Rotational averaging in the third order Liouville pathways

ad b) $\quad \left\langle (\vec{d}_1\cdot\vec{l}_1)(\vec{d}_2\cdot\vec{l}_2)(\vec{d}_3\cdot\vec{l}_3)(\vec{d}_4\cdot\vec{l}_4)\right\rangle_\Omega = ?$

$\boxed{\vec{d}_n = d_n \vec{n}_n}$

$$= d_1 d_2 d_3 d_4 \sum_{\substack{ijkl\\ \alpha\beta\gamma\delta}} l_i^{(1)} l_j^{(2)} l_k^{(3)} l_l^{(4)} \left\langle I_{ijkl\alpha\beta\gamma\delta}\right\rangle_\Omega n_\alpha^{(1)} n_\beta^{(2)} n_\gamma^{(3)} n_\delta^{(4)}$$

$$(n_i^{(1)} n_j^{(2)} n_k^{(3)} n_l^{(4)})$$

$$= d_1 d_2 d_3 d_4 \sum_{ijkl} l_i^{(1)} l_j^{(2)} l_k^{(3)} l_l^{(4)} \left\langle n_i^{(1)} n_j^{(2)} n_k^{(3)} n_l^{(4)}\right\rangle_\Omega$$

$$\boxed{\left\langle n_i^{(1)} n_j^{(2)} n_k^{(3)} n_l^{(4)}\right\rangle_\Omega = A^{(1)}\delta_{ij}\delta_{kl} + A^{(2)}\delta_{ik}\delta_{jl} + A^{(3)}\delta_{il}\delta_{jk}}$$

$$\boxed{\begin{aligned}\langle \dots \rangle_\Omega = d_1 d_2 d_3 d_4 \Big[&(\vec{l}_1\cdot\vec{l}_2)(\vec{l}_3\cdot\vec{l}_4) A^{(1)} \\ &+ (\vec{l}_1\cdot\vec{l}_3)(\vec{l}_2\cdot\vec{l}_4) A^{(2)} + (\vec{l}_1\cdot\vec{l}_4)(\vec{l}_2\cdot\vec{l}_3) A^{(3)} \Big]\end{aligned}}$$

Invariants

$$\sum_{ij} \left\langle n_i^{(1)} n_i^{(2)} n_j^{(3)} n_j^{(4)}\right\rangle_\Omega = \left\langle (\vec{n}_1\cdot\vec{n}_2)(\vec{n}_3\cdot\vec{n}_4)\right\rangle_\Omega = (\vec{n}_1\cdot\vec{n}_2)(\vec{n}_3\cdot\vec{n}_4)$$

$$\sum_{ij} \left\langle n_i^{(1)} n_i^{(2)} n_j^{(3)} n_j^{(4)}\right\rangle_\Omega = \sum_{ij}\left(A^{(1)}\delta_{ii}\delta_{jj} + A^{(2)}\delta_{ij}\delta_{ij} + A^{(3)}\delta_{ij}\delta_{ij}\right)$$

$$= A^{(1)}9 + A^{(2)}3 + A^{(3)}3$$

$$\sum_{ij} \langle n_i^{(1)} n_j^{(2)} n_i^{(3)} n_j^{(4)} \rangle = \underline{(\vec{n}_1 \cdot \vec{n}_3)(\vec{n}_2 \cdot \vec{n}_4)}$$

$$\sum_{ij} \langle n_i^{(1)} n_j^{(2)} n_i^{(3)} n_j^{(4)} \rangle = \sum_{ij} A^{(1)} \delta_{ij} \delta_{ij} + A^{(2)} \delta_{ii} \delta_{jj} + A^{(3)} \delta_{ij} \delta_{ij})$$

$$= \underline{A^{(1)} 3 + A^{(2)} 9 + A^{(3)} 3}$$

$$\sum_{ij} \langle n_i^{(1)} n_j^{(2)} n_j^{(3)} n_i^{(4)} \rangle = \underline{(\vec{n}_1 \cdot \vec{n}_4)(\vec{n}_2 \cdot \vec{n}_3)}$$

