Diagrammatic Perturbation Theory

A simplified way of keeping track of the correlation functions that contribute to the nonlinear response (for third order nonlinear spectroscopy, this can get complicated).

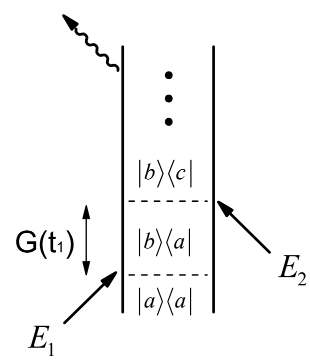
- For a multistate system, there can be many possible interaction processes.
- Not all correlation functions in the response function contribute to a particular signal ($\bar{k}_{sig}$).

Feynman diagrams and Ladder diagrams* keep track of propagation of ρ. These show repeated interaction with field followed by evolution under H_0. Interactions are shown by arrows, which propagate the density matrix from one element to another.

- Allows you to keep track of signal frequency and wavevector.
- You can write down a correlation function directly from diagram by assigning a factor for each interaction, a factor for each time evolution, and the final trace.

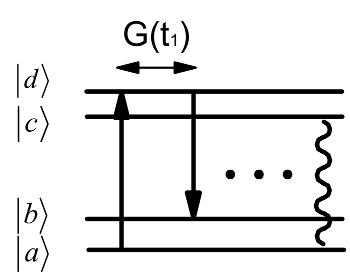
Feynman Diagrams

1. Double line represents ket and bra side of ρ
2. Time propagation upward
3. Lines intersecting diagram represent field interaction—between interactions the system evolves freely under $H_0,(G)$.



Ladder Diagrams

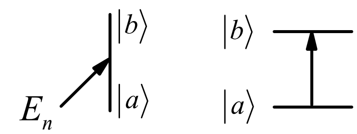
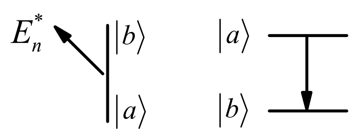
1. Multiple states arranged vertically by energy
2. Time propagates to right
3. Lines between levels indicate interaction followed by free propagation under $H_0,(G)$.

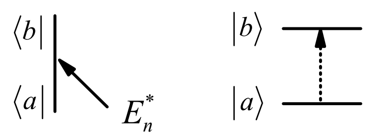
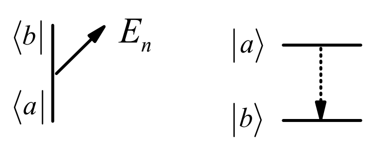


* D. Lee and A. C. Albrecht, "A unified view of Raman, resonance Raman, and fluorescence spectroscopy (and their analogues in two-photon absorption)." Adv. Infrared and Raman Spectr. **12**, 179 (1985).

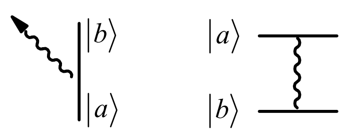
TERMS FOR FIELD-MATTER INTERACTION

- Each interaction propagates one side of ρ.
- Each interaction adds a dipole matrix element μ_{ij} to the material nonlinear response function,
- Each interaction adds input electric field factors to the polarization, which describes the frequency and wavevector of the radiated signal.

KET SIDE		Contribution to material response	Contribution to signal field
Absorption $\mu_{ba} E_n \, exp[i\mathbf{k_n r} - i\omega_n t]$		μ_{ba}	$+\mathbf{k_n}$ $+\omega_n$
Stimulated Emission $\mu_{ba} E_n^* \, exp[-i\mathbf{k_n r} + i\omega_n t]$		μ_{ba}	$-\mathbf{k_n}$ $-\omega_n$

BRA SIDE			
Absorption $\mu_{ba}^* E_n^* \, exp[-i\mathbf{k_n r} + i\omega_n t]$		μ_{ba}^*	$-\mathbf{k_n}$ $-\omega_n$
Stimulated Emission $\mu_{ba}^* E_n \, exp[i\mathbf{k_n r} - i\omega_n t]$		μ_{ba}^*	$+\mathbf{k_n}$ $+\omega_n$

FINAL TRACE: (convention: ket side)



μ_{ba}

- Bra is complex conjugate of Ket; Absorption is complex conjugate of S.E.
- Feynman: absorption: inward; emission: outward; bra: right; ket: left.
- Ladder: absorption: up; emission: down; bra: dotted; ket: solid.

