The pump – probe
Feynman and ladder diagrams:

Third order term:

$$R^{(3)}(t) = \langle \mu_t[\mu_3,[\mu_2,[\mu_1,\rho_0]]\,]\rangle$$

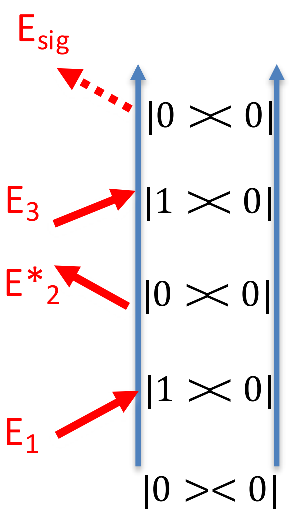
2^n *terms* and 2^{n-1} *independent terms*

$+\langle \mu_t\mu_3\mu_2\mu_1\rho_0\rangle \Rightarrow R_1$ $\qquad$ -$\langle \mu_t\mu_3\mu_2\mu_1\rho_0\rangle^* \Rightarrow R^*{}_1$

$+\langle \mu_t\mu_3\rho_0\mu_1\mu_2\rangle \Rightarrow R_2$ $\qquad$ -$\langle \mu_t\mu_3\rho_0\mu_1\mu_2\rangle^* \Rightarrow R^*{}_2$

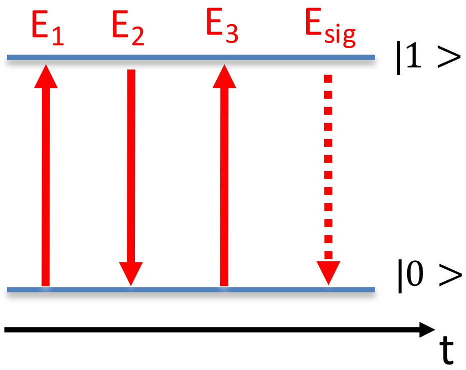
$+\langle \mu_t\mu_2\rho_0\mu_1\mu_3\rangle \Rightarrow R_3$ $\qquad$ -$\langle \mu_t\mu_2\rho_0\mu_1\mu_3\rangle^* \Rightarrow R^*{}_3$

$+\langle \mu_t\mu_1\rho_0\mu_2\mu_3\rangle \Rightarrow R_4$ $\qquad$ -$\langle \mu_t\mu_1\rho_0\mu_2\mu_3\rangle^* \Rightarrow R^*{}_4$

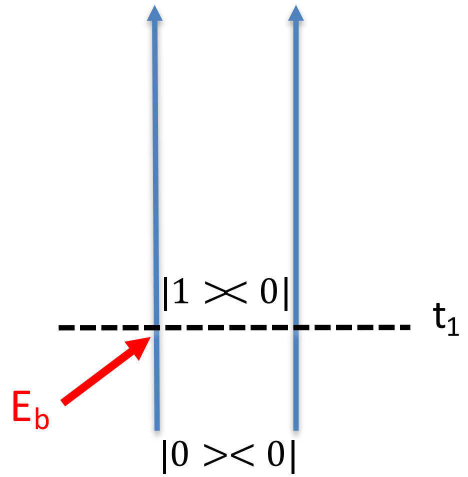


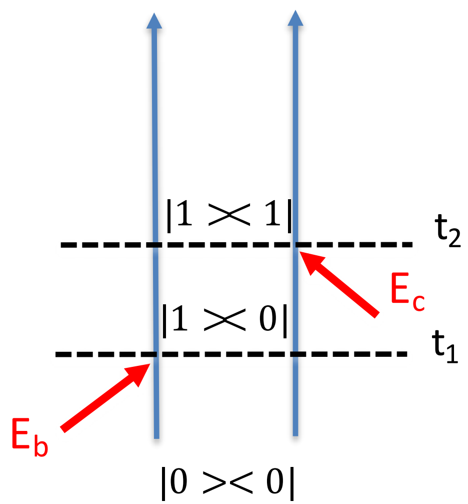
$$k_{sig} = k_1 - k_2 + k_3$$

$$\omega_{sig} = \omega_1 - \omega_2 + \omega_3$$



Why 2^n *terms* ?





