- Practical for looking at excitations with well defined spatial period/wavevector.

The first two pulses are set time-coincident, so you can't distinguish which field interacts first. Therefore, the signal will have contributions both from $k_{sig} = k_1 - k_2 + k_3$ and $k_{sig} = -k_1 + k_2 + k_3$.

That is the signal depends on $R_1+R_2+R_3+R_4$. For $k_{sig} = k_1 - k_2 + k_3$ consider the terms contributing to the polarization after the first two interactions:



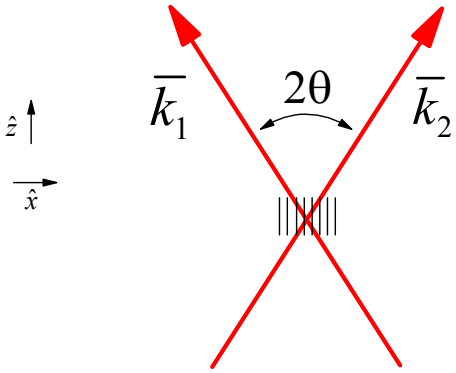

$$P_{TG} \sim R^{(3)} E_1 E_2 E_3$$

For $\tau_1 \to 0$ (pulses coincident), the first two fields create an excitation

$$P_{TG} \sim \bar{E}_1 \bar{E}_2 = E_1 E_2 \exp\left[-i(\omega_1 - \omega_2)t + i(\bar{k}_1 - \bar{k}_2)\cdot\bar{r}\right] + c.c.$$

If the beams are crossed at an angle $2\theta$:

$$\bar{k}_1 = |k_1|(\hat{z}\cos\theta + \hat{x}\sin\theta)$$
$$\bar{k}_2 = |k_2|(\hat{z}\cos\theta - \hat{x}\sin\theta)$$




Taking $\omega_1 = \omega_2$ $\left(\text{i.e., } |k_1| = |k_2| = |k| = \dfrac{2\pi n}{\lambda}\right)$, then:

$$P_{TG} \sim E_1 E_2 \exp\left[i\Delta\bar{k}\cdot\bar{x}\right]$$

$$\Delta k = \frac{4\pi n}{\lambda}\sin\theta = \frac{2\pi}{\eta}$$

$$\eta = \frac{\lambda}{2n\sin\theta} \qquad \textit{Fringe spacing}$$

This spatial modulation looks like a grating – a light/dark/light/dark pattern – with a periodicity $\eta$. Excitation with this pulse pair leads to a periodic spatial variation of the complex index of refraction of the medium. A time-delayed probe beam can scatter off this grating—constructive interference of scattered waves at Bragg angle. For $\omega_1 = \omega_2 = \omega_3 = \omega_{sig}$ this the diffraction condition is incidence of $\mathbf{k_3}$ at an angle $\theta$, leading to scattering of a signal out of the sample at an angle $-\theta$. We measure the intensity of the scattered light.

Relaxation can be expressed in terms of the dissipation of the grating pattern in the sample.

- Population relaxation leads to a decrease in its amplitude, observed as a decrease in diffraction efficiency.

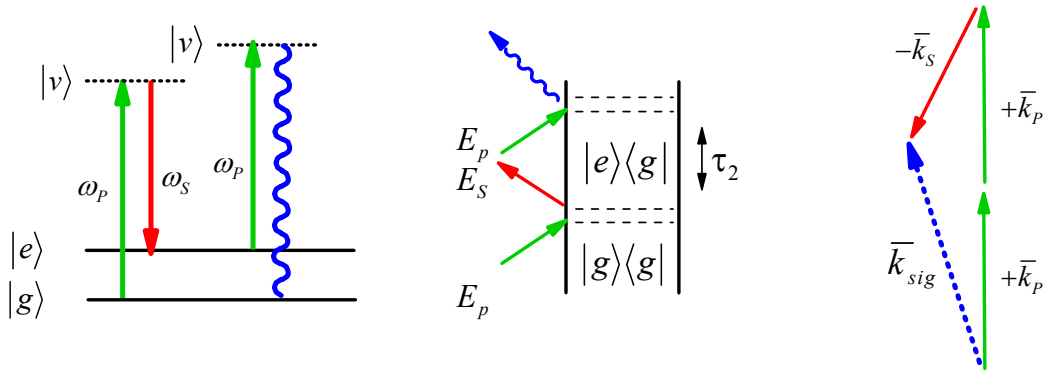
$$I_{sig} \propto \left|R^{(3)}\right|^2 \propto e^{-2\Gamma_{bb}\tau}$$

