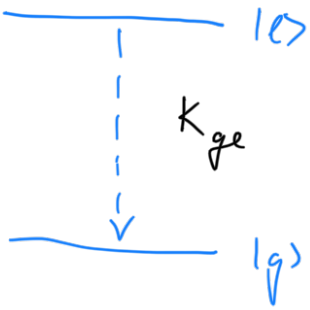
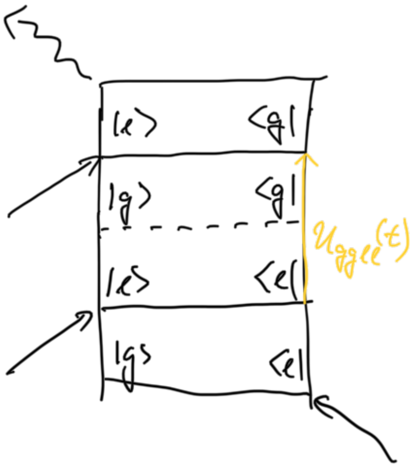
# Liouville pathways with energy relaxation processes




$$\mathcal{U}_{ggee}(t) \qquad \rho_{ee}(t) \longrightarrow \rho_{gg}(t)$$

$$\mathcal{U}_{ggee}(t) = 1 - e^{-K_{ge}t} = \int_0^t d\tau\, K_{ge}\, \mathcal{U}_{eeee}(\tau)$$

a)




$\cancel{\mathcal{U}_{eeee}(t) \approx e^{-K_{ge}t}}$

$\rho_{ee} \to \rho_{gg}$

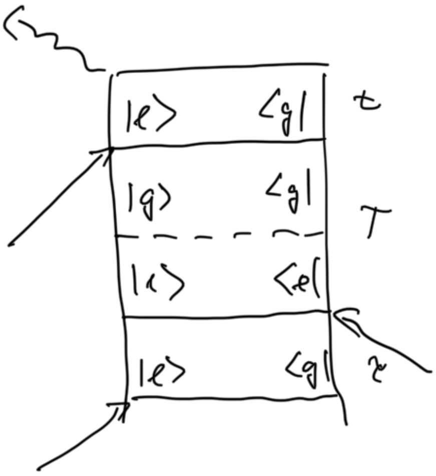
$-$

overall sign

$-$

rephasing contribution – derived from $R_2$

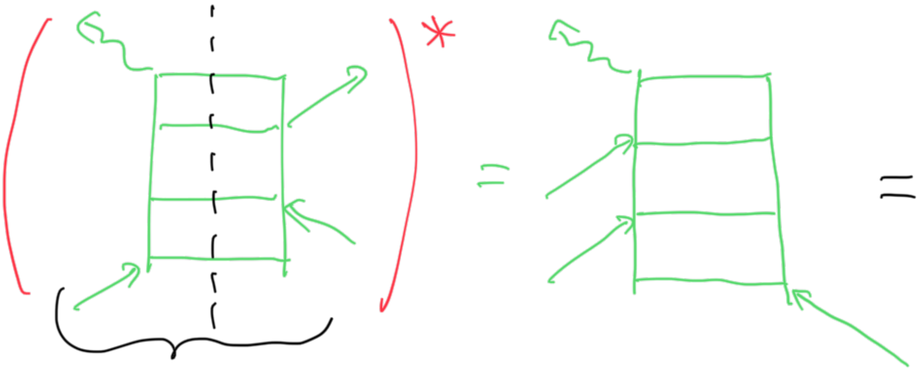
b)




non-rephasing contribution – derived from $R_1$ pathway

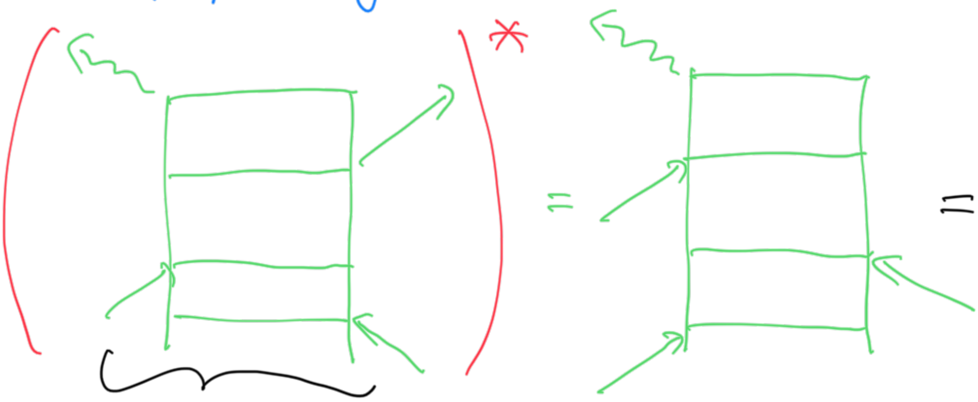
The above diagrams must correspond to $R_1^*, R_2^*, R_3^*$ or $R_4^*$.