$$= \underline{A^{(1)} 3 + A^{(2)} 3 + A^{(3)} 9}$$

$$\begin{pmatrix} 9 & 3 & 3 \\ 3 & 9 & 3 \\ 3 & 3 & 9 \end{pmatrix} \begin{pmatrix} A^{(1)} \\ A^{(2)} \\ A^{(3)} \end{pmatrix} = \begin{pmatrix} (\vec{n}_1 \cdot \vec{n}_2)(\vec{n}_3 \cdot \vec{n}_4) \\ (\vec{n}_1 \cdot \vec{n}_3)(\vec{n}_2 \cdot \vec{n}_4) \\ (\vec{n}_1 \cdot \vec{n}_4)(\vec{n}_2 \cdot \vec{n}_3) \end{pmatrix}$$

$$\begin{pmatrix} A^{(1)} \\ A^{(2)} \\ A^{(3)} \end{pmatrix} = \begin{pmatrix} 9 & 3 & 3 \\ 3 & 9 & 3 \\ 3 & 3 & 9 \end{pmatrix}^{-1} \begin{pmatrix} (\vec{n}_1 \cdot \vec{n}_2)(\vec{n}_3 \cdot \vec{n}_4) \\ (\vec{n}_1 \cdot \vec{n}_3)(\vec{n}_2 \cdot \vec{n}_4) \\ (\vec{n}_1 \cdot \vec{n}_4)(\vec{n}_2 \cdot \vec{n}_3) \end{pmatrix}$$

$$\begin{pmatrix} 9 & 3 & 3 \\ 3 & 9 & 3 \\ 3 & 3 & 9 \end{pmatrix}^{-1} = \frac{1}{30} \begin{pmatrix} 4 & -1 & -1 \\ -1 & 4 & -1 \\ -1 & -1 & 4 \end{pmatrix}$$

$$
\left\langle (\vec{d}_1\cdot\vec{l}_1)(\vec{d}_2\cdot\vec{l}_2)(\vec{d}_3\cdot\vec{l}_3)(\vec{d}_4\cdot\vec{l}_4)\right\rangle_\Omega =
$$

$$
= d_1 d_2 d_2 d_3 \begin{pmatrix} (\vec{l}_1\cdot\vec{l}_2)(\vec{l}_3\cdot\vec{l}_4) \\ (\vec{l}_1\cdot\vec{l}_3)(\vec{l}_2\cdot\vec{l}_4) \\ (\vec{l}_1\cdot\vec{l}_4)(\vec{l}_2\cdot\vec{l}_3) \end{pmatrix}^T \frac{1}{30} \begin{pmatrix} 4 & -1 & -1 \\ -1 & 4 & -1 \\ -1 & -1 & 4 \end{pmatrix} \begin{pmatrix} (\vec{u}_1\cdot\vec{u}_2)(\vec{u}_3\cdot\vec{u}_4) \\ (\vec{u}_1\cdot\vec{u}_3)(\vec{u}_2\cdot\vec{u}_4) \\ (\vec{u}_1\cdot\vec{u}_4)(\vec{u}_2\cdot\vec{u}_3) \end{pmatrix}
$$

Examples

$$
\vec{l} = \vec{l}_1 = \vec{l}_2 = \vec{l}_3 = \vec{l}_4
$$

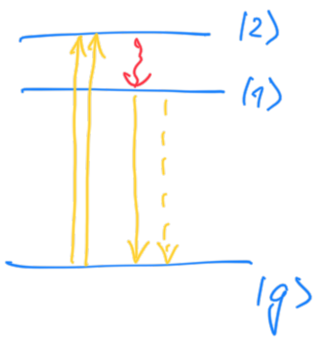
$$
\left\langle (\vec{d}_1\cdot\vec{l})(\vec{d}_2\cdot\vec{l})(\vec{d}_3\cdot\vec{l})(\vec{d}_4\cdot\vec{l})\right\rangle_\Omega = \frac{d_1 d_2 d_3 d_4}{30} \begin{pmatrix} 2 & 2 & 2 \end{pmatrix} \begin{pmatrix} (\vec{u}_1\cdot\vec{u}_2)(\vec{u}_3\cdot\vec{u}_4) \\ \vdots \end{pmatrix}
$$