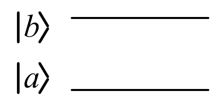
The diagram can now be used to write down correlation functions that contribute to response function:

1) Read off field factors and add propagation under H_0 between interactions (phenomenological: $G_{ij}(t) = \exp\left[-i\omega_{ij}t - \Gamma_{ij}t\right]$).

2) Add factor of (-1) for each bra side interaction (from commutators).

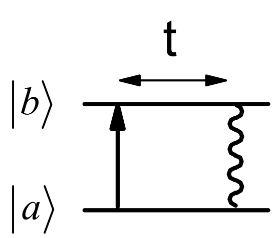
3) The radiated signal will have frequency $\sum_i \omega_i = \omega_{sig}$ and wave vector $\sum_i \bar{k}_i = \bar{k}_{sig}$

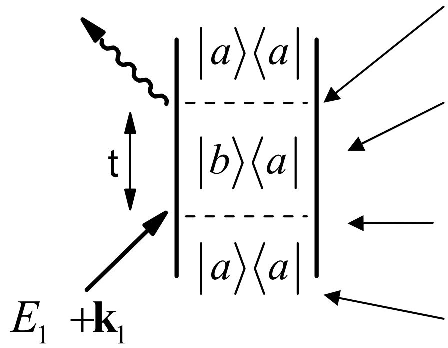
<u>EXAMPLE</u>: **Linear Response for Two-level System**
…starting with population in *a*



<u>ket side</u>

$$C(t) = Tr\left[\mu(t)\mu(0)\rho_{eq}\right]$$





(4) Act on ket with μ and take trace.

(3) Propagate under H_0; $G_{ab} = e^{-i\omega_{ba}t - \Gamma_{ba}t}$.

(2) Act on ket with μ(0) to create ρ_{ba}.

(1) Start in ρ_{aa} (add factor of p_a).

Working from bottom up

$$C(t) = p_a\left[\mu_{ba}\right]\left[e^{-i\omega_{ba}t - \Gamma_{ba}t}\right]\left[\mu_{ab}\right]$$

$$= p_a\left|\mu_{ba}\right|^2 e^{-i\omega_{ba}t - \Gamma_{ba}t}$$

The product of incident fields (response/polarization):

$$E_1\, e^{-i\omega_1 t + i\bar{k}_1\cdot\bar{r}} \quad\Rightarrow\quad P(t)e^{-i\omega_{sig}t + i\bar{k}_{sig}\cdot\bar{r}}$$

$$\omega_{sig} = \omega_1 \quad \bar{k}_{sig} = \bar{k}$$

Starting in *b* gives same result.

