5.74 Introductory Quantum Mechanics II

Spring 2009

11.5. CHARACTERIZING FLUCTUATIONS

Eigenstate vs. system/bath perspectives

From our earlier work on electronic spectroscopy, we found that there are two equivalent ways of describing spectroscopic problems, which can be classified as the eigenstate and system/bath perspectives. Let's summarize these before turning back to nonlinear spectroscopy, using electronic spectroscopy as the example:

1) Eigenstate: The interaction of light and matter is treated with the interaction picture Hamiltonian $H = H_0 + V(t)$. H_0 is the full material Hamiltonian, expressed as a function of nuclear and electronic coordinates, and is characterized by eigenstates which are the solution to $H_0|n\rangle = E_n|n\rangle$. In the electronic case $|n\rangle = |e, n_1, n_2 \ldots\rangle$ represent labels for a particular vibronic state. The dipole operator in $V(t)$ couples these states. Given that we have such detailed knowledge of the matter, we can obtain an absorption spectrum in two ways. In the time domain, we know

$$C_{\mu\mu}(t) = \sum_n p_n \langle n|\mu(t)\mu(0)|n\rangle = \sum_{n,m} p_n |\mu_{nm}|^2 e^{-i\omega_{mn}t} \tag{1}$$

The absorption lineshape is then related to the Fourier transform of $C(t)$,

$$\sigma(\omega) = \sum_{n,m} p_n |\mu_{nm}|^2 \frac{1}{\omega - \omega_{nm} - i\Gamma_{nm}} \tag{2}$$

where the phenomenological damping constant Γ_{nm} was first added into eq. (1). This approach works well if you have an intimate knowledge of the Hamiltonian if your spectrum is highly structured and if irreversible relaxation processes are of minor importance.

2) System/Bath: In condensed phases, irreversible dynamics and featureless lineshapes suggest a different approach. In the system/bath or energy gap representation, we separate our Hamiltonian into two parts: the system H_s contains a few degrees of freedom Q which we treat in detail, and the remaining degrees of freedom (q) are in the bath H_B. Ideally, the interaction between the two sets $H_{SB}(qQ)$ is weak.

$$H_0 = H_S + H_B + H_{SB}. \tag{3}$$

Spectroscopically we usually think of the dipole operator as acting on the system state, i.e. the dipole operator is a function of Q. If we then know the eigenstates of H_S, $H_S|n\rangle = E_n|n\rangle$ where $|n\rangle = |g\rangle$ or $|e\rangle$ for the electronic case, the dipole correlation function is

$$C_{\mu\mu}(t) = |\mu_{eg}|^2 e^{-i\langle\omega_{eg}\rangle t}\left\langle \exp\left[-i\int_0^t H_{SB}(t')dt'\right]\right\rangle \tag{4}$$

The influence of the dark states in H_B is to modulate or change the spectroscopic energy gap ω_{eg} in a form dictated by the time-dependent system-bath interaction. The system-bath approach is a natural way of treating condensed phase problems where you can't treat all of the nuclear motions (liquid/lattice) explicitly. Also, you can imagine hybrid approaches if there are several system states that you wish to investigate spectroscopically.

Energy Gap Fluctuations

How do transition energy gap fluctuations enter into the nonlinear response? As we did in the case of linear experiments, we will make use of the second cumulants approximation to relate dipole correlation functions to the energy gap correlation function $C_{eg}(\tau)$. Remembering that for the case of a system-bath interaction that that linearly couples the system and bath nuclear coordinates, the cumulant expansion allows the linear spectroscopy to be expressed in terms of the lineshape function $g(t)$

$$C_{\mu\mu}(t) = |\mu_{eg}|^2 e^{-i\omega_{eg}t} e^{-g(t)} \tag{5}$$

$$g(t) = \int_0^t dt'' \int_0^{t''} dt' \underbrace{\frac{1}{\hbar^2}\left\langle \delta H_{eg}(t')\delta H_{eg}(0)\right\rangle}_{C_{eg}(t')} \tag{6}$$

$$C_{eg}(\tau) = \left\langle \delta\omega_{eg}(\tau)\delta\omega_{eg}(0)\right\rangle \tag{7}$$