- Spatial diffusion processes along $x$ erase the fringe pattern.
- Rapid heating by the excitation pulses can launch counter propagating acoustic waves along $x$ , which can modulate the diffracted beam at a rate given by the acoustic velocity.

## CARS (Coherent Anti-Stokes Raman Scattering)

Used to drive ground state vibrations with optical pulses or cw fields.

- Two fields, with a frequency difference equal to a vibrational transition energy, are used to excite the vibration.
- The first field is the "pump" and the second is the "Stokes" field.
- A second interaction with the pump frequency lead to a signal that radiates at the anti-Stokes frequency: $\omega_{sig} = 2\omega_P - \omega_S$ and the signal is observed background-free next to the transmitted pump field: $\bar{k}_{sig} = 2\bar{k}_P - \bar{k}_S$.




The experiment is described by $R_1$ and $R_4$, and the polarization is

$$R^{(3)} = \bar{\mu}_{ev}\bar{\mu}_{vg}\, e^{-i\omega_{eg}\tau-\Gamma_{eg}\tau}\,\bar{\mu}_{gv}\bar{\mu}_{ve}$$
$$= \bar{\alpha}_{eg} e^{-i\omega_{eg}\tau-\Gamma_{eg}\tau}\bar{\alpha}_{ge}$$

The CARS experiment is similar to a linear experiment in which the lineshape is determined by the Fourier transform of $C(\tau) = \langle \bar{\alpha}(\tau)\bar{\alpha}(0)\rangle$.

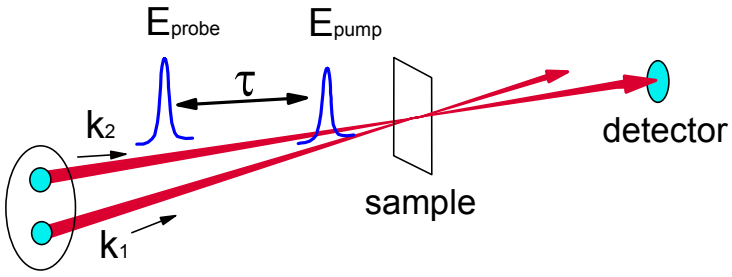
The same processes contribute to Optical Kerr Effect Experiments and Impulsive Stimulated Raman Scattering.

## PUMP-PROBE (or transient absorption)

- Follow population relaxation or wavepacket dynamics/quantum beats.

This is perhaps the most widely used third-order nonlinear experiment. Two pulses are crossed in a sample. An intense pump-pulse excited the system from equilibrium, and you watch the induced changes as a variation of intensity on a transmitted probe pulse.

Here the third order signal is emitted on top of the transmitted field. A decrease in absorption arises from a signal that is out of phase with the transmitted probe.




Similar to the transient grating, the first and second interaction are with the pump pulse, and the final (third) interaction is with the probe. The signals that can contribute to scattering along the probe are $k_{sig} = k_1 \mp k_2 + k_3$, so all correlation functions $R_1$ to $R_4$ contribute. The observed signal is

$$I_{sig} \propto \left|E_3 + E_{sig}\right|^2 = \left|E_3\right|^2 + 2E_3E_{sig} + \ldots$$