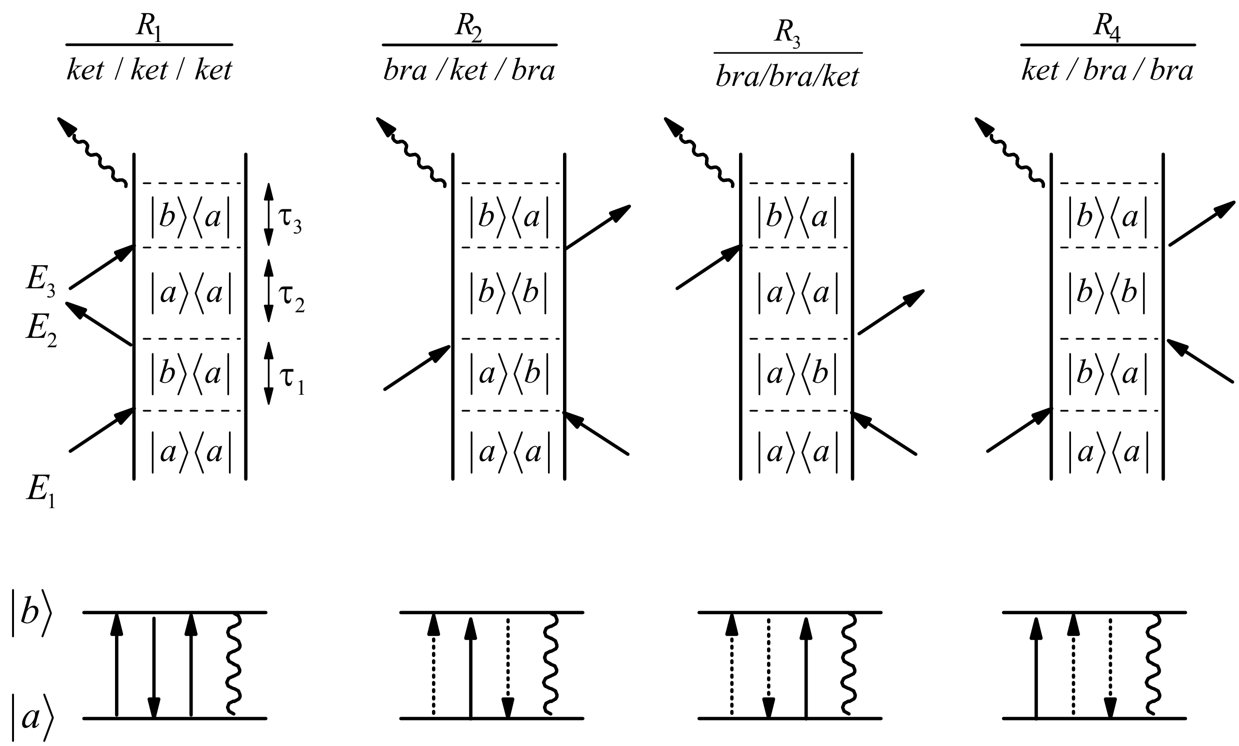
Third-Order Nonlinear Spectroscopy

Third-order nonlinearities describe most of the coherent nonlinear experiments that are used: pump-probe, transient grating, photon echoes, CARS (coherent anti-stokes Raman spec.), degenerate four wave mixing (4WM) . . .

These experiments are described by some or all of the eight correlation functions that contribute to $R^{(3)}$:

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

Let's write out the diagrams/correlation functions for a two-level system starting in ρ_{aa}, where the dipole operator couples $|b\rangle$ and $|a\rangle$.



$\omega_{sig} = +\omega_1 - \omega_2 + \omega_3$	$-\omega_1 + \omega_2 + \omega_3$	$-\omega_1 + \omega_2 + \omega_3$	$+\omega_1 - \omega_2 + \omega_3$
$k_{sig} = +k_1 - k_2 + k_3$	$-k_1 + k_2 + k_3$	$-k_1 + k_2 + k_3$	$+k_1 - k_2 + k_3$

Now let's write out the correlation function, R_2 (photon echoes, pump-probes, DFWM):

$$R_2 = \mu_{ab}\, G_{ba}\left(\tau_3\right) \mu_{ba} G_{bb}\left(\tau_2\right) \mu_{ba} G_{ab}\left(\tau_1\right) \mu_{ab}\, \rho_{aa} \qquad \text{set } \rho_{eq} \Rightarrow \rho_{aa}$$

$$R_2 = \left(-1\right)^2 p_a \left(\mu_{ab}\right)\left[e^{-i\omega_{ba}\tau_3 - \Gamma_{ba}\tau_3}\right]\left(\mu_{ba}\right)\left(e^{\cancel{-i\omega_{bb}\tau_2} - \Gamma_{bb}\tau_2}\right)\left(\mu_{ba}\right)\left[e^{-i\omega_{ba}\tau_1 - \Gamma_{ab}\tau_1}\right]\left(\mu_{ba}\right)$$

$$= p_a \left|\mu_{ab}\right|^4 \left[e^{-i\omega_{ab}\left(\tau_1 - \tau_3\right) - \Gamma_{ba}\left(\tau_1 + \tau_3\right) - \Gamma_{bb}\left(\tau_2\right)}\right]$$

The diagrams also give the input field contributions as

$$\bar{E}_1 \bar{E}_2 \bar{E}_3 = \left(E_1^*\, e^{+i\omega_1 t - i\bar{k}_1 \cdot \bar{r}}\right)\left(E_2\, e^{-i\omega_2 t + i\bar{k}_2 \cdot r}\right)\left(E_3\, e^{+i\omega_3 t - i\bar{k}_3 \cdot \bar{r}_3}\right)$$

$$= E_1^*\, E_2\, E_3\, e^{-\omega_{sig} t + i\bar{k}_{sig} \cdot \bar{r}}$$

$$\omega_{sig} = -\,\omega_1 + \omega_2 + \omega_3 \qquad k_{sig} = -\,\bar{k}_1 + \bar{k}_2 + \bar{k}_3$$

This dictates the direction that the field radiates.

For R_2: $P^{(3)} \sim R_2\left(E_1 E_2 E_3\right) \Rightarrow E_{sig}$

In the delta-function pulse limit, this response function with the field factors equals the polarization.

