Liouville pathways

$$\vec{P}^{(3)}(t) = \int_0^\infty d\tau_3 \int_0^\infty d\tau_2 \int_0^\infty d\tau_1 \; \overleftrightarrow{S}^{(3)}(\tau_3,\tau_2,\tau_1)\,\vec{E}(t-\tau_3)\vec{E}(t-\tau_3-\tau_2) \times \vec{E}(t-\tau_3-\tau_2-\tau_1)$$

Two-level system:

$$\vec{S}^{(3)}(\tau_3,\tau_2,\tau_1) = (i)^3 \frac{\vec{d}\,d^3}{\hbar^3}\, tr\{\hat{m}\, \mathcal{U}_0(\tau_3)\mathcal{M}\,\mathcal{U}_0(\tau_2)\mathcal{M}\,\mathcal{U}_0(\tau_1) \times \mathcal{M}\rho(-\infty)\}$$

$$\mathcal{M}\hat{A} = [\hat{m},\hat{A}] \qquad m = |g\rangle\langle e| + |e\rangle\langle g|$$

8 term inside $S^{(3)}$

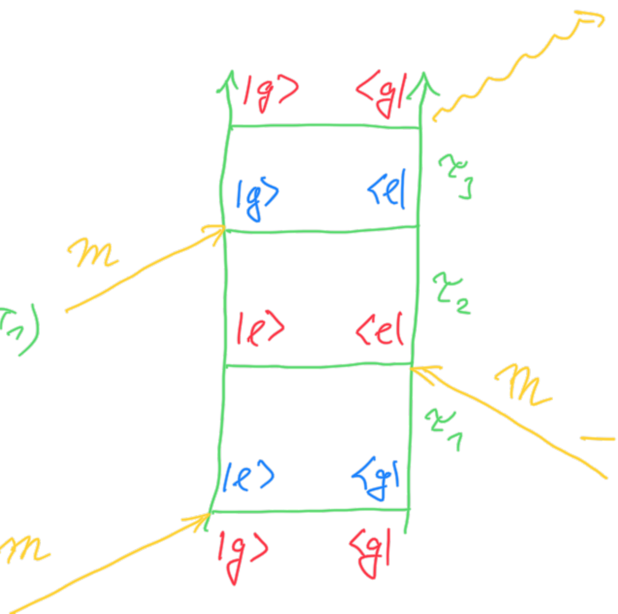
$$\vec{S}^{(3)}(\tau_3,\tau_2,\tau_1) = \sum_{n=1}^{8} \vec{R}_n^{(3)}(\tau_3,\tau_2,\tau_1)$$