$g(t)$ is a complex function for which the imaginary components describe nuclear motion modulating or shifting the energy gap, whereas the real part describes the fluctuations and damping that lead to line broadening. When $C_{eg}(\tau)$ takes on an undamped oscillatory form

$C_{eg}(\tau) = De^{i\omega_0\tau}$, as we might expect for coupling of the electronic transition to a nuclear mode with frequency ω_0, we recover the expressions that we originally derived for the electronic absorption lineshape in which D is the coupling strength and related to the Frank-Condon factor.

Here we are interested in discerning line-broadening mechanisms, and the time scale of random fluctuations that influence the transition energy gap. Summarizing our earlier results, we can express the lineshape functions for energy gap fluctuations in the homogeneous and imhomogeneous limit as

1) Homogeneous. The bath fluctuations are infinitely fast, and only characterized by a magnitude:

$$C_{eg}(\tau) = \Gamma\,\delta(\tau). \tag{8}$$

In this limit, we obtain the phenomenological damping result

$$g(t) = \Gamma t \tag{9}$$

Which leads to homogeneous Lorentzian lineshapes with width Γ.

2) Inhomogeneous. The bath fluctuations are infinitely slow, and again characterized by a magnitude, but there is no decay of the correlations

$$C_{eg}(\tau) = \Delta^2. \tag{10}$$

This limit recovers the Gaussian static limit, and the Gaussian inhomogeneous lineshape where Δ is the distribution of frequencies.

$$g(t) = \tfrac{1}{2}\Delta^2 t^2. \tag{11}$$

3) The intermediate regime is when the energy gap fluctuates on the same time scale as the experiment. The simplest description is the stochastic model which describes the loss of correlation with a time scale τ_c

$$C_{eg}(\tau) = \Delta^2 \exp(-t/\tau_c) \tag{12}$$

which leads to

$$g(t) = \Delta^2 \tau_c^2 \left[\exp(-t/\tau_c) + t/\tau_c - 1\right] \tag{13}$$

For an arbitrary form of the dynamics of the bath, we can construct $g(t)$ as a sum over independent modes $g(t) = \sum_i g_i(t)$. Or for a continuous distribution for modes, we can

describe the bath in terms of the spectral density $\rho(\omega)$ that describes the coupled nuclear motions

$$\rho(\omega) = \frac{1}{2\pi\omega^2}\mathrm{Im}\left[\tilde{C}_{eg}(\omega)\right] \tag{14}$$

$$\begin{aligned} g(t) &= \int_{-\infty}^{+\infty} d\omega \frac{1}{2\pi\omega^2}\tilde{C}_{eg}(\omega)\left[\exp(-i\omega t) + i\omega t - 1\right] \\ &= \int_{-\infty}^{+\infty} d\omega\ \rho(\omega)\left(\coth\left(\frac{\beta\hbar\omega}{2}\right)(1-\cos\omega t) + i(\sin\omega t - \omega t)\right) \end{aligned} \tag{15}$$

To construct an arbitrary form of the bath, the phenomenological Brownian oscillator model allows us to construct a bath of *i* damped oscillators,

$$\begin{aligned} C''_{eg}(\omega) &= \sum_i \xi_i C_i''(\omega) \\ C_i''(\omega) &= \frac{\hbar}{m_i}\frac{\omega\Gamma_i}{\left(\omega_i^2 - \omega^2\right)^2 + 4\omega^2\Gamma_i^2} \end{aligned} \tag{16}$$

Here ξ_i is the coupling coefficient for oscillator *i*.

