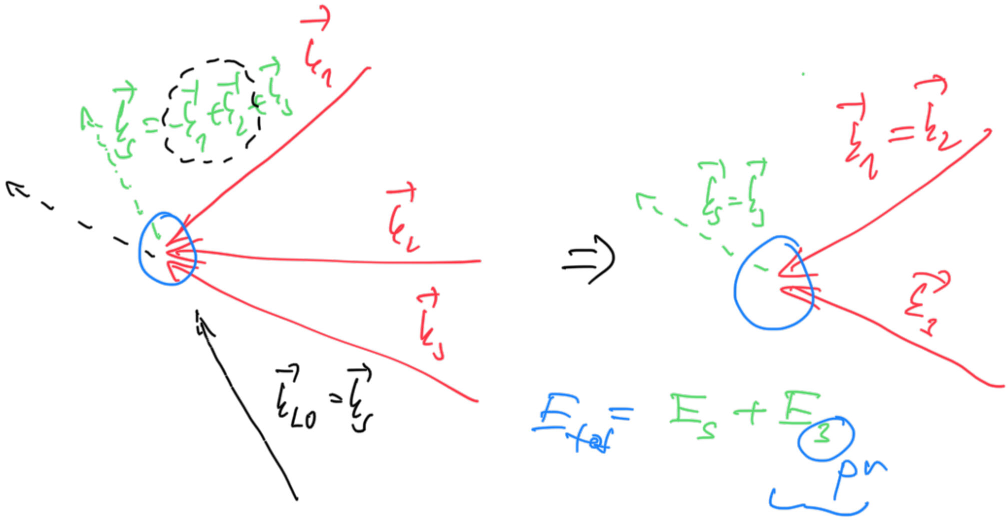
Pump-probe spectroscopy



$$E_{tot} = E_s + \underbrace{E^{(3)}_{pr}}_{E_{pr}}$$

Signal field

$$E_s(t) \approx i\omega \left(P^{(1)}(t) + P^{(3)}(t)\right) h$$

$$E_s(\omega) \approx i\omega \left(P^{(1)}(\omega) + P^{(3)}(\omega)\right) h$$

$$= i\omega \left(\varepsilon_0 \chi^{(1)}(\omega) E_{pr}(\omega) + \varepsilon_0 \chi^{(3)}(\omega; T, \tau) E_{pr}(\omega)\right)$$

$$\frac{\Delta I}{I_0} = \frac{I - I_0}{I_0}$$

$$I_0 \approx |E_{pr}(\omega)|^2$$

when pump is zero

$$\approx |E_{pr}(\omega) + E^{(1)}(\omega)|^2$$

probe is zero

$$I \approx |E_{pr}(\omega) + E^{(1)}(\omega) + E^{(3)}(\omega)|^2$$

depends on E_{pr}

$$I \approx |E_{pr}(\omega) + E^{(1)}(\omega)|^2 + |E^{(3)}(\omega)|^2 + 2\mathrm{Re}\left(\left(E_{pr}^*(\omega) + E^{(1)*}(\omega)\right) \times E^{(3)}(\omega)\right)$$

$$\approx I_0 + \text{very small} + \underline{2\,\mathrm{Re}\, E_{pr}^*(\omega)\, E^{(3)}(\omega)} + \text{very small}$$

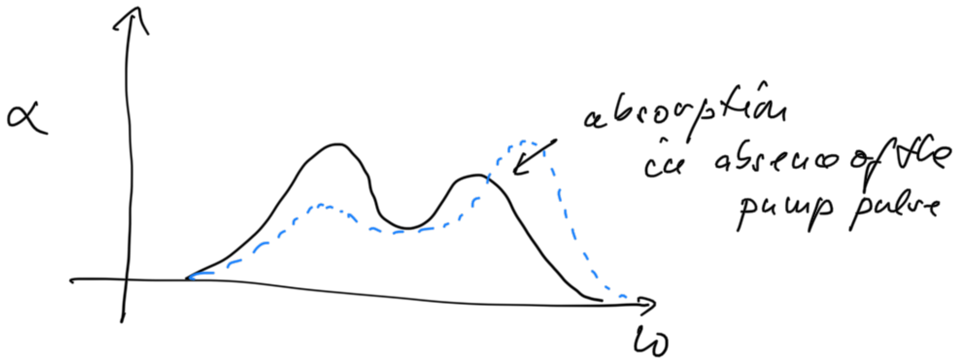
$$\frac{\Delta I}{I_0} = \frac{2\,\mathrm{Re}\, E_{pr}^*(\omega)\, E^{(3)}(\omega)}{|E_{pr}(\omega)|^2} = \frac{\varkappa\, 2\,\mathrm{Re}\, E_{pr}^*(\omega)\, i\omega\, \varepsilon_0\, \chi^{(3)}(\omega)\, E_{pr}(\omega)\, h}{\cancel{|E_{pr}(\omega)|^2}} \quad \sim \cancel{|E_{pr}|^2}$$

