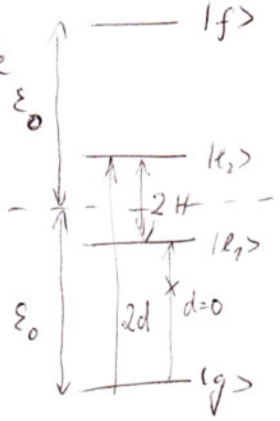
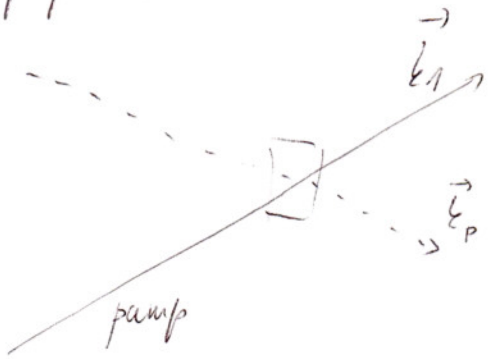
Let us investigate simple model systems with simple models for the energy gap correlation function

Relaxation in H-aggregates - studied by pump-probe

First three excited states would look like



Let us measure the life time of the state $|e_2\rangle$ by pump probe



Absorption without pump

$$\sigma(\omega) \approx \int_0^\infty dt\, e^{-g(t)+i(\omega-\omega_{eg})t}$$

Absorption of the probe after pulse can be calculated from $P(\omega)$ that is a result of interaction with $-\vec{E}_1 + \vec{E}_1 + \vec{E}_p$

biglets

$\vec{E}_1, \vec{E}_1$ 2 pulses at the same time

$t_1 = 0$

relaxation

$$P(t,T,0) \approx i\left[\bar{R}_2(t,T,0) + \bar{R}_3(t,T,0)\right] e^{-i\omega t} E_p^3$$

$$\bar{R}_2(t,T,0) \approx e^{-g^*(t) + g^*(T) - g(T) - \left[g^*(T+t) - g(T+t)\right]} \times e^{-kT}$$

q-is -(q+ic)

$$\bar{R}_3(t,T,0) \approx e^{-g(t)}$$

$$\bar{R}_3(t,T,0) = i|d|^4 e^{-g^*(t)} e^{-i\omega_{eg}t}$$

$$\bar{R}_2(t,T,0) = i|d|^4 e^{-g^*(t)} e^{-2i\,\mathrm{Im}\{g(T)-g(T+t)\}} e^{-Kt} e^{-i\omega_{eg}t}$$

$$g(t) = \Gamma t$$

↙

$$\bar{R}_3(t,T,0) = |d|^4 e^{-\Gamma t}$$

$$\bar{R}_2(t,T,0) = |d|^4 e^{-\Gamma t} e^{-KT}$$

$$P(t,T,0) = -i|d|^4 e^{-\Gamma t}\left(1+e^{-KT}\right) e^{-i\omega_{eg}t}$$

$$P(\omega,T,0) = -i|d|^4\left(1+e^{-KT}\right)\int_{-\infty}^{\infty} dt\, e^{-\Gamma t + i(\omega-\omega_{eg})t}\, E_{pump}^{(2)} E_0$$

$$= -i|d|^4\left(1+e^{-KT}\right)\left[\frac{-e^{-\Gamma t + i(\omega-\omega_{eg})\infty}}{\Gamma - i(\omega-\omega_{eg})}\right]_0 E_{pm}^2 E_0 = i|d|^4 \frac{1\left(1+e^{-KT}\right)}{\Gamma - i(\omega-\omega_{eg})} =$$

$$= i|d|^4 \frac{\left(1+e^{-KT}\right)}{\Gamma^2-(\omega-\omega_{eg})^2}\left(\Gamma + i(\omega-\omega_{eg})\right) \cdot E_{pm}^2 E_0$$

$$E_p(t) = E_0\,\delta(t)\,e^{-i\omega t} \Rightarrow E_p(\omega) = E_0$$

← lineshape

$$S_{disp}(\omega) = -\frac{4\pi\omega}{n(\omega)} |d|^4 \frac{\left(1+e^{-KT}\right)\Gamma}{\Gamma^2-(\omega-\omega_{eg})^2} E_0^2 E_{pump}^2 \Big/ E_0^2$$

this is a part of the background

Two-dimensional lineshapes

$$E(t,T,\tau) = i\omega P(t,T,\tau) = i\omega\, S^{(R)}(t,T,\tau)\, e^{-i\omega(t-\tau)}\,\Theta(\tau)$$