<u>Frequency Domain Representaion</u>

A Fourier transform of $P^{(3)}(t)$ with respect to the time time intervals allows us to obtain an expression for $\chi^{(3)}(\omega_1, \omega_2, \omega_3)$:

$$P^{(3)}\left(\omega\right) = \chi^{(3)}\left(\omega; \omega_1, \omega_2, \omega_3\right) \bar{E}_1 \bar{E}_2\, \bar{E}_3$$

where $\chi^{(n)}(t) = \int_0^\infty d\tau_n\, e^{i\Omega_n\tau_n} \cdots \int_0^\infty d\tau_1\, e^{i\Omega_1\tau_1}\, R^{(n)}(\tau_1, \tau_2, \ldots \tau_n)$ and $\Omega_n = \sum_{i=1}^{n} \omega_i$.

In general, $R^{(3)}$ is a sum over many correlation function and includes a sum over states. Also, to describe frequency domain experiments, we have to permute over all time orderings. Most general: the eight terms in $R^{(3)}$ lead to 48 terms for $\chi^{(3)}$.

An example of one term for the R_2 example we just did ($\omega_{sig} = -\omega_1+\omega_2+\omega_3$), in which the damping is treated phenomenologically:

$$\chi^{(3)}(\omega_1, \omega_2, \omega_3) = |\mu_{ba}|^4 \frac{1}{\omega_1 - \omega_{ba} - i\Gamma_{ba}} \cdot \frac{1}{-(\omega_2 - \omega_1 \cancel{-\omega_{bb}}) - i\Gamma_{bb}} \cdot \frac{1}{-(\omega_3 + \omega_2 - \omega_1 - \omega_{ba}) - i\Gamma_{ba}}$$

“–” for ket

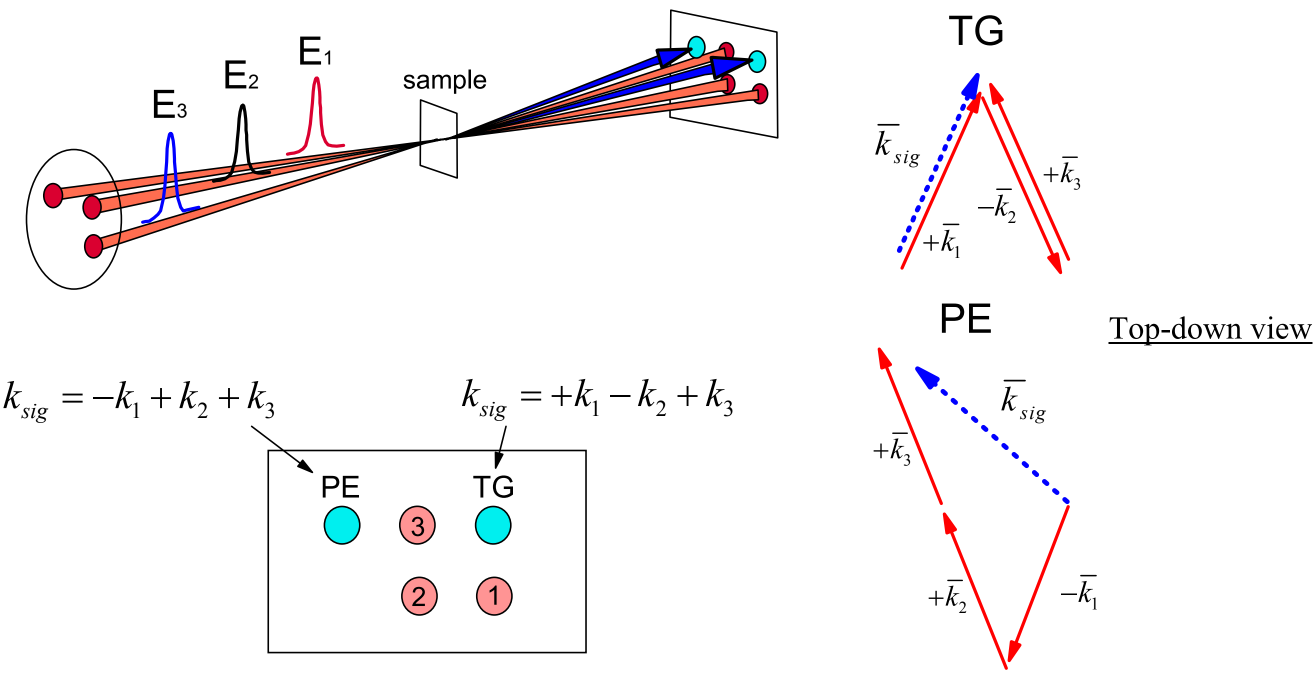
The terms are written from a diagram with each interaction and propagation adding a resonant denominator term (here reading left to right). The frequency domain response will look like a sum over terms like these.