$$= -\varkappa\omega\, \varepsilon_0\, \mathrm{Im}\, \chi^{(3)}(\omega; T, \tau)\, h$$

$$\mathrm{Re}\, i(a+ib) = -b$$

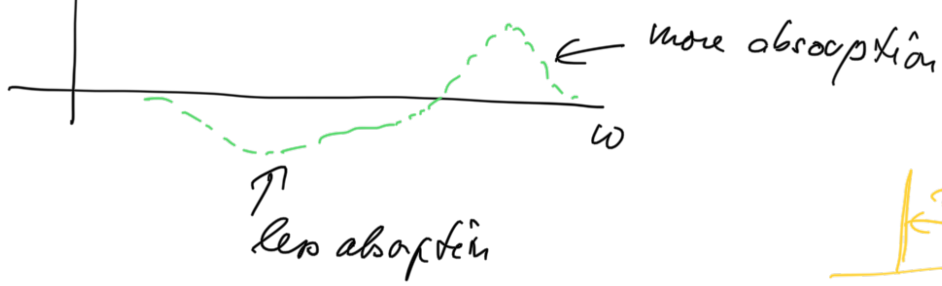
$$\frac{\Delta I}{h I_0} = -\alpha^{(3)}(\omega)$$

$$\boxed{\alpha^{(3)}(\omega) \approx \omega\, \mathrm{Im}\, \chi^{(3)}(\omega; T, \tau)}$$



$\Rightarrow$

$$\Delta\alpha = \alpha^{(1)}(\omega) + \alpha^{(3)}(\omega) - \alpha^{(1)}(\omega)$$



$$E_s(\omega) \approx i\omega P(\omega) h \propto i\omega \left(\frac{i}{\hbar}\right)^3 \int_{-\infty}^{\infty} dt\, \tilde{R}_2(t, T, \tau)\, \underline{|A_{pu}|^2 A_{pr}}$$

$$\times\, \underbrace{e^{-i\omega_{eg}(t-\tau)}\, e^{i\omega t}}_{\Downarrow\; \tilde{R}_2(\omega-\omega_{eg}, T, \tau)}$$

Linear absorption analogy

$$\alpha(\omega) \simeq \omega \, \mathrm{Im}\, \chi(\omega)$$

$$= -\frac{\mathrm{Re}\, E_0^*(\omega)(i\omega P)}{|E_0|^2} = \frac{\mathrm{Im}\, E_0^* E_0 \omega \chi}{|E_0|^2}$$

$$= \omega \chi''(\omega)$$

$$\chi^{(3)}(\omega; T, \tau) = \int_{-\infty}^{\infty} dt \left(\frac{i}{\hbar}\right)^3 \tilde{R}_2(t; T, \tau) \ldots |A_{pu}|^2$$

$$= -\frac{i}{\hbar^3} \tilde{R}_2(\omega - \omega_{eg}; T, \tau) |A_{pu}|^2$$

$$\alpha^{(3)}(\omega) \propto \mathrm{Im}\, \chi^{(3)} = \mathrm{Im}\left(-i(a+ib)\right) = -a$$

$$\alpha^{(3)}(\omega) \simeq -\frac{\omega}{\hbar^3} \mathrm{Re}\, \tilde{R}_2(\omega - \omega_{eg}; T, \tau) |A_{pu}|^2$$