Identification of pathway a)



$\equiv R_1$ $\qquad = -R_1^*$

—"— of pathway b)



$\equiv R_2$ $\qquad = -R_2^*$

## Summary of Liouville pathways for relaxing 2LS

$$R_1(t,T,\tau) = d^4\, U_{egeg}(t)\, U_{eeee}(T)\, U_{egeg}(\tau)$$

$$R_2(t,T,\tau) = d^4\, U_{egeg}(t)\, U_{eeee}(T)\, U_{gege}(\tau)$$

$$R_3(t,T,\tau) = d^4\, U_{egeg}(t)\, U_{gggg}(T)\, U_{gege}(\tau)$$

$$R_4(t,T,\tau) = d^4\, U_{egeg}(t)\, \underline{U_{gggg}}(T)\, U_{egeg}(\tau)$$

$$R_1^*(t,T,\tau) = d^4\, U_{egeg}(t)\, \underline{U_{ggee}}(T)\, U_{gege}(\tau)$$

$$R_2^*(t,T,\tau) = d^4\, U_{egeg}(t)\, U_{ggee}(T)\, U_{egeg}(\tau)$$

$$\boxed{FT[U_{egeg}(t)] = G_{eg}(\omega)}$$

## Pump-probe

$$\Delta A(\omega) \approx -\omega\, Re\left(R_1(\omega; T, \tau=0) + R_2 + R_3 + R_4 - R_1^* - R_2^*\right)$$

$$\boxed{\Delta A(T=0) \approx -\omega d^4\, Re\left[\overset{R_1}{G_{eg}(\omega)} + \overset{R_2}{G_{eg}(\omega)} + \underset{R_1^*}{G_{eg}(\omega)} + \underset{R_2^*}{G_{eg}(\omega)}\right]}$$

$- 0 \qquad - 0$

$$\boxed{\approx -4 d^4 \alpha_{eg}(\omega)}$$

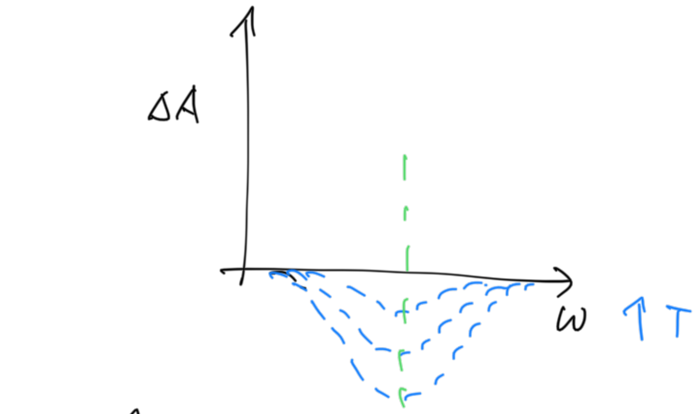
$$\Delta A(T) \approx -\omega d^4\, Re\Big[\big(G_{eg}(\omega) + G_{eg}(\omega)\big)\overset{\mathcal{U}_{eeee}(T)}{e^{-K_{ge}T}}$$

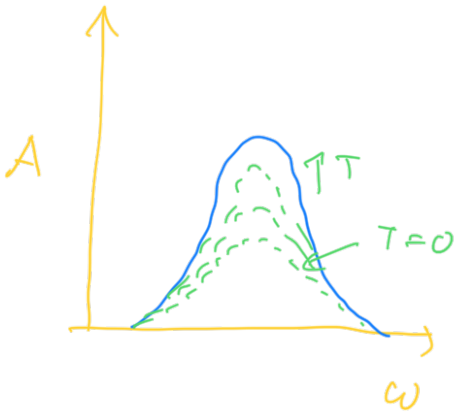
$$+ \big(\cancel{G_{eg}}(\omega) + \cancel{G_{eg}}(\omega)\big) \cdot \overset{\mathcal{U}_{gggg}(T)}{1}$$