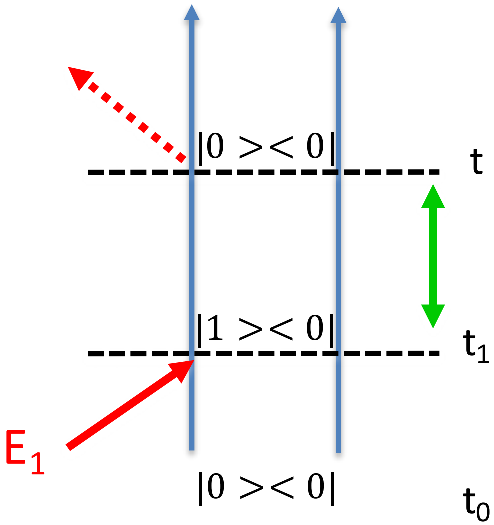
- Take three generic fields E_a, E_b, E_c
- At instant t_1 all of three can interact with the bra or ket part of the system: *6 ways*
- At time t_2, two remaining fields can interact on bra or on ket: *4 ways*
- At time t_3, one remaining fields can interact on bra or on ket: *2 ways*

$$6 * 4 * 2 = 48 \; total \; ways$$

$$2^3 = 8 \; ways$$

- Time ordering
- Resonance Condition (Bhor)
- Boltzmann factor
  (departing state must be populated)

From Feynman to correlaction function



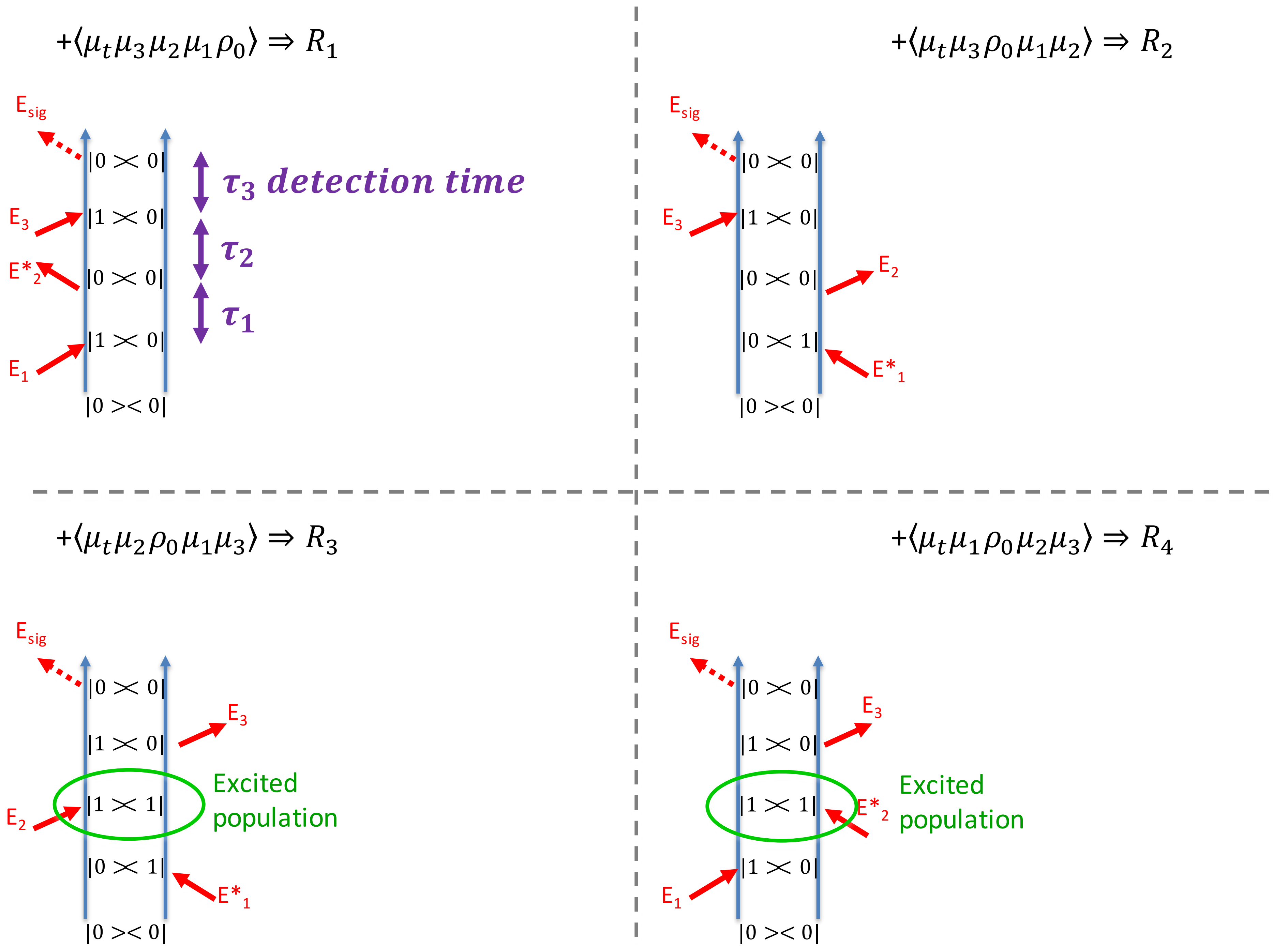
$\hat{G}(t) = UAU^{\dagger} = e^{-i\omega_{01}t-\Gamma t}$ Free-evolution super-operator

$$C(t) = p_{00}\mu_{01}e^{-i\omega_{01}t-\Gamma t}\mu_{01} = p_{00}\,\mu_{01}^2 e^{-i\omega_{01}t-\Gamma t}$$

