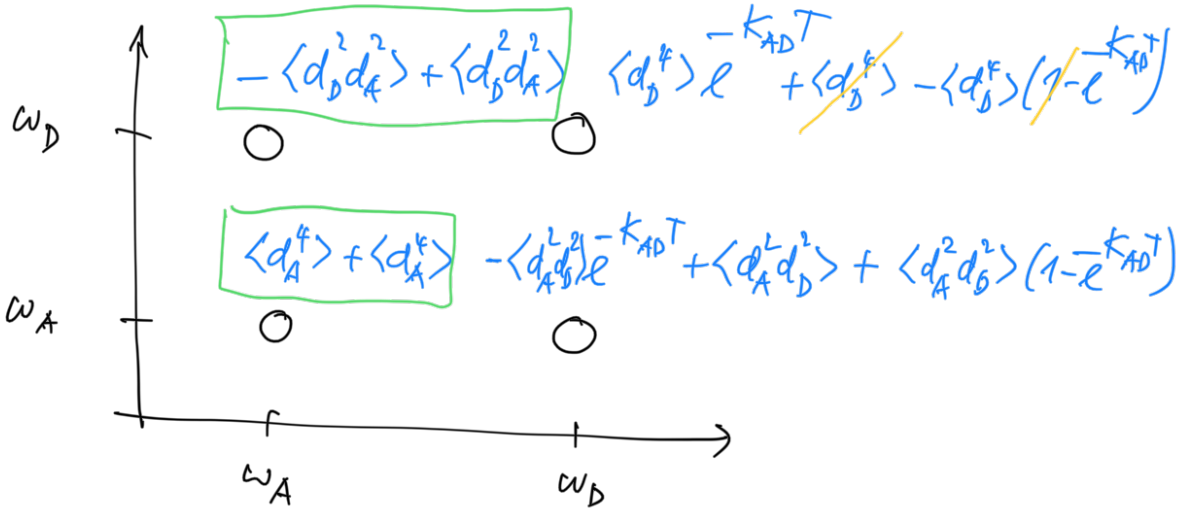
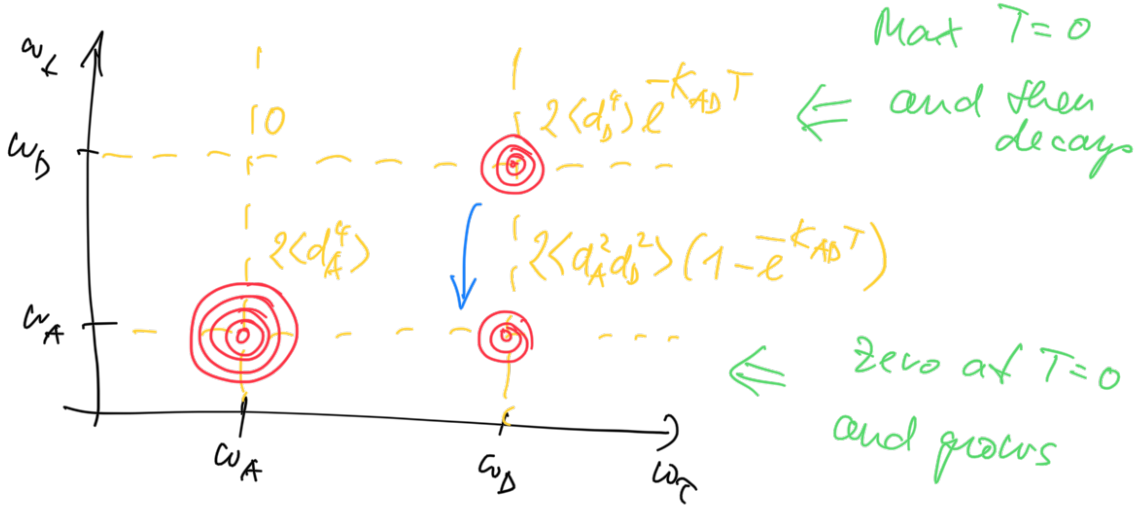
Properties of the 2D spectrum