Examples of third-order spectroscopies:

Strategy for describing an experiment:

1) Start with the wavevector and frequency of the signal field of interest.
2) (a) Time-domain: Define a time-ordering along the incident wavevectors or
   (b) Frequency domain: Define the frequencies along the incident wavevectors
3) Sum up diagrams for correlation functions that will scatter into the wave-vector matched direction, keeping only resonant terms (rotating wave approximation). In frequency: You can use ladder diagrams to determine which correlation functions yield signals that pass through your filter/monochromator.

Consider two degenerate third order experiments ($\omega_1=\omega_2=\omega_3=\omega_{sig}$):



1) Photon Echo (PE) $k_{sig} = -k_1 + k_2 + k_3 \;\Rightarrow\; R_2 + R_3$

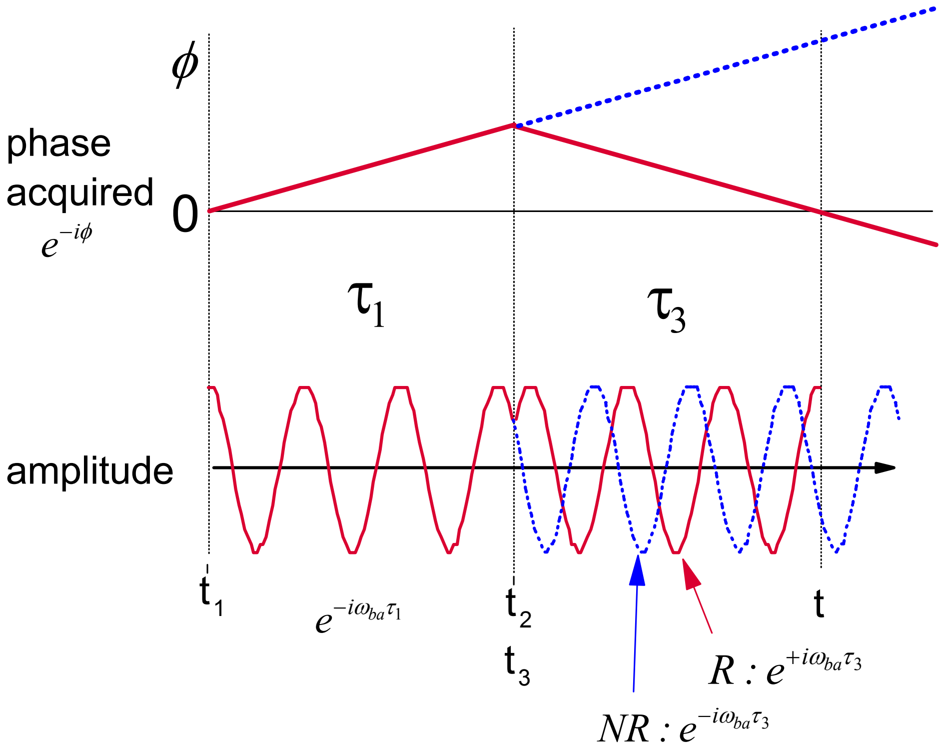
Used for relaxation: distinguish broadening mechanisms, study spectral diffusion

2) Transient Grating (TG) $k_{sig} = +k_1 - k_2 + k_3 \Rightarrow R_1 + R_4$

Population dynamics; wave packets; quantum beats.

These methods are distinguished by being rephasing (PE) or non-rephasing (TG) experiments.
Rephasing (time-reversal) terms R_1 and R_4 evolve in conjugate coherences during τ_1 and τ_3.

	τ_1		τ_3
$R_1 + R_4 \propto e^{-i\omega_{ba}(\tau_1+\tau_3)}$	$\lvert b\rangle\langle a\rvert$	$\rightarrow$	$\lvert b\rangle\langle a\rvert$
$R_2 + R_3 \propto e^{-i\omega_{ba}(\tau_1-\tau_3)}$	$\lvert a\rangle\langle b\rvert$	$\rightarrow$	$\lvert b\rangle\langle a\rvert$



For rephasing: all τ_1 phases identical at $t = t_2 - t_1$

$\tau_1 = \tau_3$