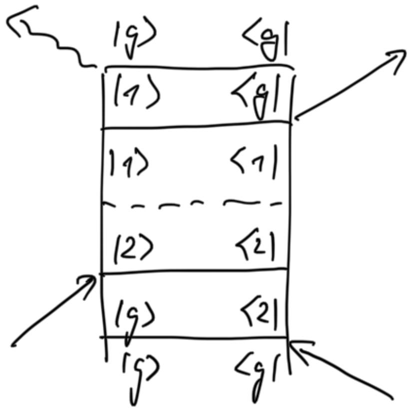
$$
= \frac{d_1 d_2 d_3 d_4}{15} \left[(\vec{u}_1\cdot\vec{u}_2)(\vec{u}_3\cdot\vec{u}_4) + (\vec{u}_1\cdot\vec{u}_3)(\vec{u}_2\cdot\vec{u}_4) + (\vec{u}_1\cdot\vec{u}_4)(\vec{u}_2\cdot\vec{u}_3) \right]
$$

if $\vec{d} = \vec{d}_1 = \vec{d}_2 = \vec{d}_3 = \vec{d}_4$

$$
\boxed{\left\langle (\vec{d}\cdot\vec{l})^4 \right\rangle_\Omega = \frac{d^4}{5}}
$$

Energy transfer

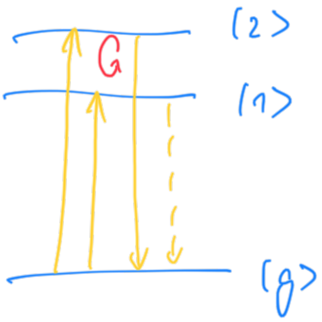


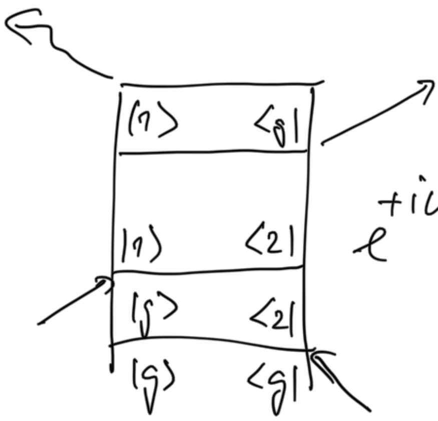


$$\left\langle (\vec{d}_2\cdot\vec{e})(\vec{d}_2\cdot\vec{e})(\vec{d}_1\cdot\vec{e})(\vec{d}_1\cdot\vec{e})\right\rangle_\Omega =$$

$$= \frac{d_1^2 d_2^2}{15}\left[1 + 2(\vec{n}_2\cdot\vec{n}_1)(\vec{n}_2\cdot\vec{n}_1)\right]$$