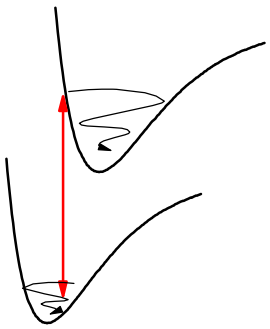
$$= I_3 + \delta I(T)$$

For a two-level system, we are sensitive to the relaxation of excited states

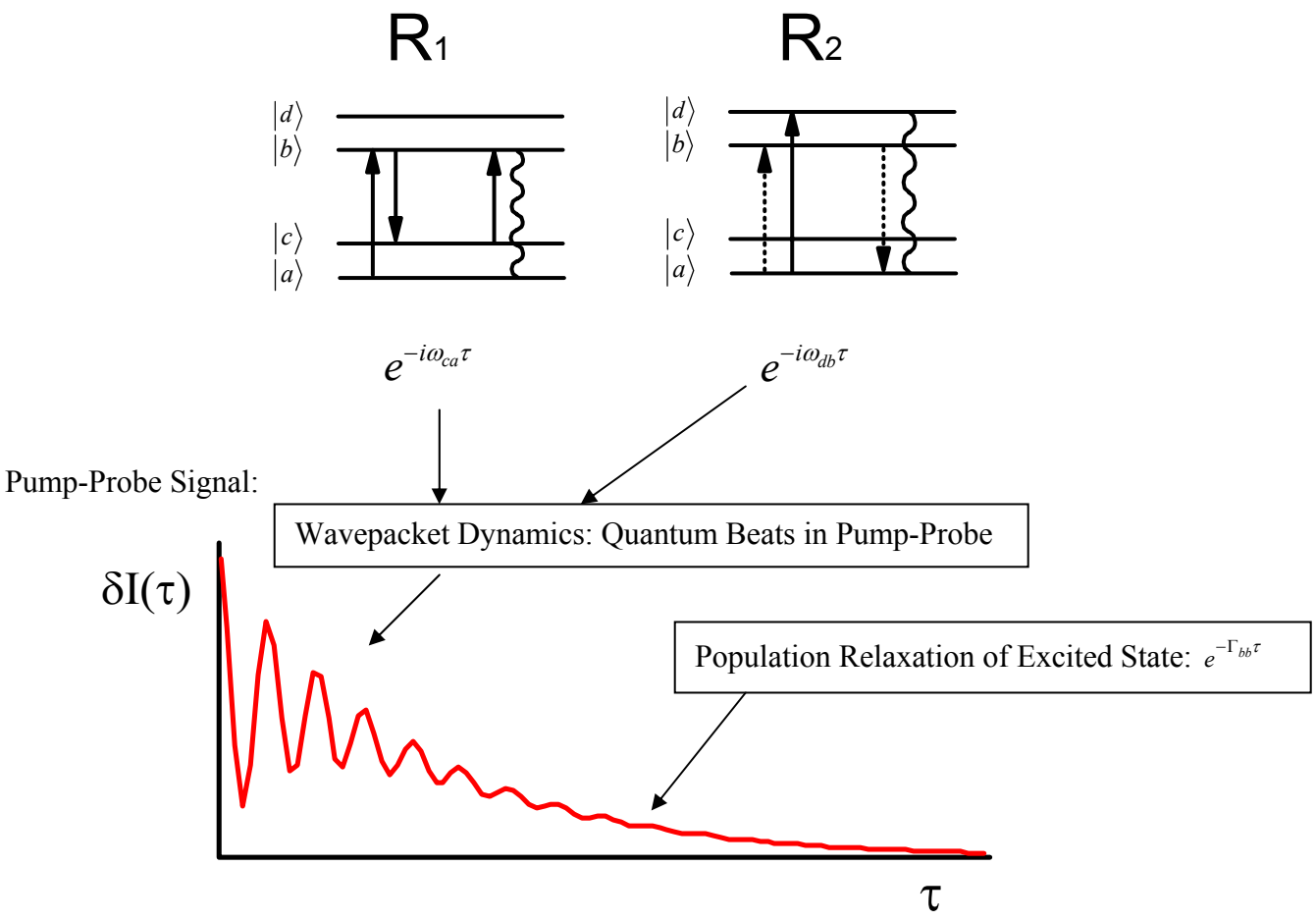
$$E_{sig} \propto R^{(3)} \propto \left|\mu_{ab}\right|^4 e^{-\Gamma_{bb}\tau}$$

Here we have set $\tau = \tau_2$.