Double-sided Feynman diagrams

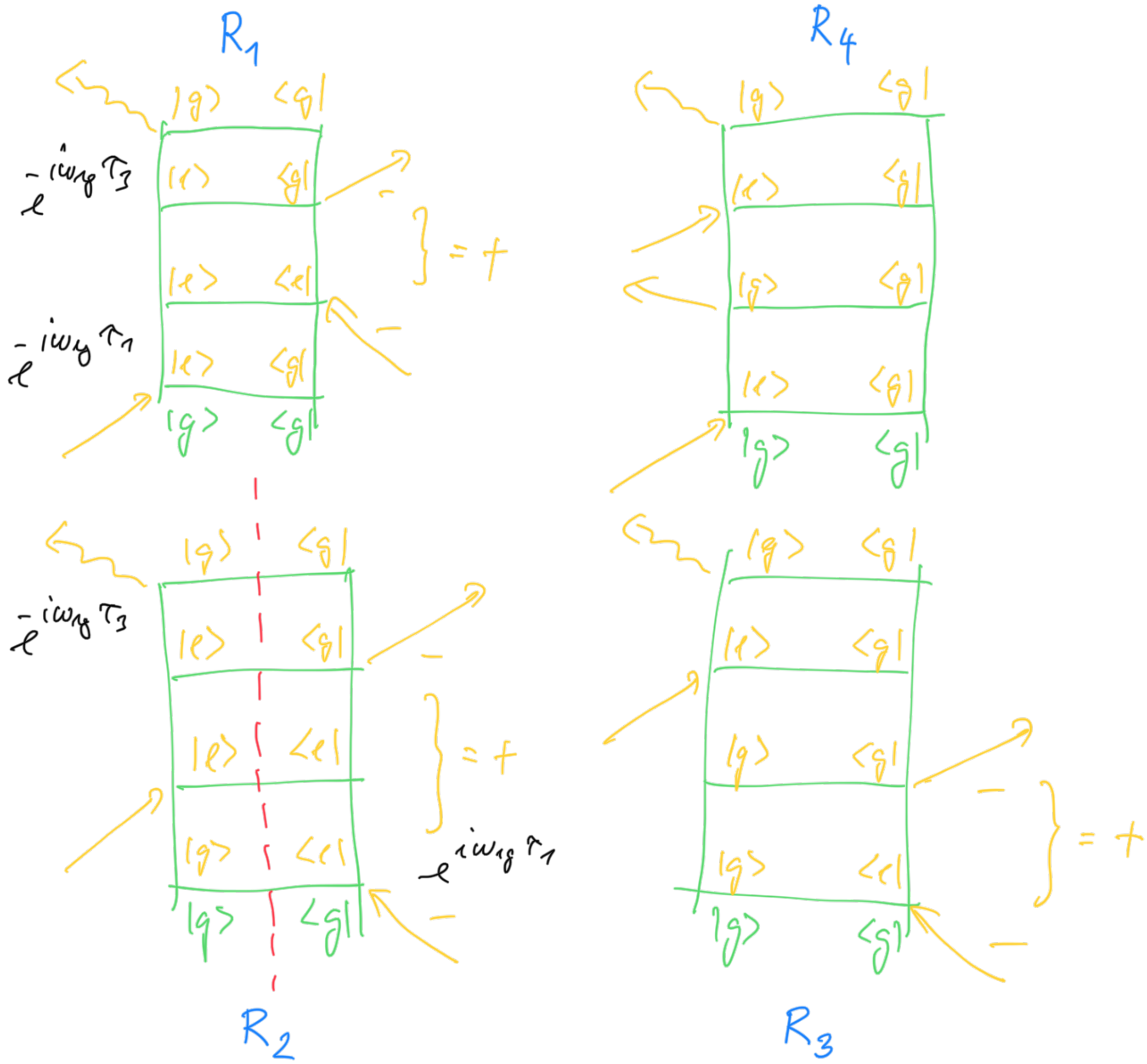
$$\hat{\rho}(-\infty) = \underline{|g\rangle}\underline{\langle g|}$$

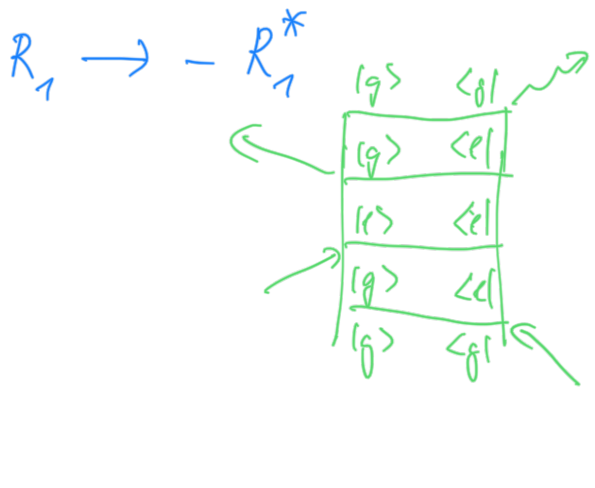
$\rightarrow \mathcal{U}_0(\tau_1)|e\rangle\langle g| \rightarrow$

$\rightarrow U_0(\tau_1)|e\rangle\langle g|U_0^\dagger(\tau_1)$



All positive sign diagrams



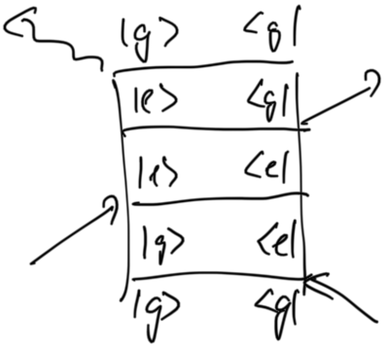


$$\vec{S}^{(3)}(\tau_3,\tau_2,\tau_1) = \sum_{n=1}^{4}\left[\vec{R}_n(\tau_3,\tau_2,\tau_1) - \vec{R}_n^{*}(\tau_3,\tau_2,\tau_1)\right]$$

Individual contributions to $\vec{S}^{(3)}$ are called $\boxed{\text{Liouville pathways}}$