Coherence

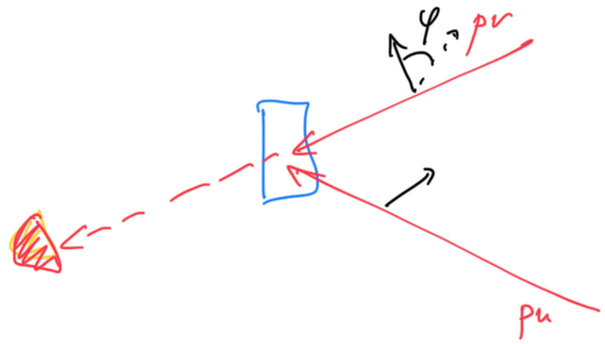




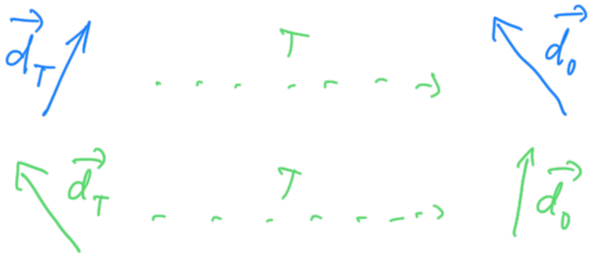
$e^{+i\omega_{21}t}$

$$\left\langle (\vec{d}_2\cdot\vec{e})(\vec{d}_1\cdot\vec{e})(\vec{d}_2\cdot\vec{e})(\vec{d}_1\cdot\vec{e})\right\rangle_\Omega = \frac{d_1^2 d_2^2}{15}\left[1 + 2(\vec{n}_1\cdot\vec{n}_2)^2\right]$$

Magic angle

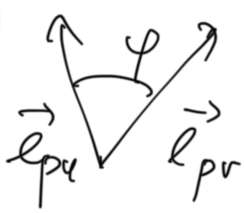


$$\boxed{\varphi = 54{,}7^\circ}$$



Pump $\quad \vec{\ell}_1 = \vec{\ell}_2 = \vec{\ell}_{pu}$

Probe $\quad \vec{\ell}_3 = \vec{\ell}_4 = \vec{\ell}_{pr}$



$$\left\langle (\vec{d}_T \cdot \vec{\ell}_{pu})(\vec{d}_T \cdot \vec{\ell}_{pu})(\vec{d}_0 \cdot \vec{\ell}_{pr})(\vec{d}_0 \cdot \vec{\ell}_{pr}) \right\rangle =$$

$$= \frac{d_T^2 d_0^2}{30} \begin{pmatrix} 1 \\ (\vec{\ell}_{pu} \cdot \vec{\ell}_{pr})^2 \\ (\vec{\ell}_{pu} \cdot \vec{\ell}_{pr})^2 \end{pmatrix}^T \begin{pmatrix} 4 & -1 & -1 \\ -1 & 4 & -1 \\ -1 & -1 & 4 \end{pmatrix} \begin{pmatrix} 1 \\ (\vec{\mu}_T \cdot \vec{\mu}_0)^2 \\ (\vec{\mu}_T \cdot \vec{\mu}_0)^2 \end{pmatrix}$$

$$= \frac{d_T^2 d_0^2}{30} \begin{pmatrix} 1 \\ \cos^2\varphi \\ \cos^2\varphi \end{pmatrix}^T \begin{pmatrix} 4 - (\vec{u}_T \cdot \vec{u}_0)^2 - (\vec{u}_T \cdot \vec{u}_0)^2 \\ -1 + 4(\vec{u}_T \cdot \vec{u}_0)^2 - (\vec{u}_T \cdot \vec{u}_0)^2 \\ -1 - (\vec{u}_T \cdot \vec{u}_0)^2 + 4(\vec{u}_T \cdot \vec{u}_0)^2 \end{pmatrix}$$

$\Delta_{T0} = \vec{u}_T \cdot \vec{u}_0$

$$= \frac{d_T^2 d_0^2}{30} \left(4 - 2\Delta_{T0}^2 + \cos^2\varphi\,(3\Delta_{T0}^2 - 1) + \cos^2\varphi\,(3\Delta_{T0}^2 - 1)\right)$$

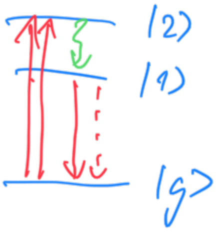
$$= \frac{d_T^2 d_0^2}{15} \left(2 - \Delta_{T0}^2 + \cos^2\varphi\,(3\Delta_{T0}^2 - 1)\right) =$$