For excited electronic states with coupled vibrations, we can launch wave packets and follow their evolution. The pump pulse creates excited state and ground state wavepackets:



- $R_1$ and $R_3$: Ground state wave packet.
- $R_2$ and $R_4$: Excited state wave packet.



## ENERGY GAP FLUCTUATIONS IN NONLINEAR SPECTROSCOPY

How do transition energy gap fluctuations enter into the nonlinear response?

For a system interacting with a fluctuating bath, we found that absorption lineshapes are given by the Fourier transform of the dipole correlation function

$$C_{\mu\mu}(t) = \left|\mu_{eg}\right|^2 e^{-i\langle\omega_{eg}\rangle t}\left\langle exp_+\left(\frac{-i}{\hbar}\int_0^t d\tau\, H_{eg}(\tau)\right)\right\rangle$$

which is written in terms of the energy gap Hamiltonian that linearly couples the system and bath nuclear coordinates. Using the cumulant expansion, we can express it as an oscillating term at the transition frequency, and a lineshape function $g(t)$ which represents the bath interaction

$$C_{\mu\mu}(t) = \left|\mu_{eg}\right|^2 e^{-i\omega_{eg}t}\, e^{-g(t)}$$

$$g(t) = \frac{1}{\hbar^2}\int_0^t dt'' \int_0^{t''} dt' \underbrace{\left\langle \delta H_{eg}(t')\delta H_{eg}(0)\right\rangle}_{C(t')}$$

$$C_{eg}(\tau) = \left\langle \delta\omega_{eg}(\tau)\delta\omega_{eg}(0)\right\rangle$$

For different forms of the energy gap fluctuations, we got different forms of our $g(t)$:

1) Bath fluctuations infinitely fast

$C_{eg}(\tau) = \Gamma\,\delta(\tau)$ *$\Gamma$ is amplitude – infinitely fast decay*

$g(t) = \Gamma t$ *Phenomenological damping result*

2) Bath fluctuations infinitely slow

$C_{eg}(\tau) = \Delta^2$ *$\Delta$ is amplitude – no decay*

$g(t) = \frac{1}{2}\Delta^2 t^2$ *Static bath - $\Delta$ is distribution of frequencies*

3) Bath correlation function decays exponentially

$C_{eg}(\tau) = \Delta^2\, exp(-t/\tau_c)$

$g(t) = \Delta^2\tau_c^2\left[\exp(-t/\tau_c) + t/\tau_c - 1\right]$ *Stochastic model*

We can construct any $g(t)$ we want:

$$g(t) = \sum_i g_i(t)$$

Alternatively, using the Brownian oscillator model, we can describe the signal in terms of the spectral density of fluctuations

$$2\pi\omega^2\rho(\omega) = C''_{eg}(\omega) = \frac{1-e^{-\beta\hbar\omega}}{2}\tilde{C}_{eg}(\omega)$$

$$g(t) = \int_{-\infty}^{+\infty} d\omega \frac{1}{2\pi}\frac{\tilde{C}_{eg}(\omega)}{\omega^2}\left[exp(-i\omega t) + i\omega t - 1\right]$$

$$= \int_{-\infty}^{+\infty} d\omega\ \rho(\omega)\left(coth\left(\frac{\beta\hbar\omega}{2}\right)(1-cos\,\omega t) + i(sin\,\omega t - \omega t)\right)$$

We can construct an arbitrary bath from Brownian oscillators:

$$C''_{eg}(\omega) = \sum_i \xi_i C''_i(\omega) \qquad \xi_i : \text{coupling coefficient}$$

$$C''_i(\omega) = \frac{\hbar}{m_i}\frac{\omega\Gamma_i}{\left(\omega_i^2 - \omega^2\right)^2 + 4\omega^2\Gamma_i^2}$$

