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 ($k_{\text{sig}}$).

Feynman diagrams and Ladder diagrams\(^*\) keep track of propagation of $\rho$. 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 $\rho$
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 $H_0, (G)$.

TERMS FOR FIELD-MATTER INTERACTION

- Each interaction propagates one side of $\rho$.
- Each interaction adds a dipole matrix element $\mu_{ij}$ 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.

<table>
<thead>
<tr>
<th>KET SIDE</th>
<th>Contribution to material response</th>
<th>Contribution to signal field</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Absorption</strong></td>
<td>( \mu_a E_a \exp(ik_a r - i\omega_a t) )</td>
<td>(</td>
</tr>
<tr>
<td><strong>Stimulated Emission</strong></td>
<td>( E_n^* )</td>
<td>(</td>
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<table>
<thead>
<tr>
<th>BRA SIDE</th>
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</thead>
<tbody>
<tr>
<td><strong>Absorption</strong></td>
<td>( \mu'_a E'_a \exp(-ik_a r + i\omega_a t) )</td>
<td>( \langle b</td>
</tr>
<tr>
<td><strong>Stimulated Emission</strong></td>
<td>( E_n^* )</td>
<td>( \langle a</td>
</tr>
</tbody>
</table>

**FINAL TRACE**: (convention: ket side)

- 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: $G_g(t) = \exp[-i\omega_g t - \Gamma_g t]$).

2) Multiply by a factor of $(-1)$ for each bra side interaction (results from commutators).

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

**EXAMPLE:** Linear Response for Two-level System

...starting with population in $a$

ket side

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

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

Working from bottom up

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

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

The product of incident fields (response/polarization):

$$E_i e^{-i\omega t + \vec{k}_i \cdot \vec{r}} \Rightarrow P(t) e^{-i\omega_{sig} t + \vec{k}_{sig} \cdot \vec{r}}$$

$$\omega_{sig} = \omega_i \quad \vec{k}_{sig} = \vec{k}$$

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 $R^{(3)}$:

$$R^{(3)} = \left( \frac{i}{\hbar} \right)^3 \sum_{\alpha=1}^{8} \left[ R_{\alpha} - R_{\alpha}^* \right]$$

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

\[
\begin{align*}
\omega_{\text{sig}} &= +\omega_1 - \omega_2 + \omega_3 & -\omega_1 + \omega_2 + \omega_3 & -\omega_1 + \omega_2 + \omega_3 & +\omega_1 - \omega_2 + \omega_3 \\
k_{\text{sig}} &= +k_1 - k_2 + k_3 & -k_1 + k_2 + k_3 & -k_1 + k_2 + k_3 & +k_1 - k_2 + k_3
\end{align*}
\]
Now let’s write out the correlation function, $R_2$ (photon echoes, pump-probes, DFWM):

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

$$R_2 = (-1)^2 p_a (\mu_{ab}) \left[ e^{-i\omega_0 (\tau_3 - \Gamma_{aa} \tau_3)} \left( \mu_{ba} \right) \left( e^{-i\omega_0 (\tau_2 - \Gamma_{bb} \tau_2)} \right) \left( \mu_{ba} \right) \right]$$

$$= p_a [\mu_{ab}] \left[ e^{-i\omega_0 (\tau_3 - \Gamma_{aa} \tau_3)} \right]$$

The diagrams also give the input field contributions as

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

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

$$\omega_{sig} = -\omega_1 + \omega_2 + \omega_3 \quad k_{sig} = -\vec{k}_1 + \vec{k}_2 + \vec{k}_3$$

This dictates the direction that the field radiates.

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

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

**Frequency Domain Representation**

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

$$P^{(3)}(\omega_{sig}) = \chi^{(3)}(\omega_{sig}; \omega_1, \omega_2, \omega_3) \bar{E}_1 \bar{E}_2 \bar{E}_3$$
where

\[ \chi^{(n)}(t) = \int_{0}^{\tau} d\tau_{n} e^{i\Omega_{\tau_{n}}} \cdots \int_{0}^{\tau_{1}} d\tau_{1} e^{i\Omega_{\tau_{1}}} \, R^{(n)}(\tau_{1}, \tau_{2}, \ldots, \tau_{n}) \]

and the Fourier transforms are performed with respect to the frequencies for which you are evolving during that period

\[ \Omega_{m} = \sum_{i=1}^{m} \omega_{i}. \]

For instance the Fourier transform conjugate variable for the third time-interval –after the third interaction– is \( \Omega_{3} = \omega_{3} + \omega_{2} + \omega_{1} \). In general, \( R^{(3)} \) is a sum over many correlation function and includes a sum over states:

\[ \chi^{(3)}(\omega_{1}, \omega_{2}, \omega_{3}) = \frac{1}{6} \left( \frac{i}{\hbar} \right)^{3} \sum_{abed} \sum_{a} P_{a} \sum_{a=1}^{4} \left[ \chi_{a} - \chi_{a}^{*} \right] \]