$$+ i\omega\, S^{(NR)}(t,T,-\tau)\, e^{-i\omega(t+\tau)}\,\Theta(-\tau)$$

$$\tilde{E}(\omega_t,T,\omega_\tau) \approx \int_0^\infty dt \int_{-\infty}^{\infty} d\tau \Big[S^{(R)}(t,T,\tau)\, e^{i\omega_t t - i\omega_\tau \tau}\, e^{-i\omega(t-\tau)}$$

$$+ S^{(NR)}(t,T,-\tau)\, e^{i\omega_t t - i\omega_\tau \tau}\, e^{-i\omega(t+\tau)} \Big]$$

$$\approx \int_0^\infty dt \int_0^\infty d\tau\; e^{+i(\omega_t-\omega)t}\, e^{-i(\omega_\tau-\omega)\tau}\, e^{-\Gamma t}\, e^{-\Gamma\tau}$$

(+) (−)

$$+ \int_0^\infty dt \int_{-\infty}^{0} d\tau\; e^{i(\omega_t-\omega)t}\, e^{-i(\omega_\tau-\omega)\tau}\, e^{-\Gamma t}\, e^{-\Gamma(-\tau)}$$

$$= \left(\frac{1}{i(\omega_t-\omega)-\Gamma}\left[e^{-\infty} - 1\right]\right)\left(\frac{1}{-i(\omega_\tau-\omega)-\Gamma}\left[e^{-\infty} - e^{0}\right]\right)$$

$$+ \int_0^\infty dt \int_0^\infty d\tau'\; e^{i(\omega_t-\omega)t}\, e^{+i(\omega_\tau-\omega)\tau'}\, e^{-\Gamma t - \Gamma\tau'}$$

(+) (+)

$$= \left(-\frac{1}{i(\omega_t-\omega)-\Gamma}\right)\left(\frac{1}{i(\omega_\tau-\omega)+\Gamma}\right) + \frac{+1}{i(\omega_t-\omega)-\Gamma}\,\frac{1}{i(\omega_\tau-\omega)-\Gamma}$$

↑ Rephasing part ↑ non-rephasing part

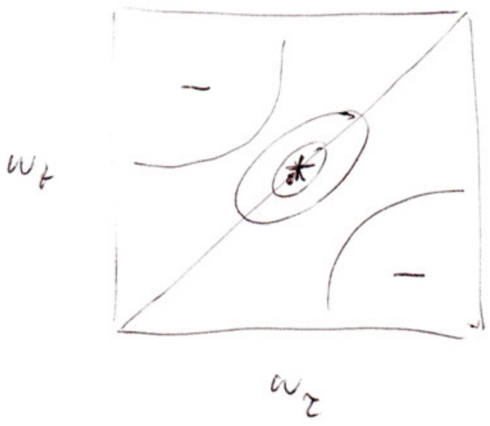
Rephasing part

$(a+ib)(a-ib) = a^2 - b^2$

$$-\frac{-\Gamma - i(\omega_t - \omega)}{\Gamma^2 - (\omega_t - \omega)^2} \cdot \frac{\Gamma - i(\omega_\tau - \omega)}{\Gamma^2 - (\omega_\tau - \omega)^2} =$$

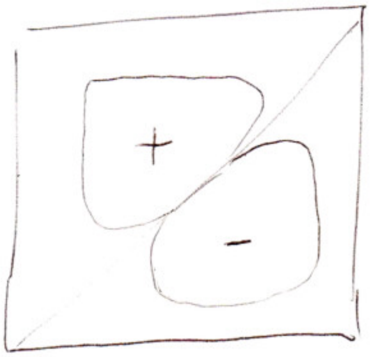
$$= \frac{\Gamma + i(\omega_t - \omega)}{\Gamma^2 - (\omega_t - \omega)^2} \cdot \frac{\Gamma - i(\omega_\tau - \omega)}{\Gamma^2 - (\omega_\tau - \omega)^2} = \frac{\Gamma^2 + (\omega_t - \omega)(\omega_\tau - \omega)}{(\Gamma^2 - (\omega_t - \omega)^2)(\Gamma^2 - (\omega_\tau - \omega)^2)}$$

$$+ i \frac{\Gamma[(\omega_t - \omega) - \omega_\tau + \omega]}{(\Gamma^2 - (\omega_t - \omega)^2)(\Gamma^2 - (\omega_\tau - \omega)^2)}$$