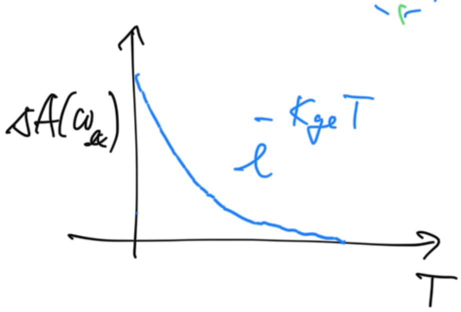
$$- \big(G_{eg}(\omega) + G_{eg}(\omega)\big)\underset{\mathcal{U}_{ggee}(T)}{\big(\cancel{1} - e^{-K_{ge}T}\big)}\Big]$$

$$\boxed{\Delta A(T) \approx -\omega d^4\, Re\left[4\, G_{eg}(\omega)\right] e^{-K_{ge}T}}$$

$$\Delta A(T \to \infty) \approx 0$$

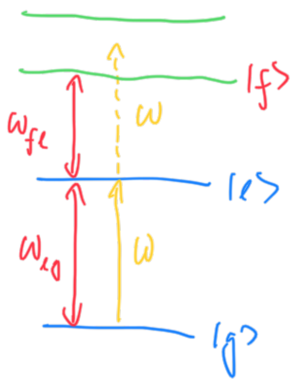


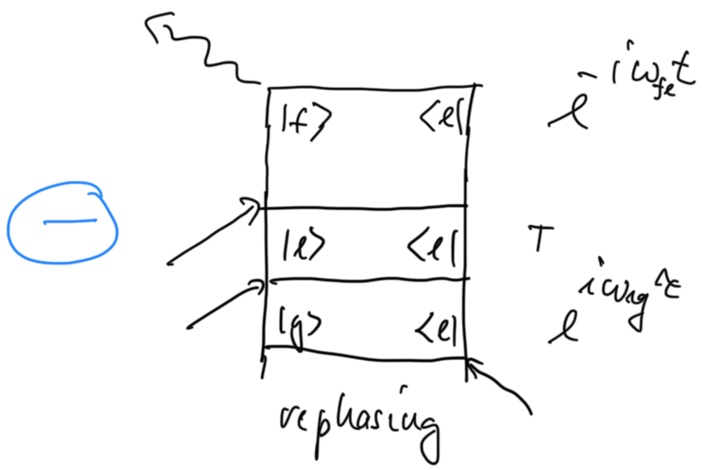




← pump-probe can measure relaxation rate $k_{ge}$

## Systems with excited state absorption

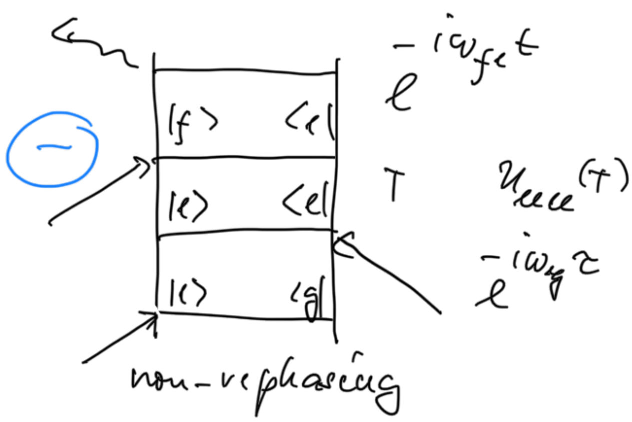



what pathways describe excited state absorption (ESA)