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 for a fluctuating two-level system can be written as a sum of correlation functions of the form

$$R_1(\tau_1,\tau_2,\tau_3) = \left(\frac{i}{\hbar}\right)^3 p_g \left|\mu_{eg}\right|^4 e^{i\omega_{eg}(\tau_1+\tau_3)}\left\langle \exp\left(-\frac{i}{\hbar}\int_0^{\tau_1} d\tau\, H_{eg}(\tau) - \frac{i}{\hbar}\int_{\tau_1+\tau_2}^{\tau_1+\tau_2+\tau_3} d\tau\, H_{eg}(\tau)\right)\right\rangle \tag{17}$$

$$R_2(\tau_1,\tau_2,\tau_3) = \left(\frac{i}{\hbar}\right)^3 p_g \left|\mu_{eg}\right|^4 e^{-i\omega_{eg}(\tau_1-\tau_3)}\left\langle \exp\left(\frac{i}{\hbar}\int_0^{\tau_1} d\tau\, H_{eg}(\tau) - \frac{i}{\hbar}\int_{\tau_1+\tau_2}^{\tau_1+\tau_2+\tau_3} d\tau\, H_{eg}(\tau)\right)\right\rangle \tag{18}$$

These are the rephasing (R_2) and non-rephasing (R_1) functions, written for a two-level system. These expressions only account for fluctuations of the energy gap while the system evolves during the coherence periods τ_1 and τ_3. Since they neglect any difference in relaxation on the ground or excited state during the population period τ_2, $R_2 = R_3$ and $R_1 = R_4$. They also ignore reorientational relaxation of the dipole. Otherwise the primary assumption to obtain this form is

the Condon approximation, in which we say that the dipole is only an operator in the system coordinates Q, and not in the bath coordinates q.

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:

$$R^{(3)}(\tau_1,\tau_2,\tau_3)=\left(\frac{i}{\hbar}\right)^3\theta(\tau_1)\theta(\tau_2)\theta(\tau_3)\sum_{\alpha=1}^{4}\left[R_\alpha(\tau_1,\tau_2,\tau_3)-R_\alpha^*(\tau_1,\tau_2,\tau_3)\right] \tag{19}$$

$$\begin{aligned}R_1 = {} & e^{-i\omega_{eg}\tau_1-i\omega_{eg}\tau_3}\left(\frac{i}{\hbar}\right)^3 p_g\left|\mu_{eg}\right|^4 \\ & \times\exp\left[-g^*(\tau_3)-g(\tau_1)-g^*(\tau_2)+g^*(\tau_2+\tau_3)+g(\tau_1+\tau_2)-g(\tau_1+\tau_2+\tau_3)\right]\end{aligned} \tag{20}$$

$$\begin{aligned}R_2 = {} & \left(\frac{i}{\hbar}\right)^3 p_g\left|\mu_{eg}\right|^4 e^{i\omega_{eg}\tau_1-i\omega_{eg}\tau_3} \\ & \times\exp\left[-g^*(\tau_3)-g^*(\tau_1)+g(\tau_2)-g(\tau_2+\tau_3)-g^*(\tau_1+\tau_2)+g^*(\tau_1+\tau_2+\tau_3)\right]\end{aligned} \tag{21}$$

$$\begin{aligned}R_3 = {} & \left(\frac{i}{\hbar}\right)^3 p_g\left|\mu_{eg}\right|^4 e^{i\omega_{eg}\tau_1-i\omega_{eg}\tau_3} \\ & \times\exp\left[-g(\tau_3)-g^*(\tau_1)+g^*(\tau_2)-g^*(\tau_2+\tau_3)-g^*(\tau_1+\tau_2)+g^*(\tau_1+\tau_2+\tau_3)\right]\end{aligned} \tag{22}$$

$$\begin{aligned}R_4 = {} & \left(\frac{i}{\hbar}\right)^3 p_g\left|\mu_{eg}\right|^4 e^{-i\omega_{eg}\tau_1-i\omega_{eg}\tau_3} \\ & \times\exp\left[-g(\tau_3)-g(\tau_1)-g(\tau_2)+g(\tau_2+\tau_3)+g(\tau_1+\tau_2)-g(\tau_1+\tau_2+\tau_3)\right]\end{aligned} \tag{23}$$

These expressions provide the most direct way of accounting for fluctuations or periodic modulation of the spectroscopic energy gap in nonlinear spectroscopies.