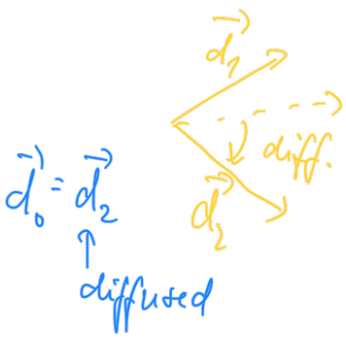
$$= \frac{d_T^2 d_0^2}{15} \left(\underbrace{[3\cos^2\varphi - 1]}_{=0\,?}\Delta_{T0}^2 + 2 - \cos^2\varphi\right)$$

$$3\cos^2\varphi = 1$$

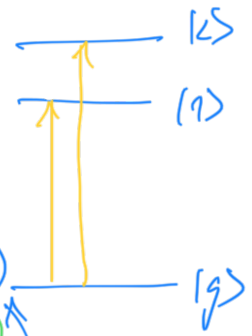
$$\cos^2\varphi = \frac{1}{3} \Rightarrow \boxed{\varphi = \arccos\left(\frac{1}{\sqrt{3}}\right) = 54{,}7^\circ}$$

Magic angle





Coherence



$$\left\langle (\vec d_1\cdot\vec e_{pu})(\vec d_2\cdot\vec e_{pu})(\vec d_3\cdot\vec e_{pr})(\vec d_4\cdot\vec e_{pr})\right\rangle_\Omega$$

$$= \frac{d_1d_2d_3d_4}{30}\begin{pmatrix}1\\(\vec e_{pu}\cdot\vec e_{pr})^2\\(\vec e_{pu}\cdot\vec e_{pr})^2\end{pmatrix}^T\begin{pmatrix}4&-1&-1\\-1&+4&-1\\-1&-1&4\end{pmatrix}\begin{pmatrix}(\vec\mu_1\cdot\vec\mu_2)(\vec\mu_3\cdot\vec\mu_4)\\(\vec\mu_1\cdot\vec\mu_3)(\vec\mu_2\cdot\vec\mu_4)\\(\vec\mu_1\cdot\vec\mu_4)(\vec\mu_2\cdot\vec\mu_3)\end{pmatrix}$$

not influenced by rotational diffusion

subject to diffusion
— have to be eliminated

$$\Delta_1 = (\vec\mu_1\cdot\vec\mu_3)(\vec\mu_2\cdot\vec\mu_4)$$

$$\Delta_2 = (\vec\mu_1\cdot\vec\mu_4)(\vec\mu_2\cdot\vec\mu_3)$$

$$\Delta = (\vec\mu_1\cdot\vec\mu_2)(\vec\mu_3\cdot\vec\mu_4)$$

$$\langle \dots \rangle_\Omega = \Delta\frac{d_1d_2d_3d_4}{30}\begin{pmatrix}1\\\cos^2\varphi\\\cos^2\varphi\end{pmatrix}^T\begin{pmatrix}4&-1&-1\\-1&4&-1\\-1&-1&4\end{pmatrix}\begin{pmatrix}1\\\frac{\Delta_1}{\Delta}\\\frac{\Delta_2}{\Delta}\end{pmatrix}$$

$$= \frac{\Delta d_1d_2d_3d_4}{30}\begin{pmatrix}1\\\cos^2\varphi\\\cos^2\varphi\end{pmatrix}^T\begin{pmatrix}4-\frac{\Delta_1+\Delta_2}{\Delta}\\-1+4\frac{\Delta_1}{\Delta}-\frac{\Delta_2}{\Delta}\\-1-\frac{\Delta_1}{\Delta}+4\frac{\Delta_2}{\Delta}\end{pmatrix}$$

$$= \Delta\frac{d_1d_2d_3d_4}{30}\left(4-\frac{\Delta_1+\Delta_2}{\Delta}+\left(\frac{4\Delta_1-\Delta_2}{\Delta}-1\right)\cos^2\varphi + \left(\frac{4\Delta_2-\Delta_1}{\Delta}-1\right)\cos^2\varphi\right)$$

$$= \Delta\frac{d_1d_2d_3d_4}{30}\left(4-2\cos^2\varphi+\frac{\Delta_1+\Delta_2}{\Delta}\underline{(3\cos^2\varphi-1)}\right)$$

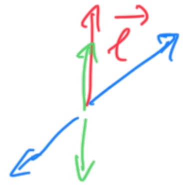
Magic angle work generally!