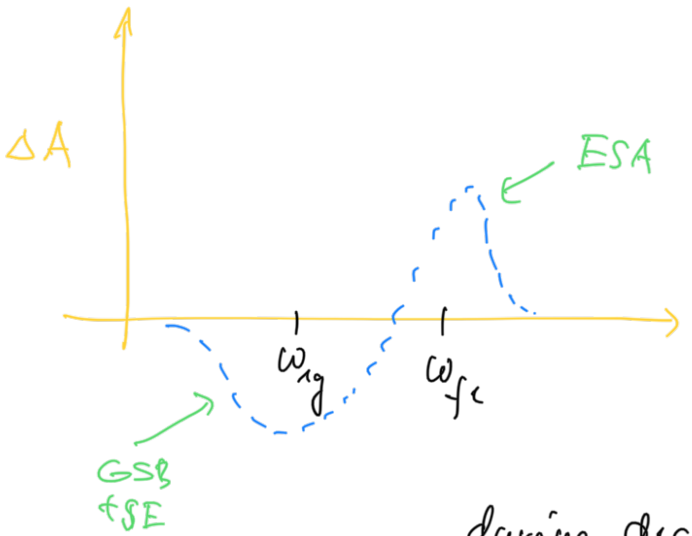

rephasing

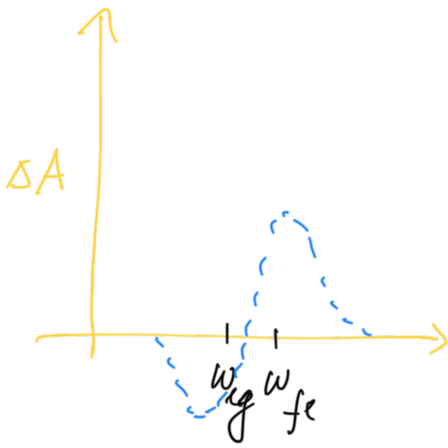
$R_1^*$




non-rephasing

$R_2^*$

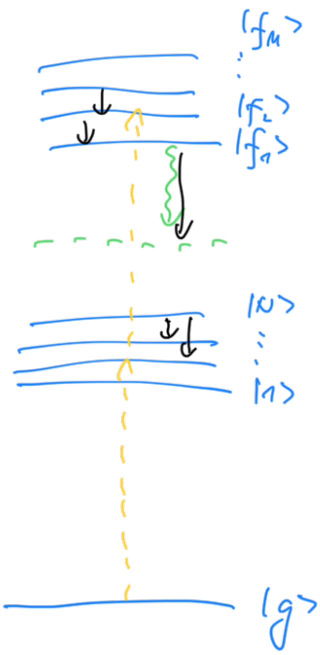



during decay of $|e\rangle$ also ESA decays

$\sim e^{-K_{ge}T}$

## General multi-level systems




$\mathcal{U}_{mnij}(t)$

Energy relaxation pathways

$$\sim \sum_{mn} d_m^2 d_n^2 \, \mathcal{U}_{mgmg}(t) \, \mathcal{U}_{\underline{nn}\,\underline{mm}}(T) \quad \mathcal{U}_{gmgm}(\tau)$$

Coherence decay pathways

$$\sim \sum_{mn} d_m^2 \, d_n^2 \, \mathcal{U}_{mgmg}(t) \, \mathcal{U}_{\underline{mn}\,\underline{mn}}(T) \, \mathcal{U}_{gngn}(\tau)$$

we assume secular approximation

$\mathcal{U}_{f_m e f_n e}(t) \rightarrow$ into ESA

# How to calculate spectra

## Absorption spectrum

$$\boxed{\alpha(\omega) \approx \omega \sum_n \left\langle \left(\vec{d}_{ng} \cdot \vec{e}\right)^2 \right\rangle_\Omega \mathrm{Re}\, G_{ng}(\omega)}$$


$$G_{ng}(\omega) = \int_{-\infty}^{\infty} dt\, \theta(t)\, \mathcal{U}_{ngng}(t)\, e^{i\omega t}$$

$$= \int_0^{\infty} dt\, \tilde{\mathcal{U}}_{ngng}(t)\, e^{-i\omega_{ng} t}\, e^{i\omega t}$$

## Pump-probe spectrum

$$\Delta A(\omega) \approx -\omega \sum_{\substack{nm \\ \varepsilon e}} \left\langle \left(\vec{d}_{g\varepsilon} \cdot \vec{e}_4\right)\left(\vec{d}_{eg} \cdot \vec{e}_3\right)\left(\vec{d}_{mg} \cdot \vec{e}_2\right)\left(\vec{d}_{ng} \cdot \vec{e}_1\right) \right\rangle_\Omega$$