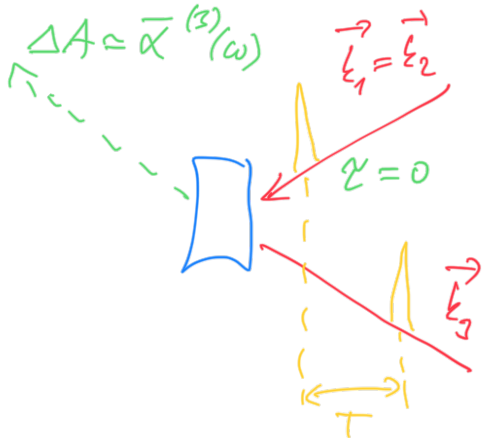
$$\alpha^{(3)}(\omega; T, \tau) \approx -\frac{\omega |A_{pu}|^2}{\hbar^3} \mathrm{Re}\, \underbrace{\mathcal{U}_{egeg}(\omega - \omega_{eg})}_{G_{eg}(\omega-\omega_{eg})} \mathcal{U}_{eeee}(T) \mathcal{U}_{gege}(\tau)$$

$T = 0 \quad \tau = 0$

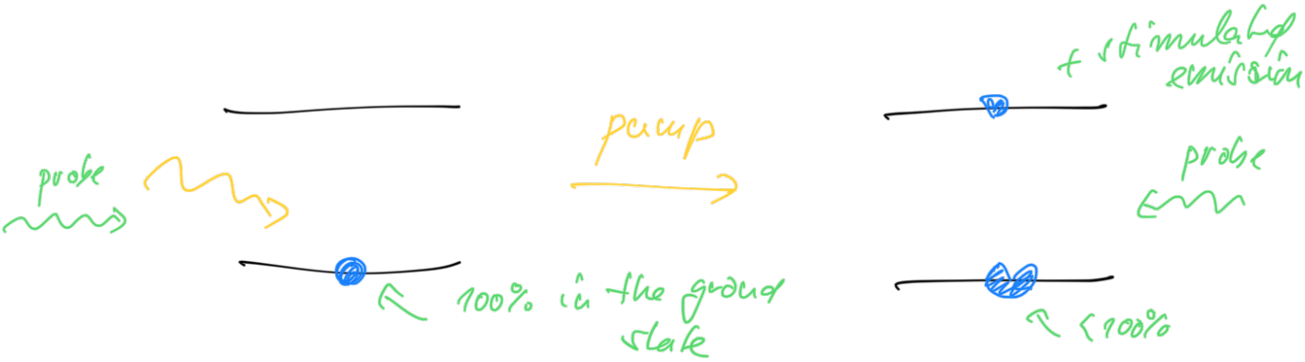
at $\tau = 0$ $\rightarrow$ no difference between rephasing and non-rephasing!

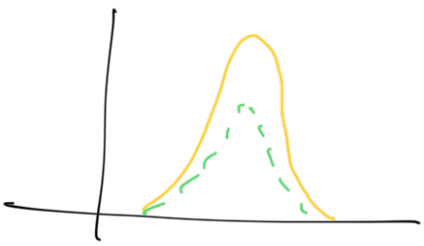
$$\bar{\alpha}^{(3)}(\omega) = \frac{\alpha^{(3)}(\omega)}{|A_{pu}|^2} \approx \ominus \frac{\omega}{\hbar^3} Re\left(G_{egeg}(\omega - \omega_{eg})\right)$$