Graphic representation of LPs

→ diagrams



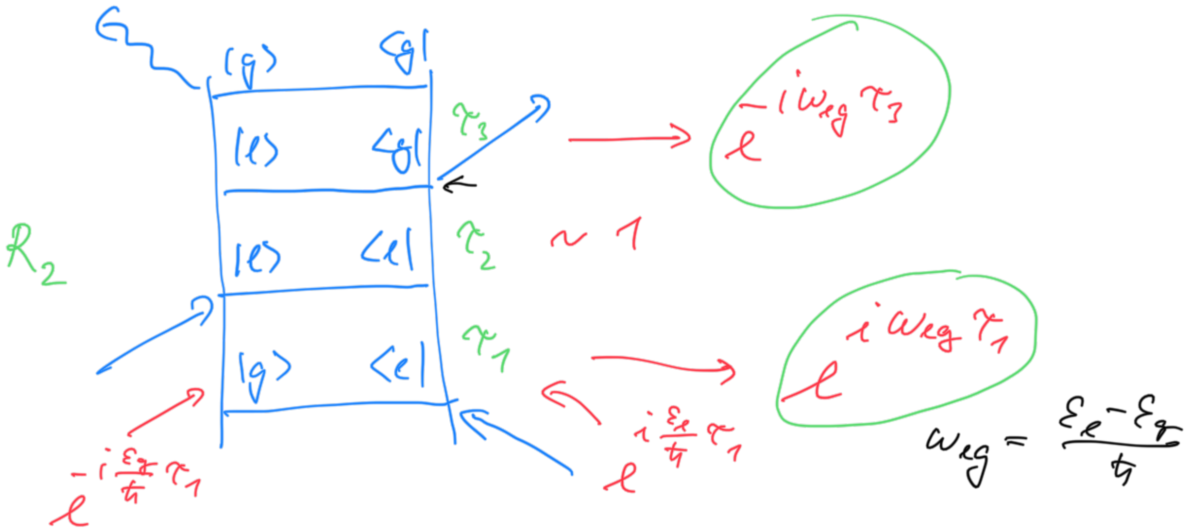
→ „pathways" in Liouville space

Hilbert space → basis: $|g\rangle$, $|e\rangle$

Liouville space → basis: $|g\rangle\langle g|$, $|g\rangle\langle e|$, $|e\rangle\langle g|$, $|e\rangle\langle e|$

$$
\begin{tikzcd}
|g\rangle\langle g| \arrow[r, "m"] & |g\rangle\langle e| \arrow[d, "m"] & \\
 & |e\rangle\langle e| \arrow[r, "m"] & |e\rangle\langle g| \arrow[d, "\hat{m}"] \\
 & & |g\rangle\langle g|
\end{tikzcd}
$$

The most important characteristic of LP is the phase factor in τ_1 and τ_3 intervals



$$R_2(\tau_3, \tau_2, \tau_1) = \left(\frac{i}{\hbar}\right)^3 d^4$$

$$tr$$

$$\left\{ \hat{m} \, \mathcal{U}_{egeg}(\tau_3) \overset{\approx 1}{\mathcal{U}_{eeee}(\tau_2)} |e\rangle\langle e| \hat{m} \left(\mathcal{U}_{gege}(\tau_1) \, |g\rangle\langle g| \hat{m} |e\rangle\langle e| \right) \hat{m} |g\rangle\langle g| \right\}$$

$$= \left(\frac{i}{\hbar}\right)^3 d^4 \, \mathcal{U}_{egeg}(\tau_3) \, \mathcal{U}_{eeee}(\tau_2) \, \mathcal{U}_{gege}(\tau_1)$$

$$= \left(\frac{i}{\hbar}\right)^3 d^4 \, \underbrace{\tilde{\mathcal{U}}_{egeg}(\tau_3)}_{e^{-iw_{eg}\tau_3}} \, \tilde{\mathcal{U}}_{eeee}(\tau_2) \, \underbrace{\tilde{\mathcal{U}}_{gege}(\tau_1)}_{e^{iw_{ge}\tau_1}}$$

$$R_2(\tau_3,\tau_2,\tau_1) = \left(\frac{i}{\hbar}\right)^3 d^4\, \tilde{R}_2(\tau_3,\tau_2,\tau_1)\, e^{-i\omega_{eg}(\tau_3 - \tau_1)}$$

$$R_1(\tau_3,\tau_2,\tau_1) = \left(\frac{i}{\hbar}\right)^3 d^4\, \tilde{R}_1(\tau_3,\tau_2,\tau_1)\, e^{-i\omega_{eg}(\tau_3 + \tau_1)}$$

$$R_3(\tau_3,\tau_2,\tau_1) = \left(\frac{i}{\hbar}\right)^3 d^4\, \tilde{R}_3(\tau_3,\tau_2,\tau_1)\, e^{-i\omega_{eg}(\tau_3 - \tau_1)}$$

$$R_4(\tau_3,\tau_2,\tau_1) = \left(\frac{i}{\hbar}\right)^3 d^4\, \tilde{R}_4(\tau_3,\tau_2,\tau_1)\, e^{-i\omega_{eg}(\tau_3 + \tau_1)}$$