SE $\sim R_2 + R_1$

$$\times \mathrm{Re} \Big\{ 2\, G_{\varepsilon g}(\omega)\, \mathcal{U}_{\varepsilon e\, nm}(T) \left(\delta_{nm}\delta_{\varepsilon e} + (1-\delta_{nm})\delta_{\varepsilon n}\delta_{em}\right) +$$

$FT[\mathcal{U}_{kgkg}(t)]$

GSB $\sim R_3 + R_4$

$$+ 2\, G_{\varepsilon g}(\omega)\, \delta_{nm}\delta_{\varepsilon e}$$

$$- 2\, G_{\varepsilon g}(\omega)\, \mathcal{U}_{ggnn}(T)\, \delta_{nm}\delta_{\varepsilon e} \Big\}$$

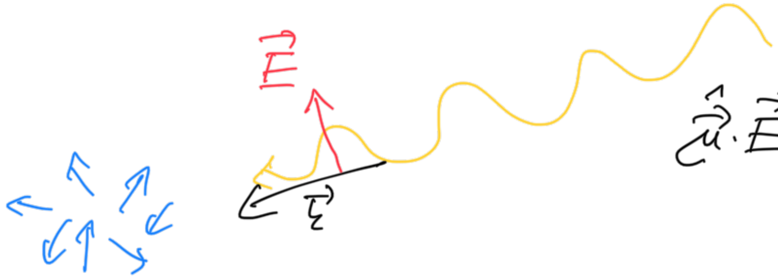
GSB filling $\sim R_1^* + R_2^*$ with relaxation to $|g\rangle$

$$+ \omega \sum_{\substack{nm \\ f\varepsilon e}} \left\langle \left(\vec{d}_{\varepsilon f} \cdot \vec{e}_4\right)\left(\vec{d}_{fe} \cdot \vec{e}_3\right)\left(\vec{d}_{ng} \cdot \vec{e}_2\right)\left(\vec{d}_{gm} \cdot \vec{e}_1\right) \right\rangle_\Omega$$

$$\times 2\mathrm{Re} \left\{ G_{f\varepsilon}(\omega)\, \mathcal{U}_{\varepsilon e\, nm}(T) \left[\delta_{nm}\delta_{\varepsilon e} + (1-\delta_{nm})\delta_{\varepsilon n}\delta_{em}\right] \right\}$$

ESA

# Rotational averaging over transition dipole moment directions




$$\hat{\vec{\mu}}\cdot\vec{E} \approx \vec{d}\cdot\vec{E} = |\vec{d}||\vec{E}|\,\vec{n}\cdot\vec{e}$$

$\vec{e}$ ... in the laboratory frame fixed

$\vec{n}$ ... different for each molecule
- in the molecular frame of reference

We assume isotropic distribution of directions

$$\langle \vec{n} \rangle_\Omega \equiv 0$$

## In absorption

secular approximation

$$\left\langle (\vec{d}_n\cdot\vec{e})(\vec{d}_n\cdot\vec{e}) \right\rangle_\Omega = |\vec{d}|^2 \left\langle (\vec{n}\cdot\vec{e})^2 \right\rangle$$

## In pump-probe (and other non-linear spectra)

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

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

four different polarizations: $\vec{e}_1, \vec{e}_2, \vec{e}_3, \vec{e}_4$ ... fixed in space

four different orientations of $\vec{d}$, mutually fixed but arbitrarily rotated ad a)

$$(\vec{d}_1\cdot\vec{\ell}_1)(\vec{d}_2\cdot\vec{\ell}_2) = d_1 d_2 (\vec{n}_1\cdot\vec{\ell}_1)(\vec{n}_2\cdot\vec{\ell}_2)$$

$$= d_1 d_2 \sum_{ij} (n_i^{(1)} \ell_i^{(1)})(n_j^{(2)} \ell_j^{(2)})$$

$$= d_1 d_2 \sum_{ij} (\ell_i^{(1)} \ell_j^{(1)}) \underbrace{(n_i^{(1)} n_j^{(2)})}_{\uparrow \text{ tensor}}$$

$$\langle(\vec{d}_1\cdot\vec{\ell}_1)(\vec{d}_2\cdot\vec{\ell}_2)\rangle_\Omega = d_1 d_2 \sum_{ij} (\ell_i^{(1)} \ell_j^{(2)}) \langle n_i^{(1)} n_j^{(2)}\rangle_\Omega$$