$$\approx R_2 + R_3 + R_4 + R_1$$



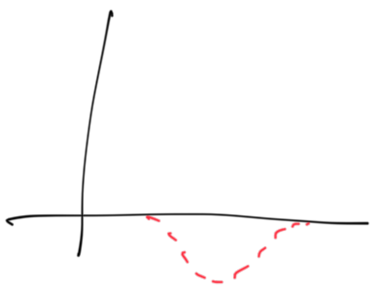
Two-level system





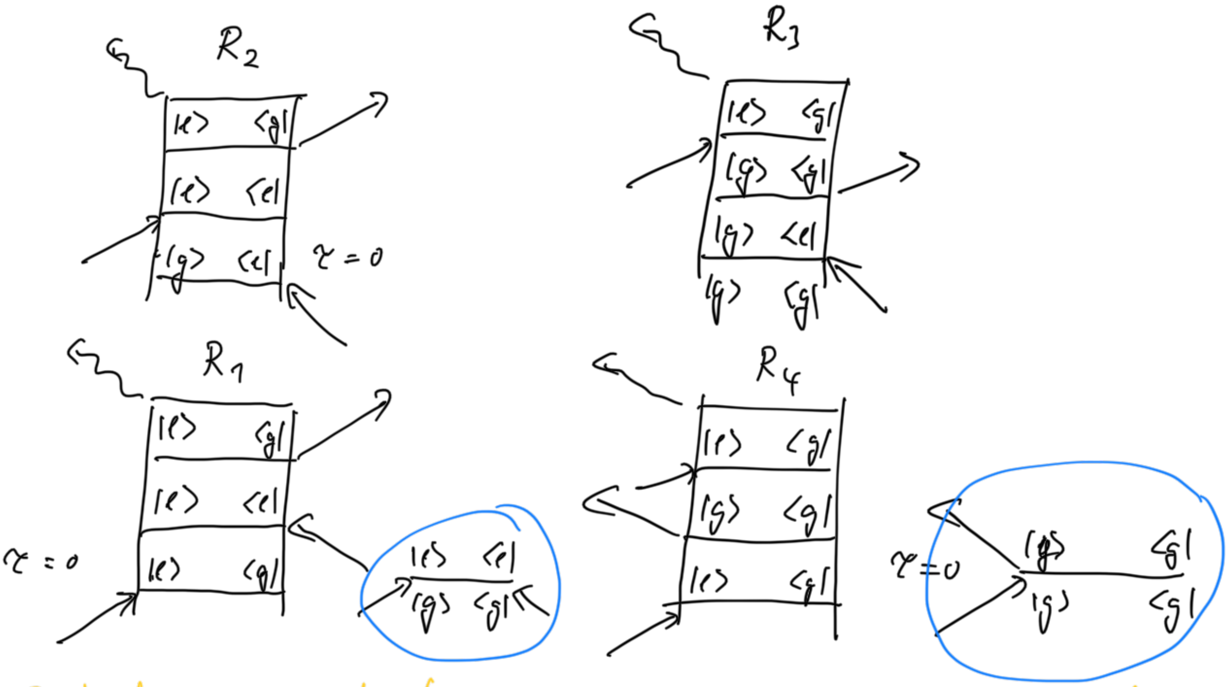
$\Delta A = \bar{\alpha}^{(3)}$

overall minus sign



Liouville pathways in pump-probe

$\tau = 0$ … impulsive limit $E(t) \approx \delta(t)$



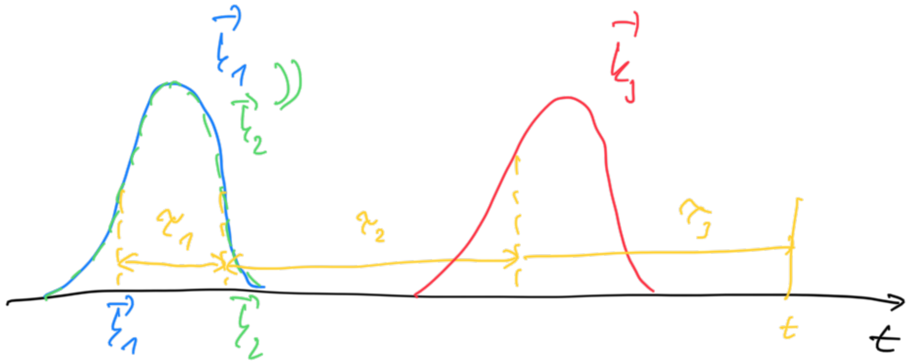
Rephasing + non-rephasing signal
– goes through the state |e>

Rephasing + non-rephasing signal
– goes through the state |g>

PP:

$-\vec{k}_1 + \vec{k}_2 + \vec{k}_3 \longrightarrow$ order $1-2-3 \rightarrow$ rephasing

$\vec{k}_1 \equiv \vec{k}_2$ order $2-1-3 \rightarrow$ non-rephas.

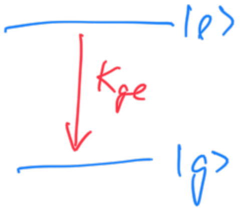


Stimulated emission

$$R^{(SE)} = \overset{\text{reph}}{R_2} + \overset{\text{non-rephasing}}{R_1} \approx \mathcal{U}_{egeg}(t)\,\underline{\mathcal{U}_{eeee}(T)}\,\underbrace{\mathcal{U}_{gege}(\tau=0)}_{}^{\approx 1}$$

$$R^{(GSB)} = R_3 + R_4 \approx \mathcal{U}_{egeg}(t)\,\underline{\mathcal{U}_{gggg}(T)}\,\mathcal{U}_{gege}(\tau=0)^{\approx 1}$$