amplitudes of the peaks





Max $T=0$ ⇐ and then decays

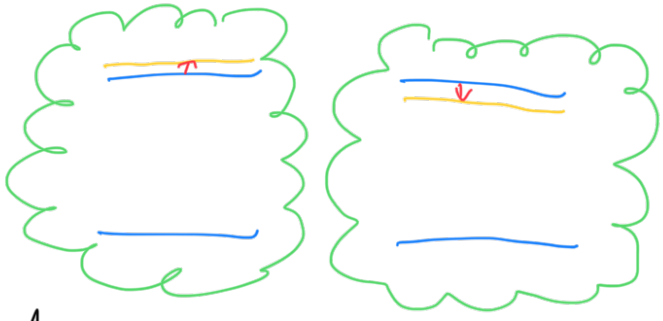
⇐ zero at $T=0$ and grows

at $T=0$, there are no crosspeaks!

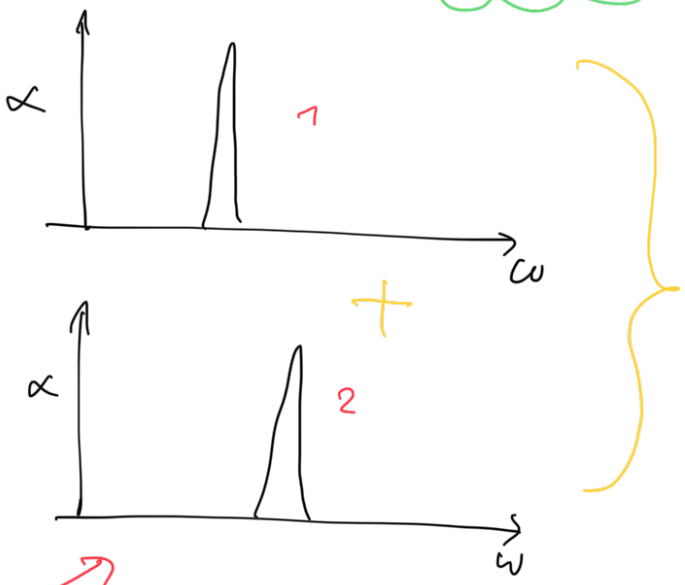
2DFT spectroscopy can observe/quantify energy transfer.

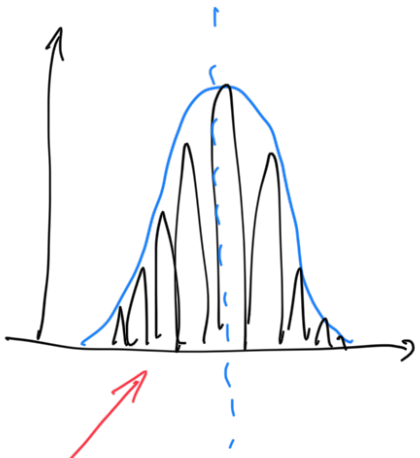
Energetic Disorder in 2DFT Spectroscopy

Energetic disorder



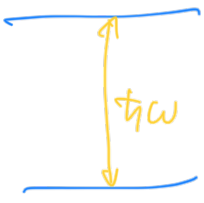
Different molecules have different environments
⇒ different transition energies

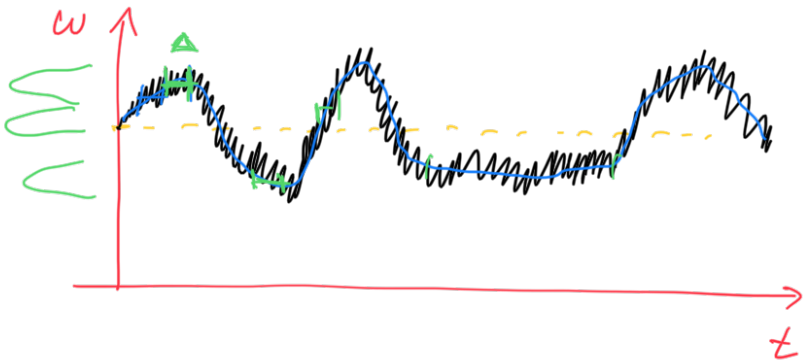




Inhomogeneously broadened lineshape

Homogeneously broadened —ll—





Ensemble spectrum?