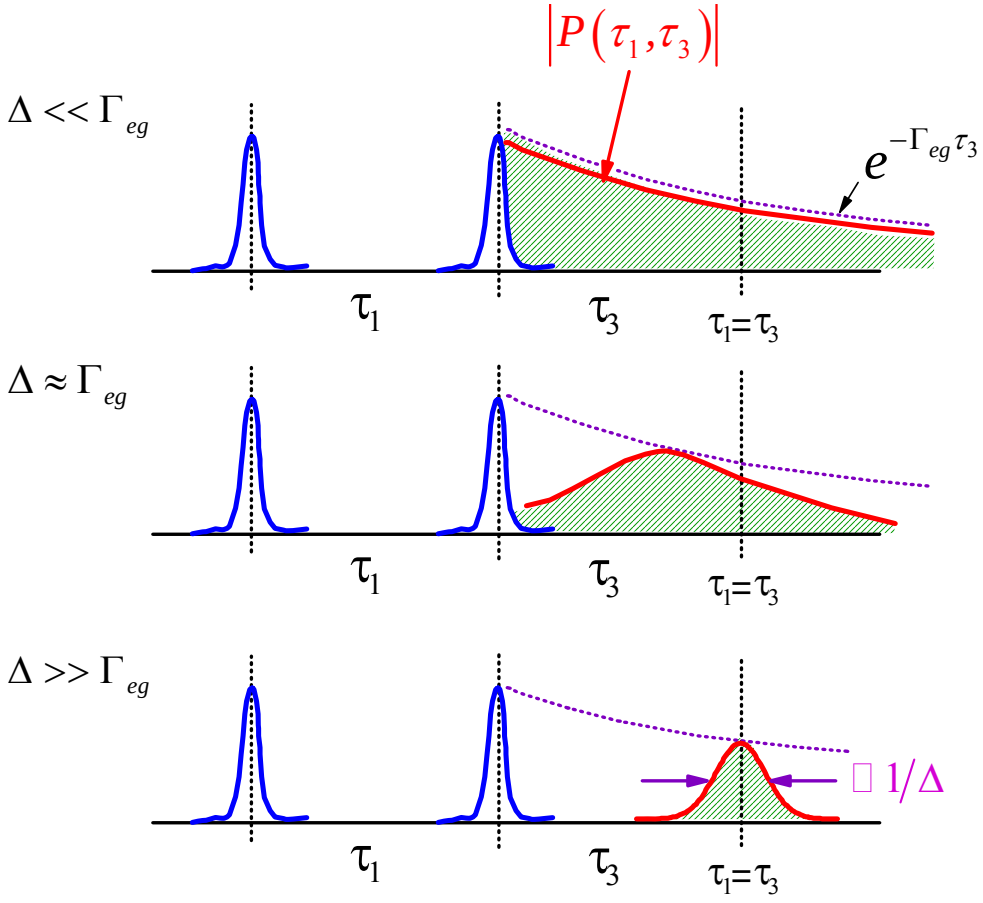
Example: For the two-pulse photon echo experiment on a system with inhomogeneous broadening:

- 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 $R_2=R_3=\left(\frac{i}{\hbar}\right)^3 p_g\left|\mu_{eg}\right|^4 e^{i\omega_{eg}\tau_1-i\omega_{eg}\tau_3}\exp\left[-2g(\tau_3)-2g(\tau_1)+g(\tau_1+\tau_3)\right]$.
- Substituting $g(t)$ into this expression gives the same result as before.

$$R^{(3)}\propto e^{-i\omega_{eg}(\tau_1-\tau_3)}e^{-\Gamma_{eg}(\tau_1+\tau_3)}e^{-(\tau_1-\tau_3)^2\Delta^2/2} \tag{24}$$

How can you characterize fluctuations and spectral diffusion?