## Nonlinear Response with the Energy Gap Hamiltonian

In a manner that parallels our description of the linear response from a system coupled to a bath, the nonlinear response can also be partitioned into a system, bath and energy gap Hamiltonian, leading to similar averages over the fluctuations of the energy gap. The nonlinear response can be written as a sum of correlation functions such as

$$R_2(\tau_1,\tau_2,\tau_3) = \left(\frac{i}{\hbar}\right)^3 p_g \left|\mu_{eg}\right|^4 e^{-i\omega_{eg}(\tau_1-\tau_3)}\left\langle exp_+\left(\frac{i}{\hbar}\int_0^{\tau_1} d\tau\, H_{eg}(\tau) - \frac{i}{\hbar}\int_{\tau_1+\tau_2}^{\tau_1+\tau_2+\tau_3} d\tau\, H_{eg}(\tau)\right)\right\rangle$$

This is the rephasing function $R_2$ written for a two-level system.

Using the cumulant expansion, the third order response function for a two-level system can be rewritten in terms of our four correlation functions and the lineshape function for the system:

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

$$R_1=e^{-i\omega_{eg}\tau_1-i\omega_{eg}\tau_3}\,exp\left[-g^*(\tau_3)-g(\tau_1)-g^*(\tau_2)+g^*(\tau_2+\tau_3)+g(\tau_1+\tau_2)-g(\tau_1+\tau_2+\tau_3)\right]$$

$$R_2=e^{i\omega_{eg}\tau_1-i\omega_{eg}\tau_3}\,exp\left[-g^*(\tau_3)-g^*(\tau_1)+g(\tau_2)-g(\tau_2+\tau_3)-g^*(\tau_1+\tau_2)+g^*(\tau_1+\tau_2+\tau_3)\right]$$

$$R_3=e^{i\omega_{eg}\tau_1-i\omega_{eg}\tau_3}\,exp\left[-g(\tau_3)-g^*(\tau_1)+g^*(\tau_2)-g^*(\tau_2+\tau_3)-g^*(\tau_1+\tau_2)+g^*(\tau_1+\tau_2+\tau_3)\right]$$

$$R_4=e^{-i\omega_{eg}\tau_1-i\omega_{eg}\tau_3}\,exp\left[-g(\tau_3)-g(\tau_1)-g(\tau_2)+g(\tau_2+\tau_3)+g(\tau_1+\tau_2)-g(\tau_1+\tau_2+\tau_3)\right]$$

In this way, you can incorporate fluctuations (interactions with a bath/spectral diffusion) into nonlinear spectroscopies.