- non-interacting molecules contribute additively !!!

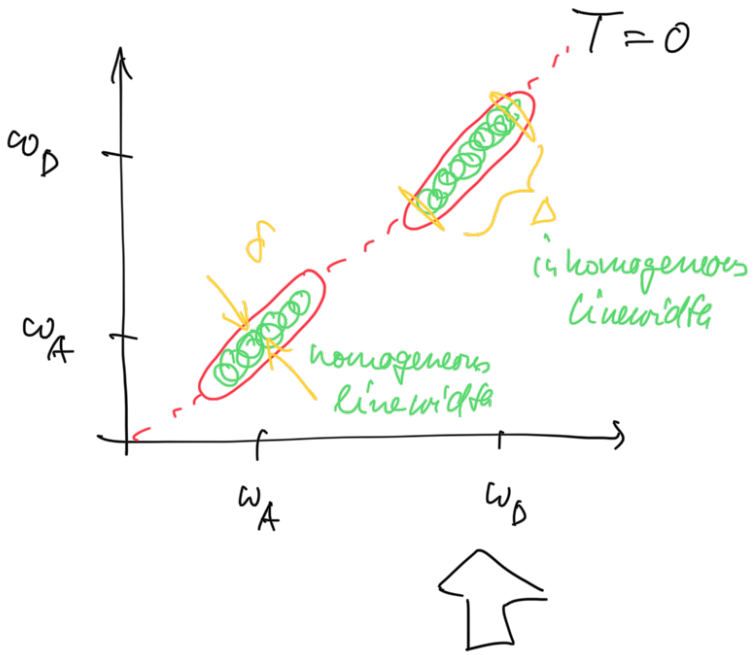
Ensemble of non-interacting entities has a spectrum which is a SUM of individual spectra !

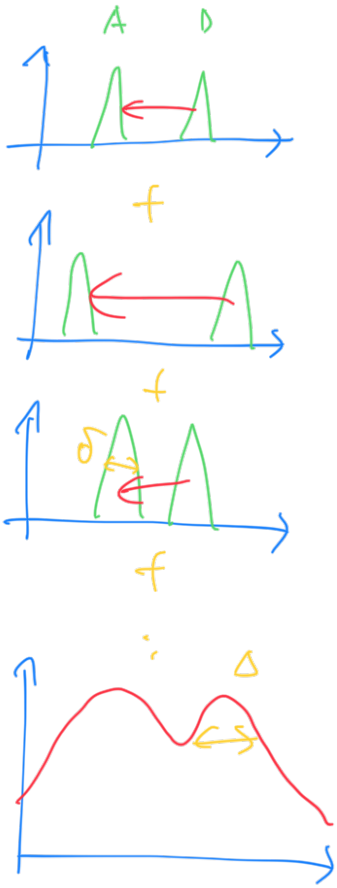
- absorption spectrum
- 2DFT spectrum

Proof for 2DFT spectrum:

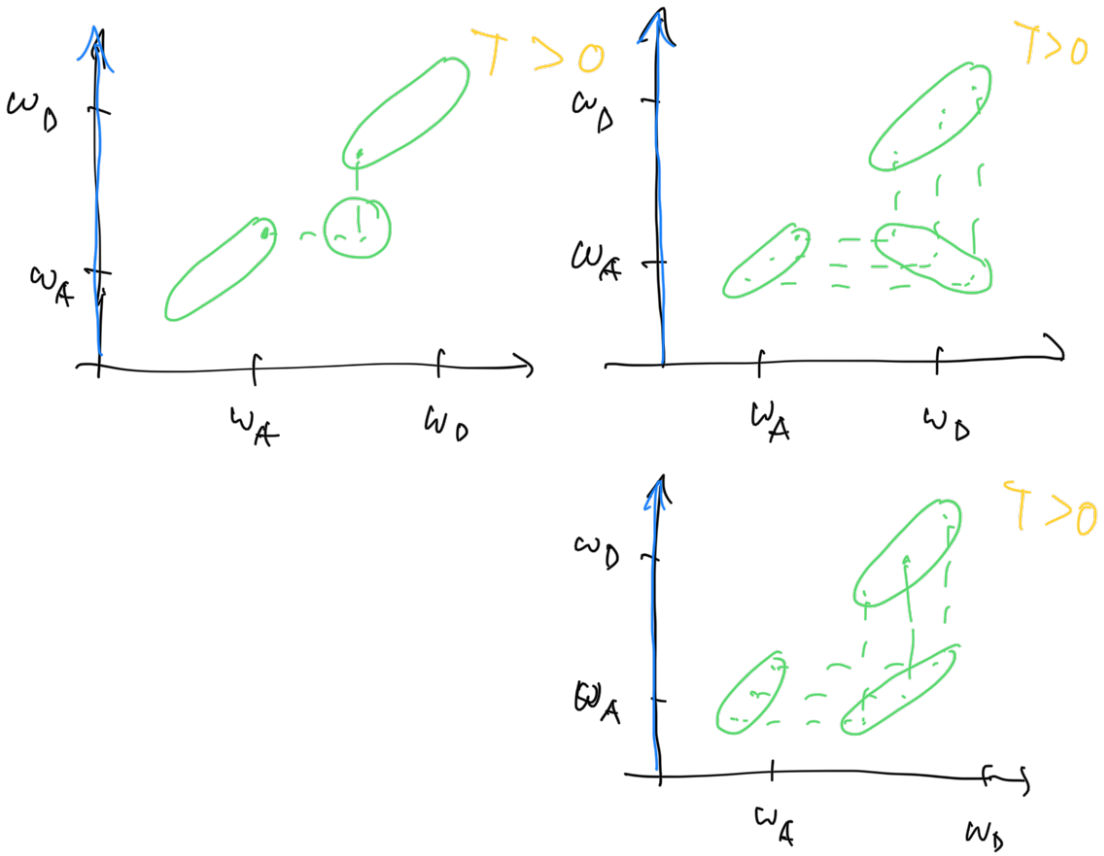
$K_{AD} = 0 \Rightarrow$ no crosspeaks

2DFT spectrum with disorder





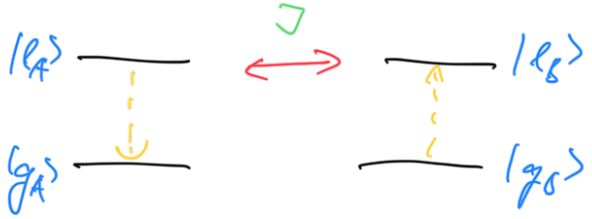
Other inhomogeneities!



Excitonic interaction in 2DFT spectroscopy

What we mean by interaction?