The rephasing ability of the photon echo experiment provides a way of characterizing memory of the energy gap transition frequency initially excited by the first pulse. For a static inhomogeneous lineshape, perfect memory of transition frequencies is retained through the experiment, whereas homogeneous broadening implies extremely rapid dephasing. So, let's first examine the polarization for a two-pulse photon echo experiment on a system with homogeneous and inhomogeneous broadening by varying Δ/Γ_{eg}. Plotting the polarization as proportional to the response in eq. (24):



We see that following the third pulse, the polarization (red line) is damped during τ_3 through homogeneous dephasing at a rate Γ_{eg}, regardless of Δ. However in the inhomogeneous case $\Delta >> \Gamma_{eg}$, any inhomogeneity is rephased at $\tau_1 = \tau_3$. The shape of this echo is a Gaussian with width $\sim 1/\Delta$. The shape of the echo polarization is a competition between the homogeneous damping and the inhomogeneous rephasing.

Normally, one detects the integrated intensity of the radiated echo field. Setting the pulse delay $\tau_1 = \tau$,

$$S(\tau) \propto \int_0^\infty d\tau_3 \left| P^{(3)}(\tau, \tau_3) \right|^2 \tag{25}$$

$$S(\tau) = \exp\left(-4\Gamma_{eg}\tau - \frac{\Gamma_{eg}^{\,2}}{\Delta^2} \right) \cdot \mathrm{erfc}\left(-\Delta\tau + \frac{\Gamma_{eg}}{\Delta} \right), \tag{26}$$

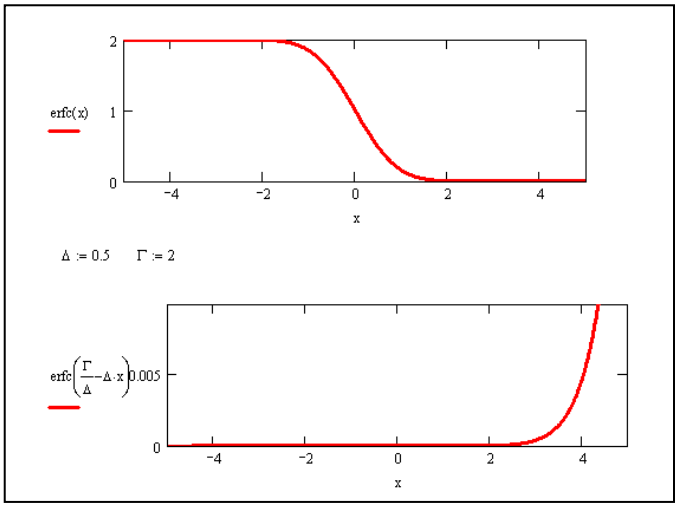
where *erfc*(*x*) = *1*–*erf*(*x*) is the complementary error function. For the homogeneous and inhomogeneous limits of this expression we find

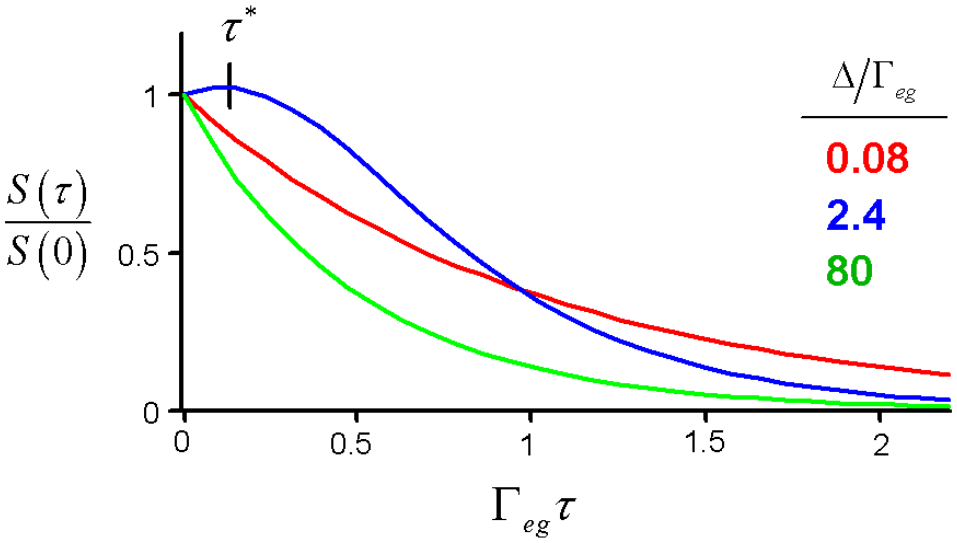
$$\Delta << \Gamma_{eg} \quad \Rightarrow \quad S(\tau) \propto e^{-2\Gamma_{eg}\tau} \tag{27}$$