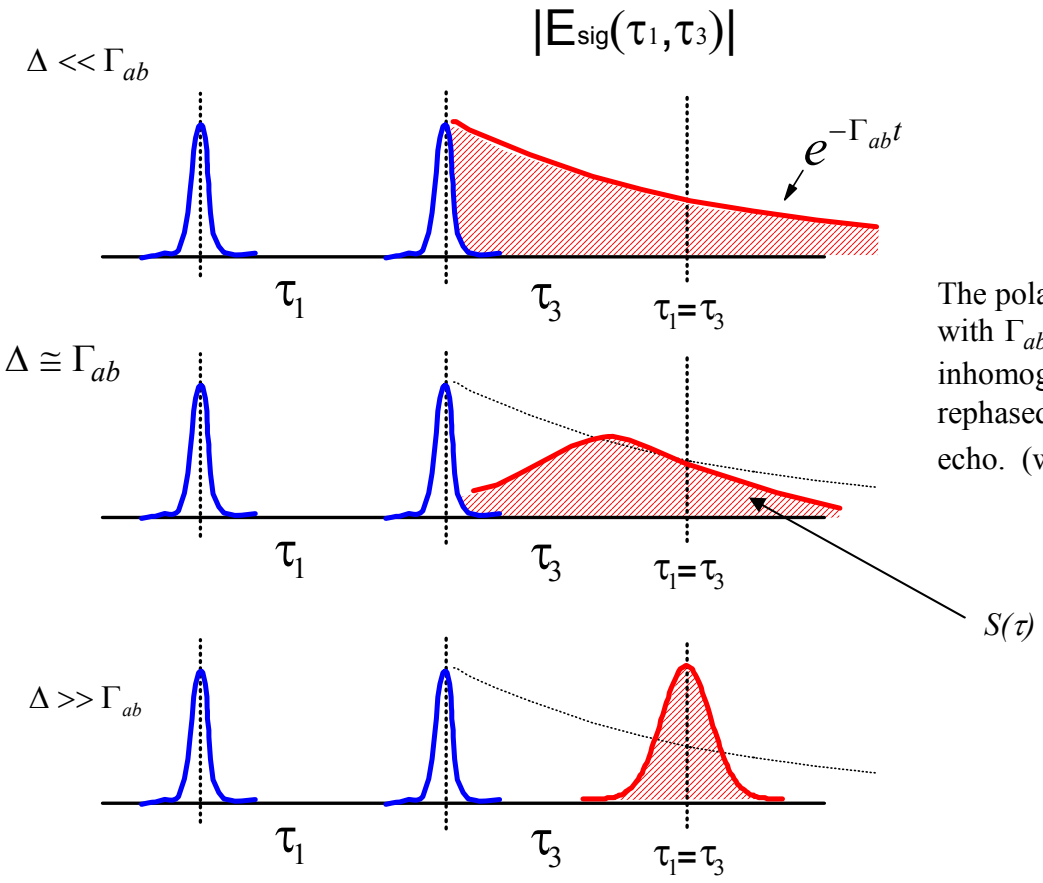
**Example:** For the two-pulse photon echo experiment example on p. 159:

- Set $g(t)=\Gamma_{eg}t+\frac{1}{2}\Delta^2t^2$. For this simple model *g(t)* is real.
- Set $\tau_2=0$, giving $R_2=R_3=e^{i\omega_{eg}\tau_1-i\omega_{eg}\tau_3}\,exp\left[-2g(\tau_3)-2g(\tau_1)+g(\tau_1+\tau_3)\right]$
- Substituting the *g(t)*expression we get the same result as before.

$$R^{(3)}\propto e^{-i\omega_{eg}(\tau_1-\tau_3)}\,e^{-\Gamma_{eg}(\tau_1+\tau_3)}\,e^{-(\tau_1-\tau_3)^2\Delta^2/2}$$

## How can you measure spectral diffusion?

Back to the photon echo experiment… First, let's examine the polarization for a system with homogeneous and inhomogeneous broadening for varying $\Delta / \Gamma_{ab}$:




The polarization damps with $\Gamma_{ab}$, but any inhomogeneity is rephased at $\tau_1 = \tau_3$: An echo. (width ~ $1/\Delta$)

Normally you detect the integrated intensity of this echo field.

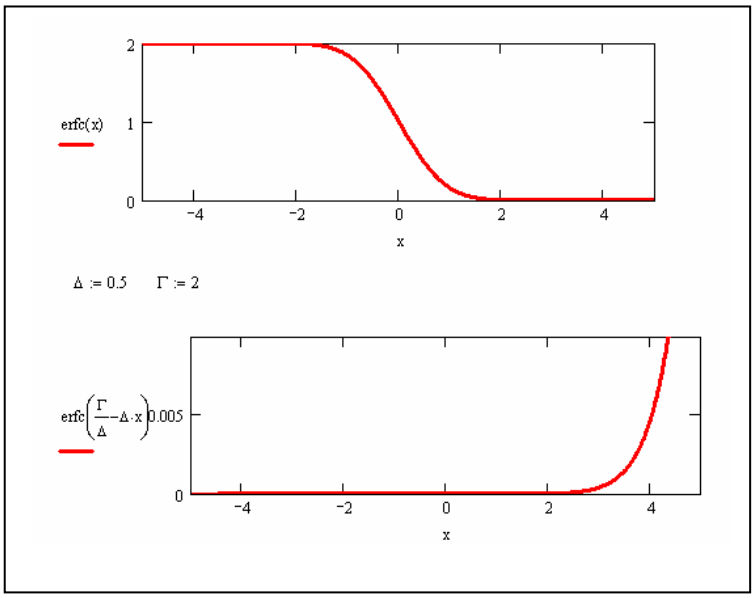
$$S(\tau) \propto \left| \int_0^\infty d\tau_3 \; P^{(3)}(\tau, \tau_3) \right|^2$$