- coupling



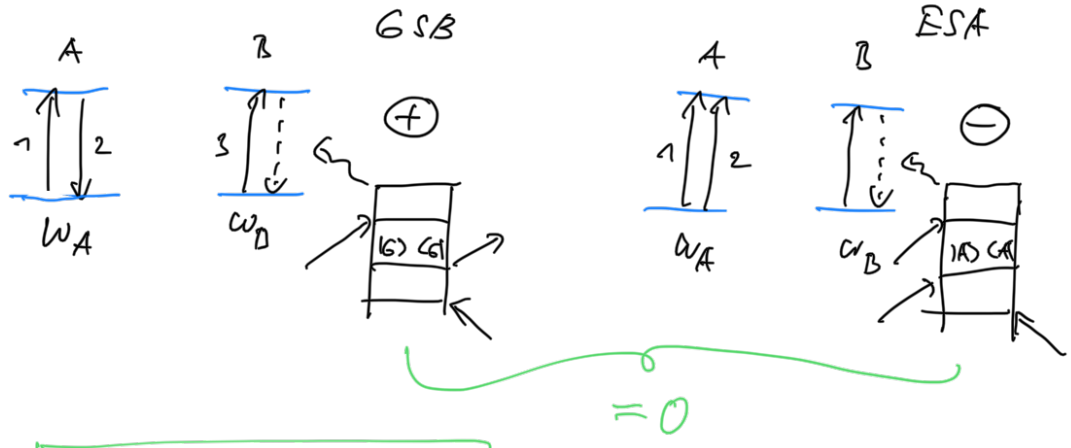
$$H = \begin{pmatrix} \varepsilon_g^A + \varepsilon_g^B & 0 & 0 & 0 \\ 0 & \varepsilon_e^A + \varepsilon_g^B & J & 0 \\ 0 & J & \varepsilon_g^A + \varepsilon_e^B & 0 \\ 0 & 0 & 0 & \varepsilon_e^A + \varepsilon_e^B \end{pmatrix}$$

if $J = 0$

molecules A and B independent

- cross-peaks are 0! at $T=0$ and $T>0$

In collective states:



if $|J| > 0$ (large)

Eigenstates of the Hamiltonian are DELOCALIZED

$$H = \begin{pmatrix} \varepsilon_A & J \\ J & \varepsilon_B \end{pmatrix} \qquad \varepsilon_A = \varepsilon_B = \varepsilon$$