Two different types of phase factors

$e^{-i\omega_{eg}(\tau_3 - \tau_1)}$ ... rephasing phase factor

$\boxed{\tau_1 = \tau_3} \Rightarrow e^{-i\omega_{eg}(\tau_3 - \tau_1)} \approx 1$

$e^{-i\omega_{eg}(\tau_3 + \tau_1)}$ ... non-rephasing phase factor

Polarization

$$\vec{P}(t) = \left(\frac{i}{\hbar}\right)^3 \vec{d}\, d^3 \int_0^\infty d\tau_3 \int_0^\infty d\tau_2 \int_0^\infty d\tau_1 \sum_{n=1}^{4} \left(R_n(\tau_3,\tau_2,\tau_1) - R_n^* \right)$$
$$\times E(t-\tau_3)\, E(t-\tau_3-\tau_2)\, E(t-\tau_3-\tau_2-\tau_1)$$

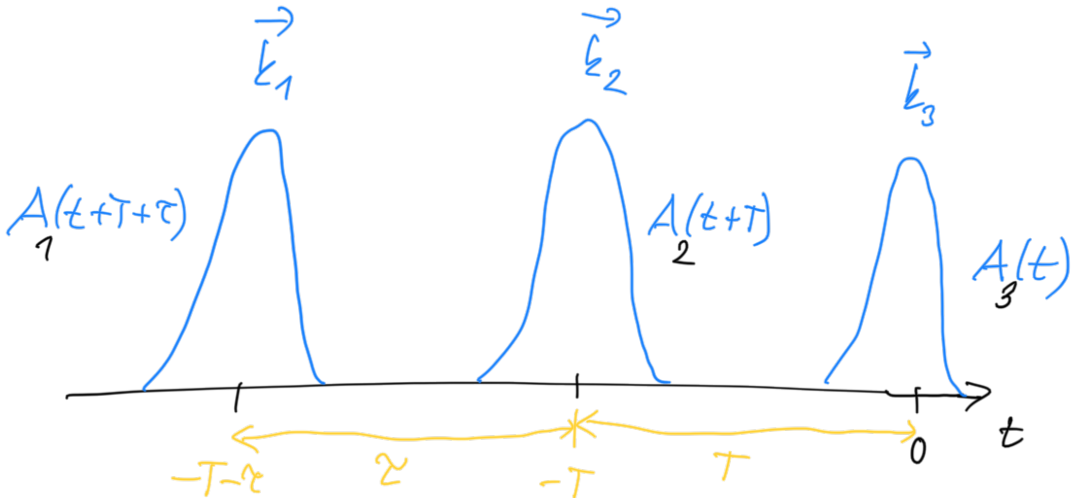
$\Rightarrow$ single contribution

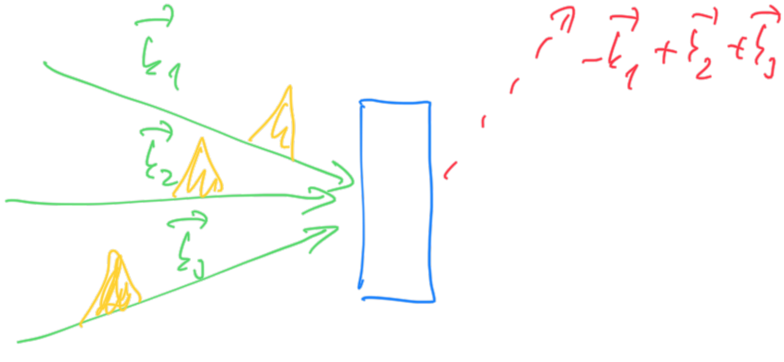
$$\int_0^\infty d\tau_3 \int_0^\infty d\tau_2 \int_0^\infty d\tau_1 \, \tilde{R}_2(\tau_3,\tau_2,\tau_1)\, e^{-i\omega_{eg}(\tau_3-\tau_1)} \; E(\dots)E(\dots)E(\dots)$$

also contains $e^{i\omega\tau_1}$ etc.