Special care of even-order spectroscopies

$$\left\langle (\vec{d}_1\cdot\vec{e}_1)(\vec{d}_2\cdot\vec{e}_2)\right\rangle_\Omega \neq 0$$

$$\left\langle (\vec{d}_1\cdot\vec{e}_1)(\vec{d}_2\cdot\vec{e}_2)(\vec{d}_3\cdot\vec{e}_3)(\vec{d}_4\cdot\vec{e}_4)\right\rangle_\Omega \neq 0$$

$$\left\langle (\vec{d}_1\cdot\vec{e})\right\rangle_\Omega = 0$$



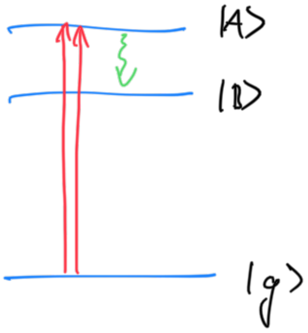
$$\left\langle (\vec{d}_1\cdot\vec{e})(\vec{d}_2\cdot\vec{e})(\vec{d}_3\cdot\vec{e})\right\rangle_\Omega = 0 \ !$$

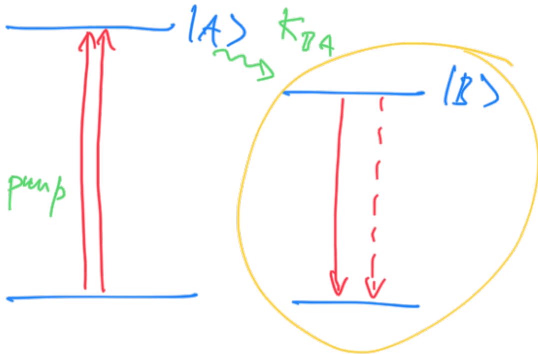
$$\vec{k}_s = \vec{k}_1 + \vec{k}_2 \ \rightarrow \ \omega_s = \omega_1 + \omega_2$$

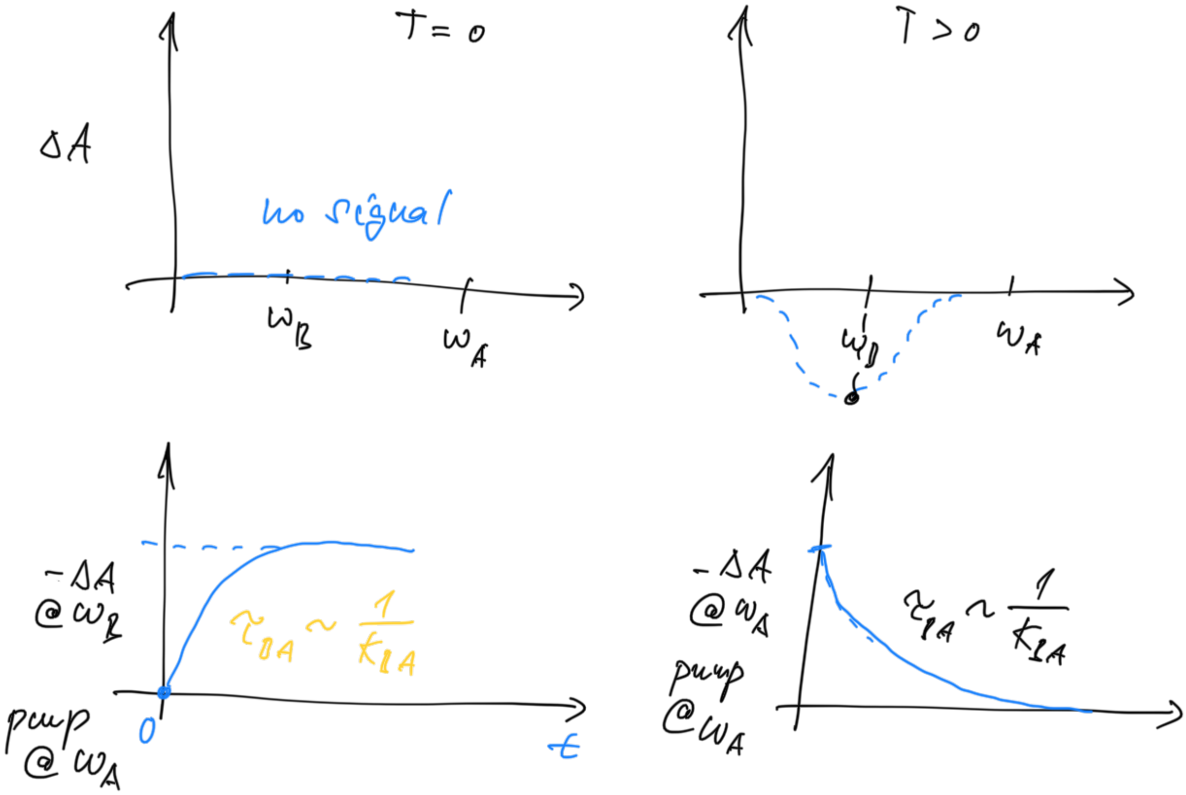
$$e^{i(\vec{k}_1+\vec{k}_2)\cdot\vec{r} - i(\omega_1+\omega_2)t}$$