Eigenstates

$$|+\rangle = \frac{1}{\sqrt{2}}\left(|A\rangle + |B\rangle\right)$$

$$|-\rangle = \frac{1}{\sqrt{2}}\left(|A\rangle - |B\rangle\right)$$

$$H|\psi\rangle = E|\psi\rangle \quad \Rightarrow$$

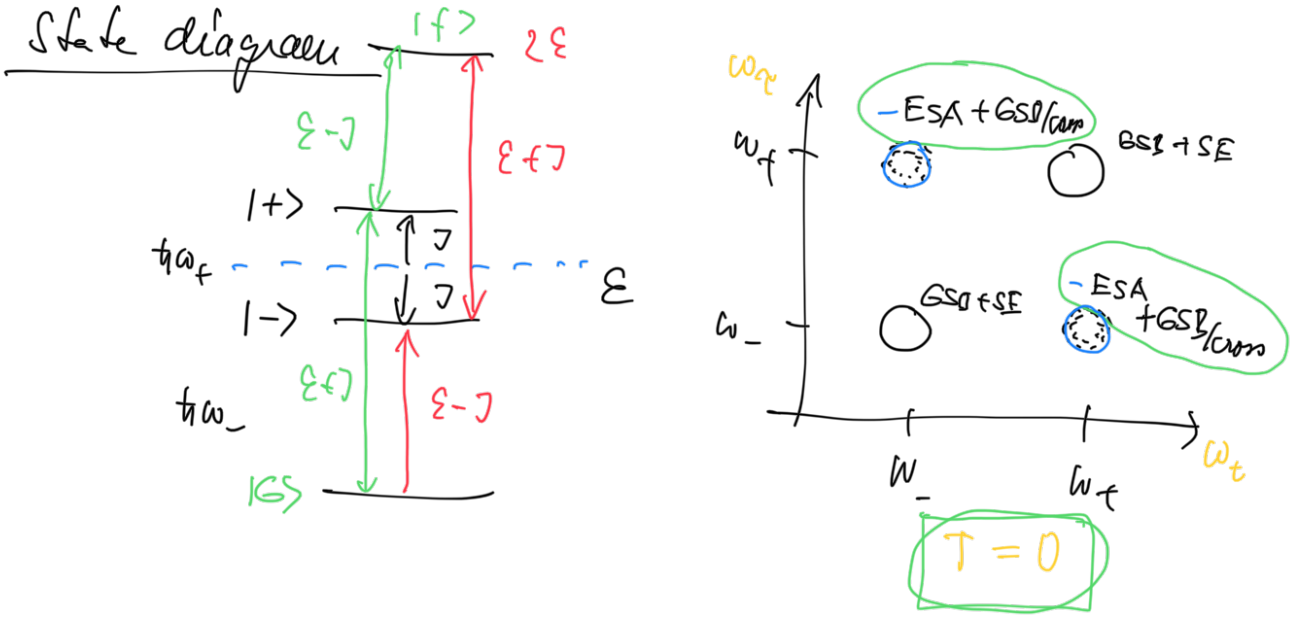
$|A\rangle + |B\rangle$

$$\begin{pmatrix} \varepsilon & J \\ J & \varepsilon \end{pmatrix}\begin{pmatrix} 1 \\ 1 \end{pmatrix} = \begin{pmatrix} \varepsilon + J \\ \varepsilon + J \end{pmatrix} = (\varepsilon + J)\begin{pmatrix} 1 \\ 1 \end{pmatrix}$$

$$\varepsilon_+ = \varepsilon + J$$

$$\begin{pmatrix} \varepsilon & J \\ J & \varepsilon \end{pmatrix}\begin{pmatrix} 1 \\ -1 \end{pmatrix} = \begin{pmatrix} \varepsilon - J \\ J - \varepsilon \end{pmatrix} = (\varepsilon - J)\begin{pmatrix} 1 \\ -1 \end{pmatrix}$$

$$\varepsilon_- = \varepsilon - J$$



Transition dipole moment operator

$$\hat{\vec{\mu}} = \vec{d}_A\,|A\rangle\langle G| + \vec{d}_B\,|B\rangle\langle G| + \vec{d}_B\,|f\rangle\langle A| + \vec{d}_A\,|f\rangle\langle B| + \text{h.c.}$$

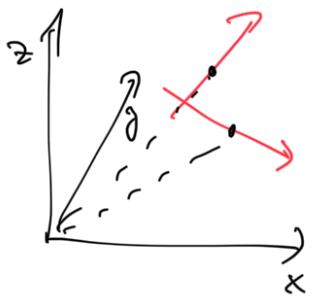
$$|A\rangle = \frac{1}{\sqrt{2}}\left(|+\rangle + |-\rangle\right)$$

$$|B\rangle = \frac{1}{\sqrt{2}}\left(|+\rangle - |-\rangle\right)$$

$$\hat{\vec{\mu}} = \left[\frac{\vec{d}_A}{\sqrt{2}}\left(|+\rangle + |-\rangle\right) + \frac{\vec{d}_B}{\sqrt{2}}\left(|+\rangle - |-\rangle\right)\right]\langle G| + |f\rangle\left[\frac{\vec{d}_B}{\sqrt{2}}\left(\langle +| + \langle -|\right) + \frac{\vec{d}_A}{\sqrt{2}}\left(\langle +| - \langle -|\right)\right]$$

$$\vec{d}_+ = \frac{\vec{d}_A + \vec{d}_B}{\sqrt{2}}\,|+\rangle\langle G| + \frac{\vec{d}_A - \vec{d}_B}{\sqrt{2}}\,|-\rangle\langle G| \qquad \left(\frac{\vec{d}_A - \vec{d}_B}{\sqrt{2}} = \vec{d}_-\right)$$

$$\vec{d}_+ = \frac{\vec{d}_B + \vec{d}_A}{\sqrt{2}}\,|f\rangle\langle +| + \frac{\vec{d}_B - \vec{d}_A}{\sqrt{2}}\,|f\rangle\langle -| \qquad \left(\frac{\vec{d}_B - \vec{d}_A}{\sqrt{2}} = -\vec{d}_-\right)$$



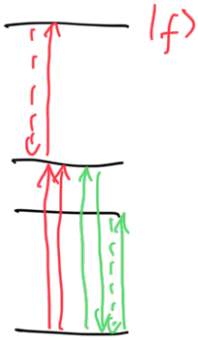
$\vec{d}_A = \vec{d}_B$

$\uparrow\uparrow \Rightarrow \vec{d}_+ = \sqrt{2}\,\vec{d}_A$

$\vec{d}_- = 0$

What is the amplitude of the crosspeaks ?