$$\Delta >> \Gamma_{eg} \quad \Rightarrow \quad S(\tau) \propto e^{-4\Gamma_{eg}\tau} \tag{28}$$

In either limit, the inhomogeneity is removed from the measured decay.

In the intermediate case, we observe that the leading term in eq. (26) decays whereas the second term rises with time. This reflects the competition between homogeneous damping and the inhomogeneous rephasing. As a result, for the intermediate case ($\Delta \approx \Gamma_{ab}$) we find that the integrated signal $S(\tau)$ has a maximum signal for $\tau > 0$.

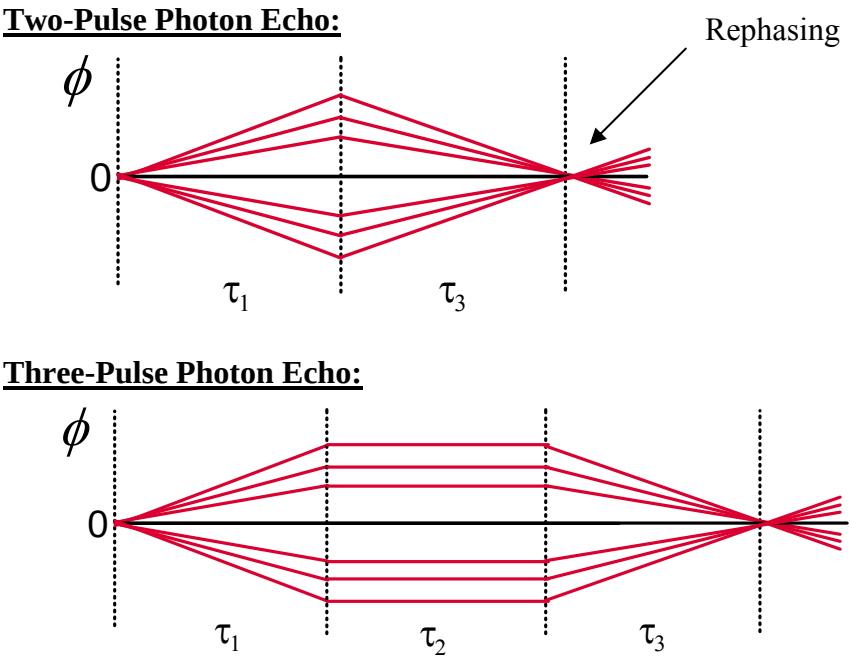




The delay of maximum signal, τ^*, is known as the peak shift. The observation of a peak shift is an indication that there is imperfect ability to rephrase. Homogenous dephasing, i.e. fluctuations fast on the time scale of τ, are acting to scramble memory of the phase of the coherence initially created by the first pulse.