$$\boxed{\omega \sim \omega_{eg}}$$

General third-order pulse organization





$$E(t) = A_1(t+T+\tau)\, e^{-i\omega(t+T+\tau)+i\vec{k}_1\cdot\vec{r}}$$
$$+ A_2(t+T)\, e^{-i\omega(t+T)+i\vec{k}_2\cdot\vec{r}}$$
$$+ A_3(t)\, e^{-i\omega t+i\vec{k}_3\cdot\vec{r}} + c.c.$$

6 terms

$E(t-\tau_3)E(t-\tau_3-\tau_2)E(t-\tau_3-\tau_2-\tau_1) \sim 6^3 = 216$ terms

$$EEE \sim e^{i(\pm\vec{k}_1\pm\vec{k}_2\pm\vec{k}_3)\cdot\vec{r}-i(\pm\omega\pm\omega\pm\omega)t}$$
$$\sim e^{-i\omega t} \qquad \boxed{\vec{k}_s = -\vec{k}_1+\vec{k}_2+\vec{k}_3}$$

Order of the pulses

$$E(t-\tau_3) \approx e^{i\vec{k}_3\cdot\vec{r}}\, A_3(t-\tau)\, e^{-i\omega(t-\tau_3)+i\vec{k}_3\cdot\vec{r}}$$
$$E(t-\tau_3-\tau_2) \approx e^{i\vec{k}_2\cdot\vec{r}}\, A_2(t+T-\tau_3-\tau_2)\, e^{-i\omega(t+T-\tau_3-\tau_2)}\, e^{+i\vec{k}_2\cdot\vec{r}}$$
$$E(t-\tau_3-\tau_2-\tau_1) \approx e^{-i\vec{k}_1\cdot\vec{r}}\, A_1^*(t+T+\tau-\tau_3-\tau_2-\tau_1)\, e^{+i\omega(t+T+\tau-\tau_3-\tau_2-\tau_1)} \times e^{-i\vec{k}_1\cdot\vec{r}}$$

One of the 8×216 contributions to $\vec{P}$

$$\simeq \int_0^\infty d\tau_3 \int_0^\infty d\tau_2 \int_0^\infty d\tau_1\, \underline{\tilde{R}_2(\tau_3,\tau_2,\tau_1)}\, e^{-i\omega_{eg}(\tau_3-\tau_1)}$$
$$\times\, \underline{A_3(t-\tau_3)\, A_2(t+T-\tau_3-\tau_2)\, A_1^*(t+T+\tau-\tau_3-\tau_2-\tau_1)}$$

$$\times e^{-i\omega(t-\tau_3)-i\omega(\cancel{t+T}-\cancel{\tau_3}-\cancel{\tau_2})+i\omega(\cancel{t+T}+\tau-\cancel{\tau_3}-\cancel{\tau_2}-\tau_1)}$$

$$\times e^{i(\vec{k}_1+\vec{k}_2+\vec{k}_3)\cdot\vec{r}}$$

$$= e^{-i\omega(t-\tau)}\int_0^\infty d\tau_3\int_0^\infty d\tau_2\int_0^\infty d\tau_1\ \hat{R}_2(\tau_3,\tau_2,\tau_1)A_3(t-\tau_3)A_2(t+T-\tau_3-\tau_2)$$

$$\times A_1^*(t+T+\tau-\tau_3-\tau_2-\tau_1)$$

$$\times e^{-i\omega_{eg}(\tau_3-\tau_1)}\ e^{i\omega(\tau_3-\tau_1)}$$

transition freq. frequency of laser

$$\boxed{\omega_{eg}\approx\omega}$$

Two-level system + exact resonance

$$\omega_{eg}=\omega$$

$$P(t)\sim e^{-i\omega_{eg}(t-\tau)}\int_0^\infty d\tau_3\int_0^\infty d\tau_2\int_0^\infty d\tau_1\ \hat{R}_2(\tau_3,\tau_2,\tau_1)$$

$$\times A_3(t-\tau_3)A_2(t+T-\tau_3-\tau_2)$$

$$\times A_1^*(t+T+\tau-\tau_3-\tau_2-\tau_1)$$

$$A(t)=A_0\delta(t)\longrightarrow$$  ← very short pulse

$$A_3(t-\tau_3)\longrightarrow\tau_3\equiv t$$

$$A_2(t+T-\tau_3-\tau_2)\to A_2(T-\tau_2)\to\tau_2\equiv T$$

$$A_1^*(t+T+\tau-\tau_3-\tau_2-\tau_1)\to A_1^*(\tau-\tau_1)\to\tau_1\equiv\tau$$

$$P(t) = \left(\frac{i}{\hbar}\right)^3 d^4 e^{-i\omega_{eg}(t-\tau)} \tilde{R}_2(t,T,\tau) A_0^3 e^{i(-\vec{k}_1+\vec{k}_2+\vec{k}_3)\cdot\vec{r}} + \ldots \text{ other terms}$$