- ESA + GSB/cross



$-\langle d_+^4 \rangle + \langle d_+^2 d_-^2 \rangle \neq 0$

Summary : 2D spectrum

1) Shows delocalization (resonance couplings) by the presence of crosspeaks at $T=0$

2) Shows energy transfer by evolution of crosspeak peak amplitude at $T>0$

3) Reveals homogeneous and inhomogeneous linewidths (↑ if evolves in time T)

Electronic coherence in 2DFT spectroscopy

$|\Psi(t=0)\rangle = a|+\rangle + b|-\rangle$ ← pure

$\Rightarrow \hat{\rho}(t) = |\Psi(t=0)\rangle\langle\Psi(t=0)| =$

$= \begin{pmatrix} |a|^2 & a^*b \\ ab^* & |b|^2 \end{pmatrix} = \begin{pmatrix} \rho_{++} & \rho_{+-} \\ \rho_{-+} & \rho_{--} \end{pmatrix}$

$\rho_{+-}(t) \approx \rho_{+-}(0)\, e^{i\omega_{+-}t}\, e^{-\gamma t}$

$\rho_{+-} \to 0$

$\rho(t > \tau_d) = \begin{pmatrix} \rho_{++} & 0 \\ 0 & \rho_{--} \end{pmatrix} = \rho_{++}|+\rangle\langle+| + \rho_{--}|-\rangle\langle-|$

mixed

T-evolution of pathway "going through" excited state.