$$\sum_{ij} (S^{-1})_{ki} \underset{\underset{a\,\delta_{ij}}{\shortparallel}}{A_{ij}} S_{jl} = a \sum_{ij} (S^{-1})_{ki} \delta_{ij} S_{jl} =$$

$$= a \sum_i (S^{-1})_{ki} S_{il} = a\,\delta_{kl}$$

$$\boxed{\langle n_i^{(1)} n_j^{(2)}\rangle = a\,\delta_{ij}}$$

$$\langle(\vec{d}_1\cdot\vec{\ell}_1)(\vec{d}_2\cdot\vec{\ell}_2)\rangle_\Omega = d_1 d_2 \sum_{ij} (\ell_i^{(1)} \ell_j^{(2)}) \sum_{\alpha\beta} \langle T_{i\alpha} n_\alpha^{(1)} T_{j\beta} n_\beta^{(2)}\rangle_\Omega$$

$$= d_1 d_2 \sum_{\substack{ij\\ \alpha\beta}} (\ell_i^{(1)} \ell_j^{(2)}) \underbrace{\langle T_{i\alpha} T_{j\beta}\rangle_\Omega}_{I_{ij\alpha\beta}} n_\alpha^{(1)} n_\beta^{(2)}$$

$$I_{ij\alpha\beta} = a\,\delta_{ij} \ldots \quad ?$$

$$\sum_i n_i^{(1)} n_i^{(2)} = \text{const} = \underbrace{\sum_i \sum_{\alpha\beta} I_{ii\alpha\beta} n_\alpha^{(1)} n_\beta^{(2)} = \sum_\alpha n_\alpha^{(1)} n_\alpha^{(2)}}$$

$$\sum_\alpha \Big(\sum_\beta \underbrace{\sum_i I_{ii\alpha\beta}}_{\mathcal{H}_{\alpha\beta}} n_\beta^{(2)} - n_\alpha^{(2)}\Big) n_\alpha^{(1)} = 0$$

$$\sum_\beta \underbrace{\varkappa_{\alpha\beta}}_{=\delta_{\alpha\beta}} n_\beta^{(2)} = n_\alpha^{(2)}$$

$$\sum_i I_{ii\alpha\beta} = \delta_{\alpha\beta} \quad \rightarrow \quad \boxed{I_{ij\alpha\beta} = a\,\delta_{ij}\cdot\delta_{\alpha\beta}}$$

$$\sum_i a\,\delta_{ii}\cdot\delta_{\alpha\beta} = \delta_{\alpha\beta}$$

$$3a\,\delta_{\alpha\beta} = \delta_{\alpha\beta}$$

$$\Rightarrow \boxed{a = \frac{1}{3}}$$

$$\boxed{I_{ij\alpha\beta} = \frac{1}{3}\delta_{ij}\cdot\delta_{\alpha\beta}}$$

$$\left\langle (\vec{d}_1\cdot\vec{e}_1)(\vec{d}_2\cdot\vec{e}_2)\right\rangle_\Omega = d_1 d_2 \sum_{\substack{ij\\ \alpha\beta}} \left(\ell_i^{(1)}\ell_j^{(1)}\right)\frac{1}{3}\delta_{ij}\cdot\delta_{\alpha\beta}\left(n_\alpha^{(1)} n_\beta^{(2)}\right)$$

$$= \frac{d_1 d_2}{3}\sum_{i\alpha}\left(\ell_i^{(1)}\ell_i^{(2)}\right)\left(n_\alpha^{(1)} n_\alpha^{(2)}\right)$$

$$= \frac{d_1 d_2}{3}\left(\vec{\ell}_1\cdot\vec{\ell}_2\right)\left(\vec{n}_1\cdot\vec{n}_2\right)$$

In absorption spectroscopy

$$\vec{\ell}_1 \equiv \vec{\ell}_2$$

$$\left\langle (\vec{d}_1\cdot\vec{e})(\vec{d}_2\cdot\vec{e})\right\rangle_\Omega = \frac{d_1 d_2}{3}\left(\vec{n}_1\cdot\vec{n}_2\right)$$

secular approximation

$$\boxed{\left\langle \left(\vec{d}_n \cdot \vec{e}\right)^2 \right\rangle_\Omega = \frac{|\vec{d}_n|^2}{3}}$$