Weight factor
Boltzman population
of g state

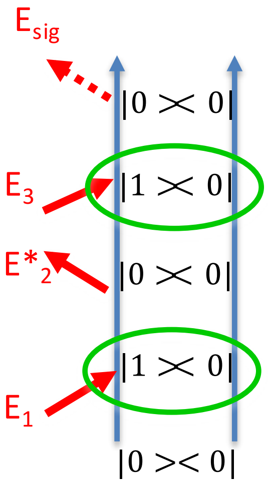
transition
probability

Oscillating coherence
+ dephasing factor



$+\langle \mu_t \mu_3 \mu_2 \mu_1 \rho_0 \rangle \Rightarrow R_1$
E_{sig}
$|0\rangle\langle 0|$
E_3
$|1\rangle\langle 0|$
E^*_2
$|0\rangle\langle 0|$
E_1
$|1\rangle\langle 0|$
$|0\rangle\langle 0|$
τ_3 detection time
τ_2
τ_1
$+\langle \mu_t \mu_3 \rho_0 \mu_1 \mu_2 \rangle \Rightarrow R_2$
E_{sig}
$|0\rangle\langle 0|$
E_3
$|1\rangle\langle 0|$
$|0\rangle\langle 0|$
E_2
$|0\rangle\langle 1|$
E^*_1
$|0\rangle\langle 0|$
$+\langle \mu_t \mu_2 \rho_0 \mu_1 \mu_3 \rangle \Rightarrow R_3$
E_{sig}
$|0\rangle\langle 0|$
E_3
$|1\rangle\langle 0|$
E_2
$|1\rangle\langle 1|$
Excited population
$|0\rangle\langle 1|$
E^*_1
$|0\rangle\langle 0|$
$+\langle \mu_t \mu_1 \rho_0 \mu_2 \mu_3 \rangle \Rightarrow R_4$
E_{sig}
$|0\rangle\langle 0|$
E_3
$|1\rangle\langle 0|$
$|1\rangle\langle 1|$
E^*_2
Excited population
E_1
$|1\rangle\langle 0|$
$|0\rangle\langle 0|$

$$+\langle \mu_t \mu_3 \mu_2 \mu_1 \rho_0 \rangle \Rightarrow R_1$$

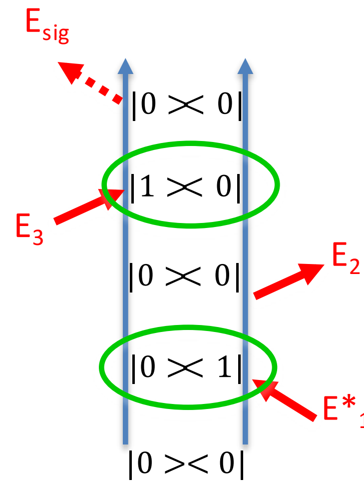


$$C(t) = p_{00}\ \mu_{01}^4 e^{i\omega_{01}\tau_1 - \Gamma_{10}\tau_1} e^{-i\omega_{00}\tau_2 - \Gamma_{00}\tau_2} e^{i\omega_{01}\tau_3 - \Gamma_{10}\tau_3}$$

$$= p_{00}\ \mu_{01}^4 e^{i\omega_{01}(\tau_3+\tau_1) - \Gamma_{10}(\tau_3+\tau_1)}$$

Non-rephasing

$$+\langle \mu_t \mu_3 \rho_0 \mu_1 \mu_2 \rangle \Rightarrow R_2$$

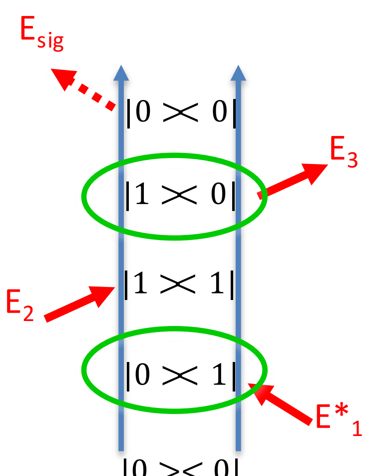


$$C(t) = p_{00}\ \mu_{01}^4 e^{-i\omega_{01}\tau_1 - \Gamma_{01}\tau_1} e^{i\omega_{00}\tau_2 - \Gamma_{00}\tau_2} e^{i\omega_{01}\tau_3 - \Gamma_{10}\tau_3}$$

$$= p_{00}\ \mu_{01}^4 e^{i\omega_{01}(\tau_3-\tau_1) - \Gamma_{10}(\tau_3-\tau_1)}$$