SE and ESA

$\Rightarrow \quad U_{--++}(T) \quad \Rightarrow \quad U_{+-+-}(T)$

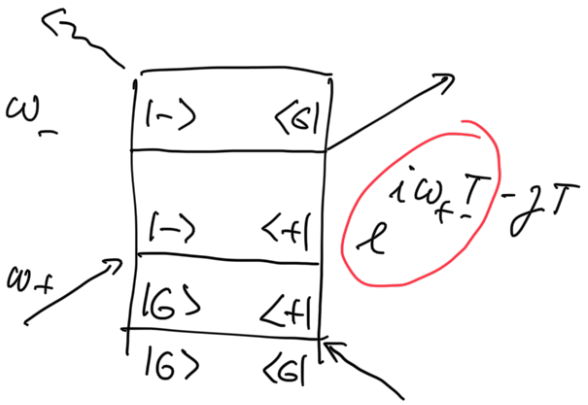
$U_{++++}(T)$

secular approximation

Additional Liouville pathways

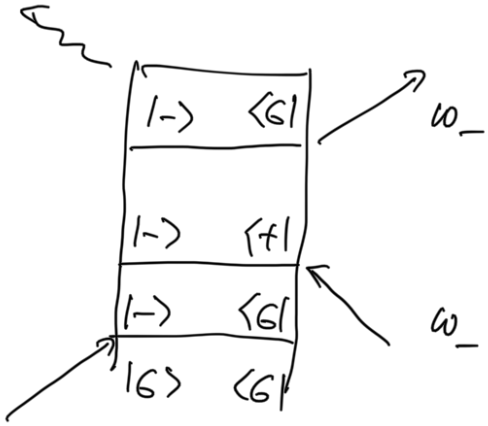
SE

R

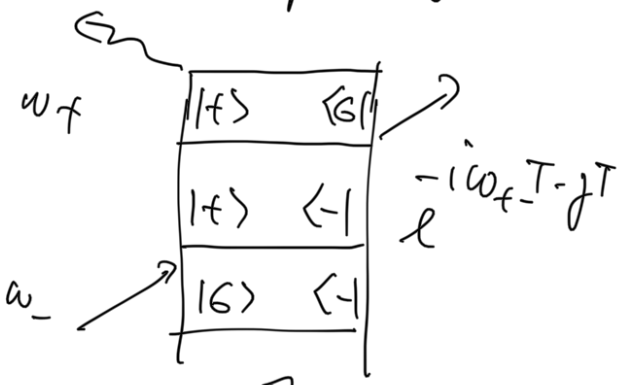


Crosspeak signal

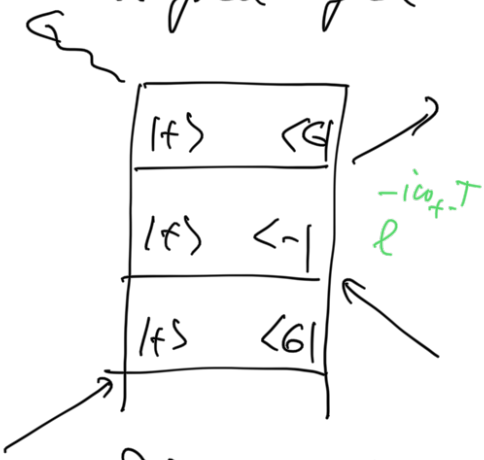
N



Diagonal signal

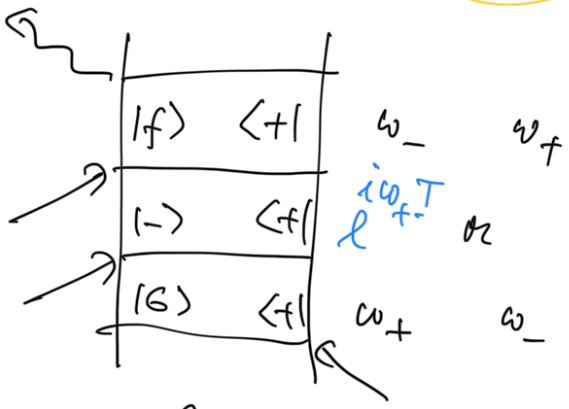


Crosspeak

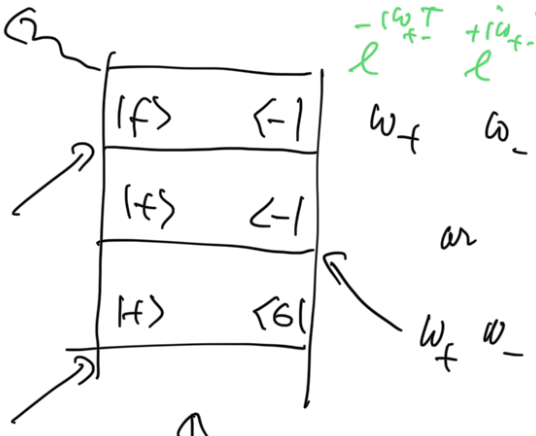


Diagonal signal

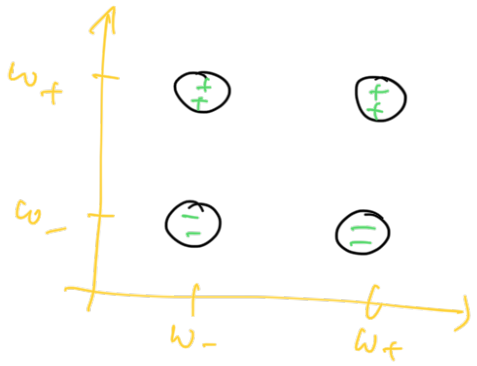
ESA



Crosspeak



Diagonal peak



We can separate R and NR signal!

→ only R signal oscillates on CP

→ only NR signal oscillates on DP

- One can measure the life-time of electronic coherence by 2DFT spectroscopy.