Phase factor of R_n → crucial for survival of the term under the integration

$\tilde{R}_3(t,T,\tau)$ will also contribute

<u>What about R_1 and R_4?</u>

$$\int_0^\infty d\tau_3 \int_0^\infty d\tau_2 \int_0^\infty d\tau_1 \ldots \underbrace{e^{-i\omega_{eg}(\tau_3+\tau_1)} e^{-i\omega(\tau_3-\tau_1)}}_{e^{-i(\omega_{eg}+\omega)\tau_3}}$$

← fast oscillation integral ~0

$R_1^* \rightarrow e^{i\omega_{eg}(\tau_3+\tau_1)}$ ← fast oscillation in τ_1

$R_4^* \rightarrow e^{i\omega_{eg}(\tau_3+\tau_1)}$

$R_2^* \rightarrow e^{i\omega_{eg}(\tau_3-\tau_1)}$ ← fast oscillations in τ_1 and τ_3

R_3^* — " —

Only $R_2 + R_3$ pathways contribute to the signal in the direction $-\vec{k}_1+\vec{k}_2+\vec{k}_3$

! order of pulses 1−2−3

Same order of pulses – different direction

$$-\vec{k}_2+\vec{k}_1+\vec{k}_3 \quad = \vec{k}_1-\vec{k}_2+\vec{k}_3$$

$$E(t-\tau_3) \simeq e^{i\vec{k}_3\cdot\vec{r}} \quad A_3(t-\tau_3)\, e^{-i\omega(t-\tau_3)+i\vec{k}_3\cdot\vec{r}}$$

$$E(t-\tau_3-\tau_2) \approx e^{-i\vec{k}_2\cdot\vec{r}} \quad A^*(t+T-\tau_3-\tau_2)\, e^{i\omega(t+T-\tau_3-\tau_2)-i\vec{k}_2\cdot\vec{r}}$$

$$E(t-\tau_3-\tau_2-\tau_1) \approx e^{i\vec{k}_1\cdot\vec{r}} \quad A(t+T+\tau-\tau_3-\tau_2-\tau_1)$$
$$\times\, e^{-i\omega(t+T+\tau-\tau_3-\tau_2-\tau_1)+i\vec{k}_1\cdot\vec{r}}$$

$$EEE \sim e^{-i\omega(t-\tau_3)+i\omega(\cancel{t}\cancel{+T}\cancel{-\tau_3}-\tau_2)-i\omega(\cancel{t}\cancel{+T}+\tau\cancel{-\tau_3}\cancel{-\tau_2}-\tau_1)}$$

$$= e^{-i\omega(t+\tau)}\; e^{i\omega(\tau_3+\tau_1)}$$

non-rephasing phase factor (it's opposite)

In the direction of $\vec{k}_1-\vec{k}_2+\vec{k}_3$, when the order of pulses is 1-2-3, we get non-rephasing pathway.

Different ordering of pulses – same direction

$$\vec{k}_s = -\vec{k}_1 + \vec{k}_2 + \vec{k}_3$$

order of pulses $\rightarrow$ 2 – 1 – 3

$$E(t-\tau_3) \simeq A_3(t-\tau_3)\, e^{-i\omega(t-\tau_3) + i\vec{k}_3\cdot\vec{r}}$$

$$E(t+T-\tau_3-\tau_2) \approx A_1^*(t+T-\tau_1-\tau_2)\, e^{i\omega(t+T-\tau_3-\tau_2) - i\vec{k}_1\cdot\vec{r}}$$

$$E(t+T+\tau-\tau_3-\tau_2-\tau_1) \approx A(t+T+\tau-\tau_3-\tau_2-\tau_1)\, e^{-i\omega(t+T+\tau-\tau_3-\tau_2-\tau_1)}\, e^{i\vec{k}_1\cdot\vec{r}}$$

$$\approx e^{-i\omega(t+\tau)}\, e^{-i\omega_{eg}(t+\tau)}$$

non-rephasing factor