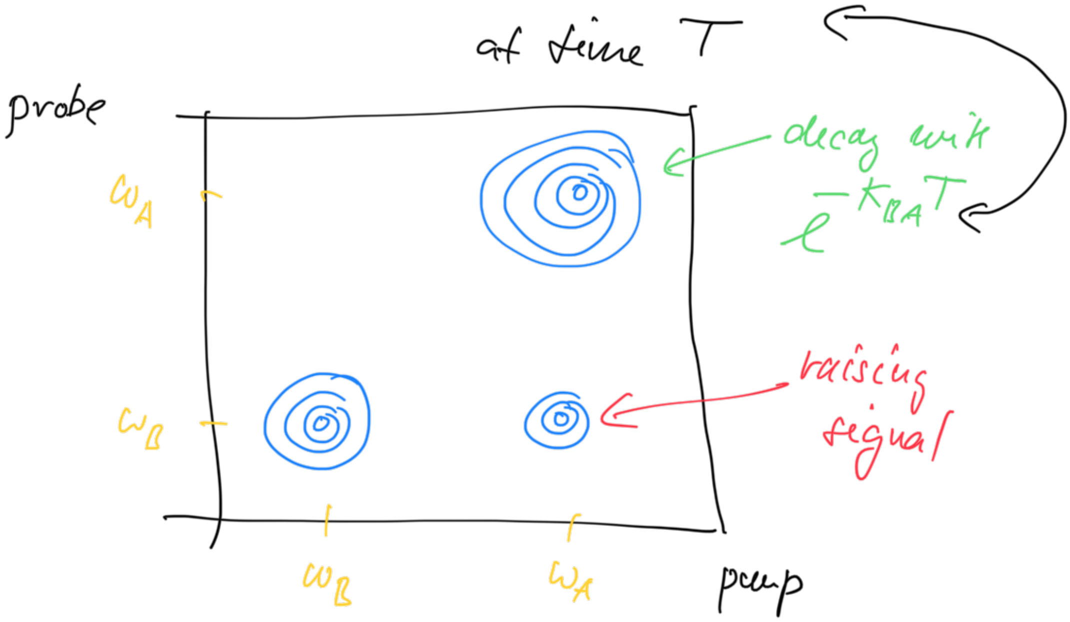
We cannot produce second harmonic (sum frequency) in an isotropic sample.

Monitoring energy transfer processes by pump-probe spectroscopy









Probing and pumping with frequency resolution ~ $\Delta\omega$

→ length of the pulse ≡ time resolution scales with $\frac{1}{\Delta\omega}$