Here \( a \) is the initial state and the sum is over all possible intermediate states. Also, to describe frequency domain experiments, we have to permute over all time orderings. Most generally, as a result of the \( 3! = 6 \) permutations of the time-ordering of the input fields 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:

\[ \chi_{2}^{*}(\omega_{1}, \omega_{2}, \omega_{3}) = \left| \mu_{ba} \right|^{4} \frac{1}{\omega_{a} - \omega_{ba} - i\Gamma_{ba}} \cdot \frac{1}{-\left( \omega_{2} - \omega_{1} - \omega_{bh} \right) - i\Gamma_{bh}} \cdot \frac{1}{-\left( \omega_{3} + \omega_{2} - \omega_{a} - \omega_{ba} \right) - i\Gamma_{ba}} \]

\[ \text{“-” for ket} \]

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.

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**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 ($\omega_1 = \omega_2 = \omega_3 = \omega_{\text{sig}}$):

1) **Photon Echo (PE)**  $k_{\text{sig}} = -k_1 + k_2 + k_3$  \[ \Rightarrow R_2 + R_3 \]
   Used for relaxation: distinguish broadening mechanisms, study spectral diffusion

2) **Transient Grating (TG)**  $k_{\text{sig}} = +k_1 - k_2 + k_3$  \[ \Rightarrow R_1 + R_4 \]
   Population dynamics; wave packets; quantum beats.

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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 $\tau_1$ and $\tau_3$.

\[ R_1 + R_4 \propto e^{-i\omega a(\tau_1 + \tau_3)} \]
\[ R_2 + R_3 \propto e^{-i\omega a(\tau_2 - \tau_3)} \]

For rephasing: all $\tau_1$ phases identical at $t = t_2 - t_1$

\[ \tau_1 = \tau_3 \]
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, \( R^{(1)} = \int d\omega_{ab} \, Z(\omega_{ab}) \, R^{(1)}(\omega_{ab}) \)

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

(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 \( (k_3 + k_2 - k_1) \)

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:

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

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

Damps with homogeneous dephasing

Peaked at \( \tau_3 = \tau_1 \)

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For $\Delta \gg \Gamma_{ab}$, $R^{(3)}$ 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 $\tau_3$:

$$I_{\text{sig}}(\tau) = |E_{\text{sig}}|^2 \propto \int_0^\infty d\tau_1 \left| P^{(3)}(\tau, \tau_3) \right|^2$$

In the inhomogeneous limit, we find

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

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 $k_{\text{sig}} = k_1 - k_2 + k_3$ and $k_{\text{sig}} = -k_1 + k_2 + k_3$.

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

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

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

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

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

$$\vec{k}_1 = |k_1| (\hat{z} \cos \theta + \hat{x} \sin \theta)$$

$$\vec{k}_2 = |k_2| (\hat{z} \cos \theta - \hat{x} \sin \theta)$$

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

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

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

$$\eta = \frac{\lambda}{2n \sin \theta} \quad \text{Fringe spacing}$$

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 $\omega_1 = \omega_2 = \omega_3 = \omega_{\text{sig}}$ this the diffraction condition is incidence of $\vec{k}_3$ 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.

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

- 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: $\omega_{\text{sig}} = 2\omega_p - \omega_s$ and the signal is observed background-free next to the transmitted pump field: $\vec{k}_{\text{sig}} = 2\vec{k}_p - \vec{k}_s$.

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

$$R^{(3)} = \mu_{eg}^* e^{-i\omega_{eg} \tau - \Gamma_{eg} \tau} \mu_{eg} e^{-i\omega_s \tau - \Gamma_{eg} \tau}$$

$$= \alpha_{eg} e^{-i\omega_{eg} \tau - \Gamma_{eg} \tau} \alpha_{ge}$$

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

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 \( k_{\text{sig}} = k_1 \mp k_2 + k_3 \), so all correlation functions \( R_1 \) to \( R_4 \) contribute. The observed signal is

\[
I_{\text{sig}} \propto \left| E_3 + E_{\text{sig}} \right|^2 = \left| E_3 \right|^2 + 2E_3 E_{\text{sig}} + \ldots
\]

\[= I_3 + \delta I(T)\]

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

\[E_{\text{sig}} \propto R^{(3)} \propto \left| \mu_{\text{at}} \right|^4 e^{-T_{\text{at}}}\]

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:
- R₁ and R₃: Ground state wave packet.
- R₂ and R₄: Excited state wave packet.

Pump-Probe Signal:

\[ \delta I(\tau) \]

Wavepacket Dynamics: Quantum Beats in Pump-Probe

Population Relaxation of Excited State: \( e^{-\Gamma_{ab}\tau} \)