Real part

Max at $\omega \equiv \omega_t$ and $\omega \equiv \omega_\tau$



Imaginary part

if $\omega_t \equiv \omega_\tau$ $\quad Im = 0$

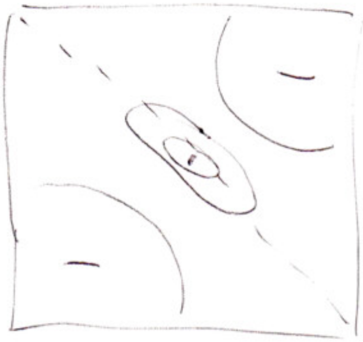
if $\omega_t > \omega_\tau$ $\quad Im +$

Non-rephasing part

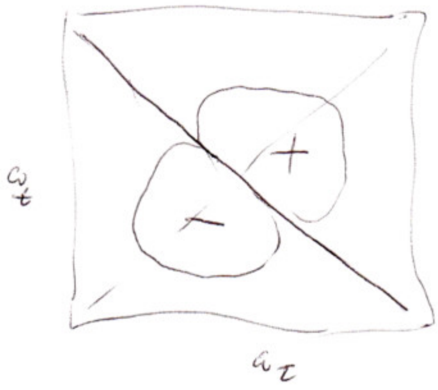
$$\frac{-\Gamma - i(\omega_t - \omega)}{\Gamma^2 - (\omega_t - \omega)^2} \cdot \frac{-\Gamma - i(\omega_\tau - \omega)}{\Gamma^2 - (\omega_\tau - \omega)^2} = \frac{\Gamma^2 + i\Gamma(\omega_t - \omega) + i\Gamma(\omega_\tau - \omega) - (\omega_\tau - \omega)(\omega_t - \omega)}{(\Gamma^2 - (\omega_t - \omega)^2)(\Gamma^2 - (\omega_\tau - \omega)^2)}$$

$$= \frac{\Gamma^2 - (\omega_\tau - \omega)(\omega_t - \omega)}{(\Gamma^2 - (\omega_t - \omega)^2)(\Gamma^2 - (\omega_t - \omega)^2)} + i \frac{\Gamma(\omega_t + \omega_\tau - 2\omega)}{(\Gamma^2 - (\omega_t - \omega)^2)(\ldots)}$$

Real part



Imaginary part

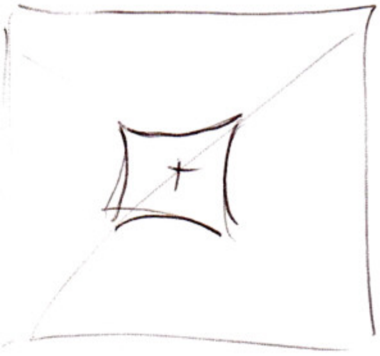


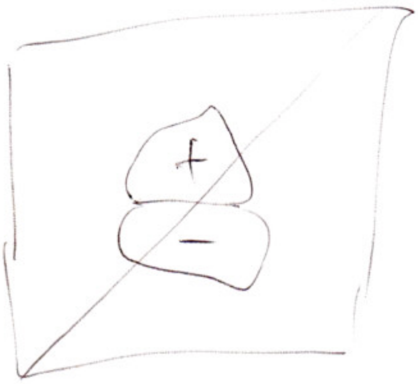
zero when $(\omega_t-\omega) = -(\omega_\tau-\omega)$

both $(\omega_t-\omega)>0$
$(\omega_\tau-\omega))>0$ $\Rightarrow$ Im >0

both $(\omega_t-\omega)<0$
$(\omega_\tau-\omega)<0$ $\Rightarrow$ Im <0

Complete spectra R + NR





The real part taken at $(\omega_t-\omega)=0$ gives

$$\frac{\Gamma^2}{\left(\Gamma^2-(\omega_t-\omega)^2\right)\left(\Gamma^2-(\omega_\tau-\omega)^2\right)} = \frac{1}{\Gamma^2-(\omega_\tau-\omega)^2}$$

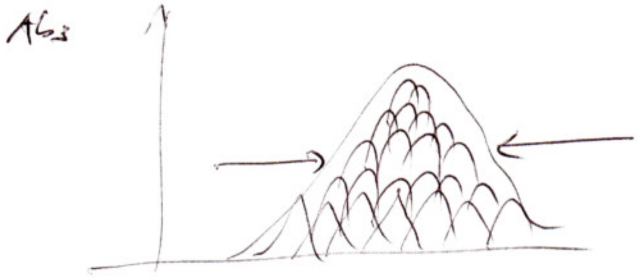
$(\omega_t-\omega)^2 = 0$

↗ homogeneous line shape.

Taking antidiagonal width just a little bit different, but approximately it gives the same result.

This remains true even if the system is inhomogeneously broadened.

Absorption spectrum and inhomogeneous broadening



inhomogeneous width is >> than the homogeneous

2D and IB