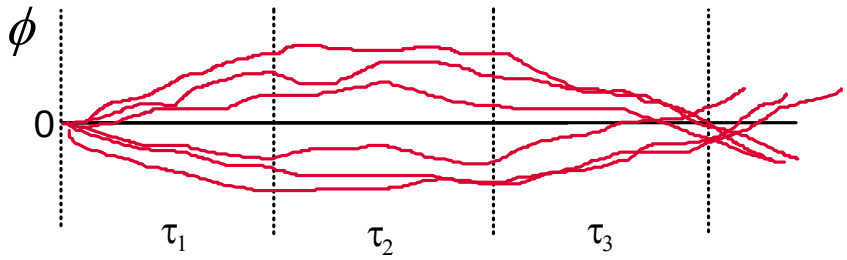
In the same way, spectral diffusion (processes which randomly modulate the energy gap on time scales equal or longer than τ) randomizes phase. It destroys the ability for an echo to form by rephasing. To characterize these processes through an energy gap correlation function, we can perform a three-pulse photon echo experiment. The three pulse experiment introduces a waiting time τ_2 between the two coherence periods, which acts to define a variable shutter speed for the experiment. The system evolves as a population during this period, and therefore there is nominally no phase acquired. We can illustrate this through a lens analogy:

Lens Analogy: For an inhomogeneous distribution of oscillators with different frequencies, we define the phase acquired during a time period through $e^{i\phi} = e^{i(\delta\omega_i t)}$.

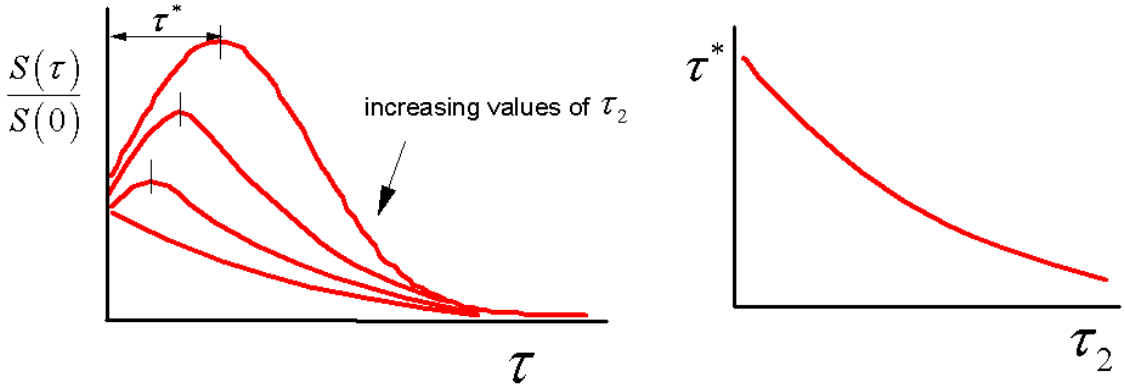


Since we are in a population state during τ_2, there is no evolution of phase. Now to this picture we can add spectral diffusion as a slower random modulation of the phase acquired during all time periods. If the system can spectrally diffuse during τ_2, this degrades the ability of the system to rephase and echo formation is diminished.

Three-Pulse Photon Echo with Spectral Diffusion:



Since spectral diffusion destroys the rephasing, the system appears more and more "homogeneous" as τ_2 is incremented. Experimentally, one observes how the peak shift of the integrated echo changes with the waiting time τ_2. It will be observed to shift toward $\tau^* = 0$ as a function of τ_2.



In fact, one can show that the peak shift with τ_2 decays with a form given by the the correlation function for system-bath interactions:

$$\tau^*(\tau_2) \propto C_{eg}(\tau) \tag{29}$$

Using the lineshape function for the stochastic model $g(t) = \Delta^2 \tau_c^2 \left[\exp(-t/\tau_c) + t/\tau_c - 1 \right]$, you can see that for times $\tau_2 > \tau_c$,

$$\tau^*(\tau_2) \propto \exp(-\tau_2/\tau_c) \Rightarrow \left\langle \delta\omega_{eg}(\tau)\delta\omega_{eg}(0) \right\rangle \tag{30}$$

Thus echo peak shift measurements are a general method to determine the form to $C_{eg}(\tau)$ or $C''_{eg}(\omega)$ or $\rho(\omega)$. The measurement time scale is limited only by the population lifetime.