$$= exp\left( -4\Gamma_{ab}\tau - \frac{\Gamma_{ab}^{\;2}}{\Delta^2} \right) \cdot erfc\left( -\Delta\tau + \frac{\Gamma_{ab}}{\Delta} \right)$$

For $\Delta >> \Gamma_{ab}$ $\quad S(\tau) \propto e^{-4\Gamma_{ab}\tau}$

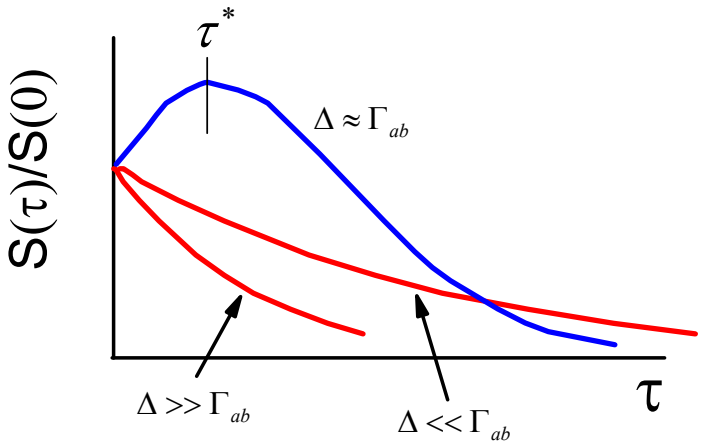
For $\Delta << \Gamma_{ab}$ $\quad S(\tau) \propto e^{-2\Gamma_{ab}\tau}$

(inhomogeneity removed!)



In between ($\Delta \cong \Gamma_{ab}$), the integrated signal *S(τ)* has a shape peaked after $\tau = 0$.

Peak of signal in τ:
τ* - the peak shift



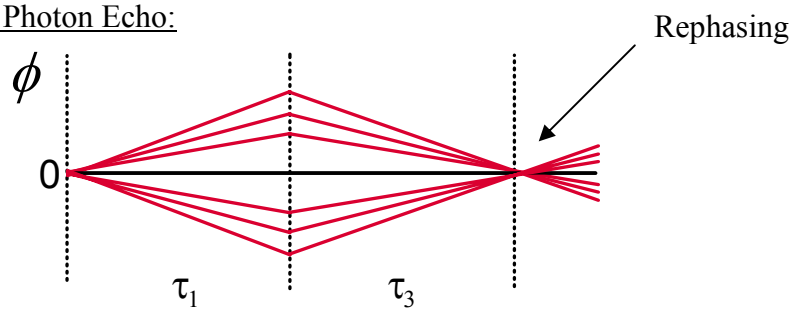

- The observation of a peak shift is an indication that there is imperfect ability to rephase. In this case, there is homogeneous dephasing competing with the rephasing of the inhomogeneity.