Finite life-time in a TLS



$$\frac{\partial}{\partial t}\begin{pmatrix} p_1(t) \\ p_2(t) \\ \vdots \end{pmatrix} = \begin{pmatrix} K_{11}(t) & K_{12}(t) & \dots \\ K_{21}(t) & K_{22}(t) & \dots \\ \vdots & & \ddots \end{pmatrix}\begin{pmatrix} p_1(t) \\ p_2(t) \\ \vdots \end{pmatrix}$$

$$\frac{\partial}{\partial t} p_1(t) = \underbrace{K_{11}(t)}_{-\sum_{n\neq 1} K_{n1}(t)}\, p_1(t) + \underline{K_{12}(t)}\, p_2(t) + \dots$$

$$\begin{pmatrix} p_1(t) \\ p_2(t) \\ \vdots \end{pmatrix} = \begin{pmatrix} U_{11}(t) & U_{12}(t) & \dots \\ U_{21}(t) & U_{21}(t) & \\ \vdots & & \ddots \end{pmatrix}\begin{pmatrix} p_1(0) \\ p_2(0) \\ \vdots \end{pmatrix}$$

$$P_1(t) = U_{11}(t)\,P_1(0) + U_{12}(t)\,P_2(0) + \dots$$

$U_{11}(t)$ ... conditional probability that the system will start in state $|1\rangle$ and after time t end in state $|1\rangle$.

$U_{12}(t)$ ... conditional probability that the system will start in state $|2\rangle$ and after time t ends up in state $|1\rangle$

$$P_n(t) = \varrho_{nn}(t)$$

$$P_n(t) = \dots + U_{nm}(t)\,P_m(t) + \dots = + \dots + \mathcal{U}_{nnmm}(t)\,\varrho_{mm}(t) + \dots + \dots$$

$\mathcal{U}_{eeee}(t)$ ... conditional probability .... start in $|e\rangle$ ... ends in $|e\rangle$

$\mathcal{U}_{gggg}(t)$ ... conditional probability .. $|g\rangle$ ... $|g\rangle$

$\mathcal{U}_{ggee}(t)$ ... conditional probability that the system starts in state $|e\rangle$ and ends up in state $|g\rangle$

$$\frac{\partial}{\partial t} P_e(t) = -K_{ge} P_e(t)$$

$$\Rightarrow \quad P_e(t) = e^{-K_{ge} t} P_e(0)$$

$$\boxed{u_{eeee}(t) = e^{-K_{ge} t}}$$

$$\boxed{u_{gggg}(t) = 1}$$

$$u_{ggee}(t) = ?$$

$$P_g(t) = u_{gggg}(t) P_g(0) + u_{ggee}(t) P_e(0)$$

We have $\quad P_e(t) + P_g(t) = 1 \quad \forall t$

$$e^{-K_{ge}t} P_e(0) + P_g(0) + u_{ggee}(t) P_e(0) = 1$$

$$e^{-K_{ge}t} P_e(0) + (\cancel{1} - P_e(0)) + u_{ggee}(t) P_e(0) = \cancel{1}$$

$$u_{ggee}(t) P_e(0) = (1 - e^{-K_{ge}t}) P_e(0)$$

$$\boxed{u_{ggee}(t) = 1 - e^{-K_{ge}t}}$$

More general expression for $u_{ggee}(t)$

- the conditional probability to jump from $|e\rangle \to |g\rangle$ in unit time $= K_{ge}$

$$\frac{\partial}{\partial t} P_g(t) = + K_{ge} P_e(t)$$

- conditional probability to jump from $|e\rangle \to |g\rangle$ in time interval $(t, t+dt)$

$\to$ $K_{ge}\, dt$

$$P_g^{(e)}(t) = \int_0^t d\tau\, K_{ge} P_e(\tau) = \int_0^t d\tau\, K_{ge}\, \mathcal{U}_{eeee}(\tau) P_e(0)$$

$\Uparrow$

$$\mathcal{U}_{ggee}(t) P_e(0) = K_{ge} \int_0^t d\tau\, \mathcal{U}_{eeee}(\tau) P_e(0)$$

$$\boxed{\mathcal{U}_{ggee}(t) = K_{ge} \int_0^t d\tau\, \mathcal{U}_{eeee}(\tau)} = K_{ge} \int_0^t d\tau\, e^{-K_{ge}\tau}$$

$$= \boxed{1 - e^{-K_{ge} t}}$$