**Spectral diffusion** randomizes phase; it destroys the ability for an echo to form by rephasing.

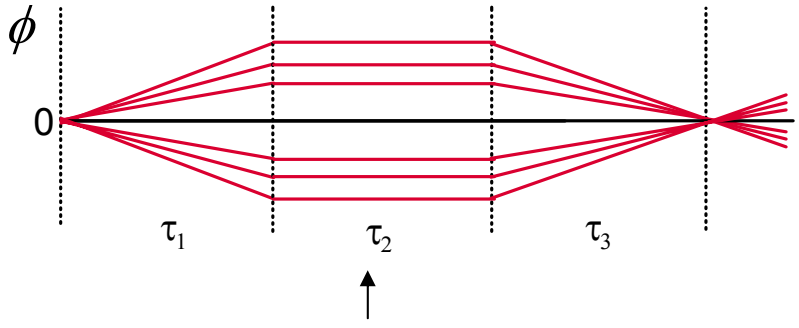
We can study this by doing the echo experiment with three pulses:

**Lens Analogy**: For a distribution of oscillators with different frequencies, define phase $e^{i\phi} = e^{i(\delta\omega_i t)}$

Two-Pulse Photon Echo:

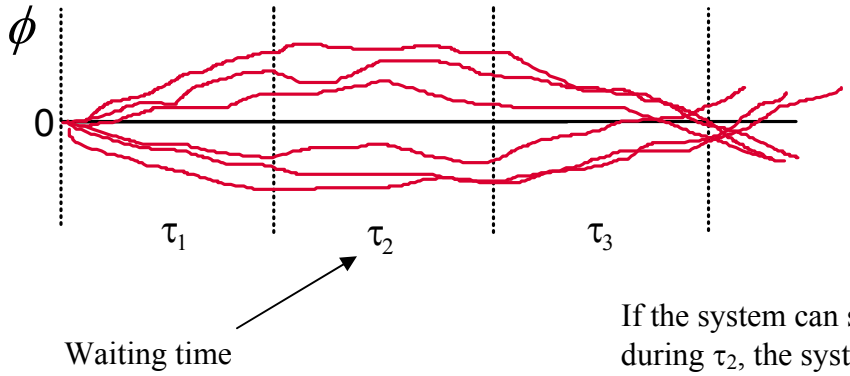



Add Extra Time Period. Three-Pulse Photon Echo:




No evolution of phase in $\tau_2$ – population $\rho_{bb}$

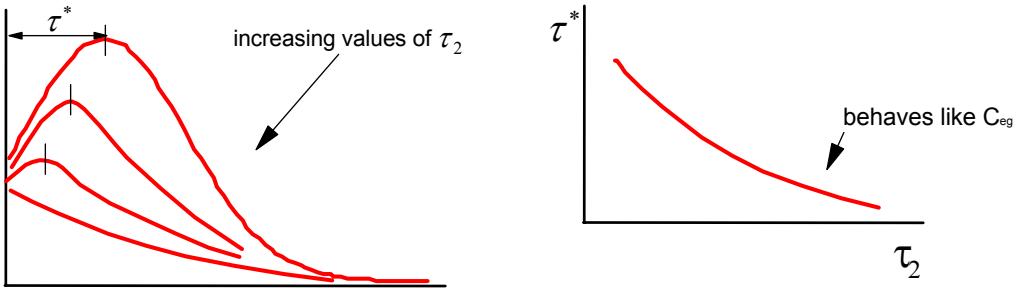
Add spectral diffusion:




If the system can spectrally diffuse during $\tau_2$, the system will rephase poorly—echo gets washed out for larger values of $\tau_2$.

- Since spectral diffusion destroys the rephasing, the system appears more and more "homogeneous" as $\tau_2$ is incremented.

- One observes that the shift of the peak of the integrated echo changes with $\tau_2$ – It shifts back to zero.




The peak of the echo τ* shifts back with a rate dictated by the correlation function for relaxation/bath interactions.

$$\tau^*(\tau_2) \propto C_{eg}(\tau)$$

If you use stochastic model $g(t) = \Delta^2 \tau_c^2 \left[ exp(-t/\tau_c) + t/\tau_c - 1 \right]$, you can see that $\tau^*(\tau_2) \propto exp(-\tau_2/\tau_c) \Rightarrow \langle \delta\omega_{eg}(\tau)\delta\omega_{eg}(0) \rangle$.

You can use this method to determine the form to $C_{eg}(\tau)$ or $C''_{eg}(\omega)$ or $\rho(\omega)$.