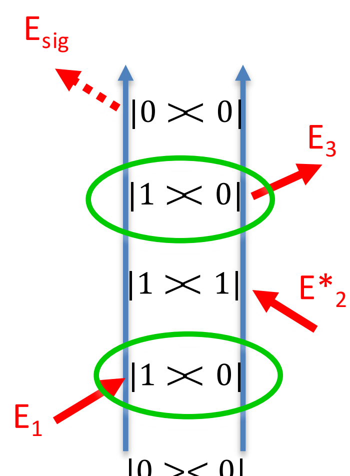
Rephasing

$$+\langle \mu_t \mu_2 \rho_0 \mu_1 \mu_3 \rangle \Rightarrow R_3$$

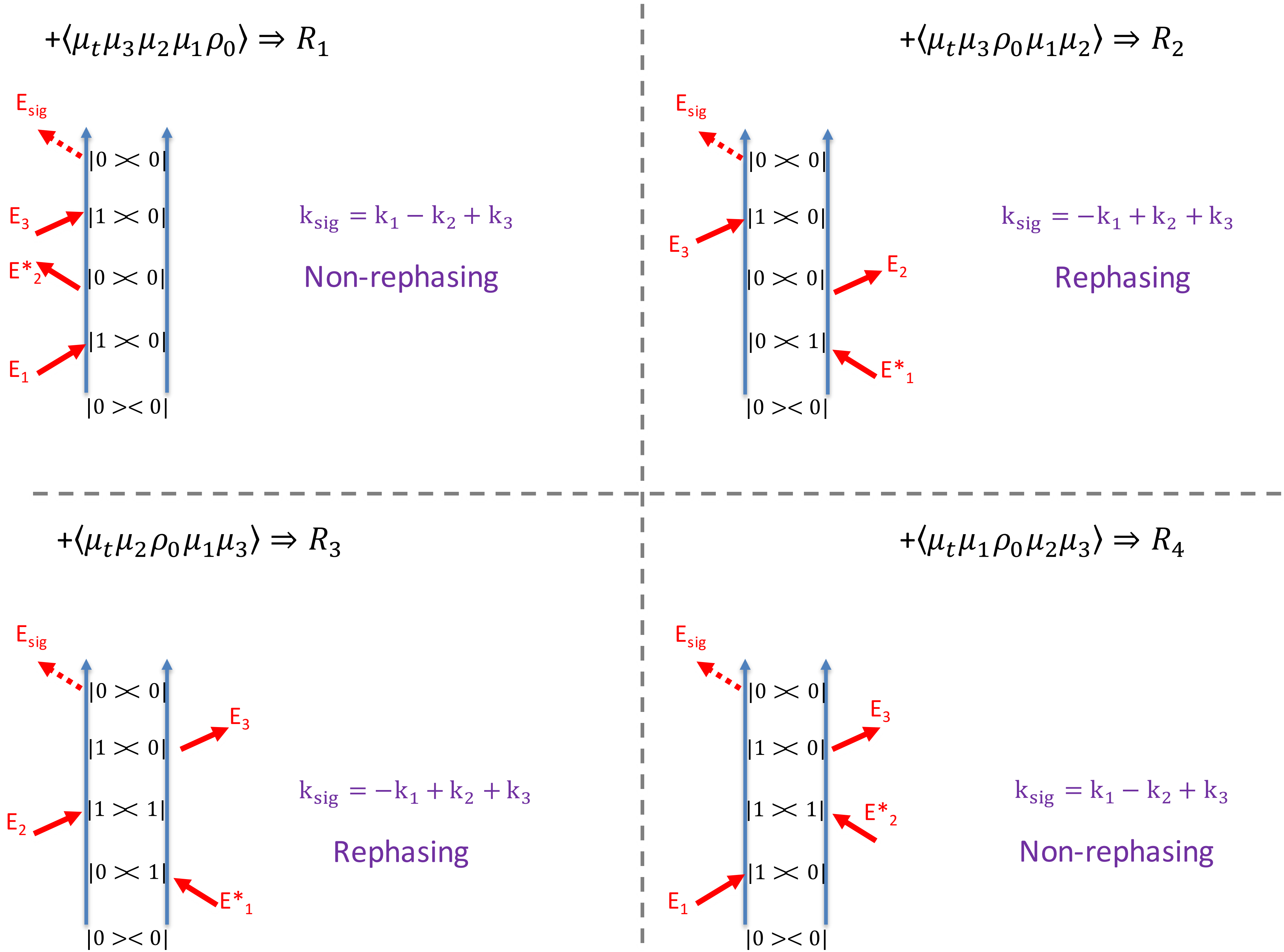


Rephasing

$$+\langle \mu_t \mu_1 \rho_0 \mu_2 \mu_3 \rangle \Rightarrow R_4$$



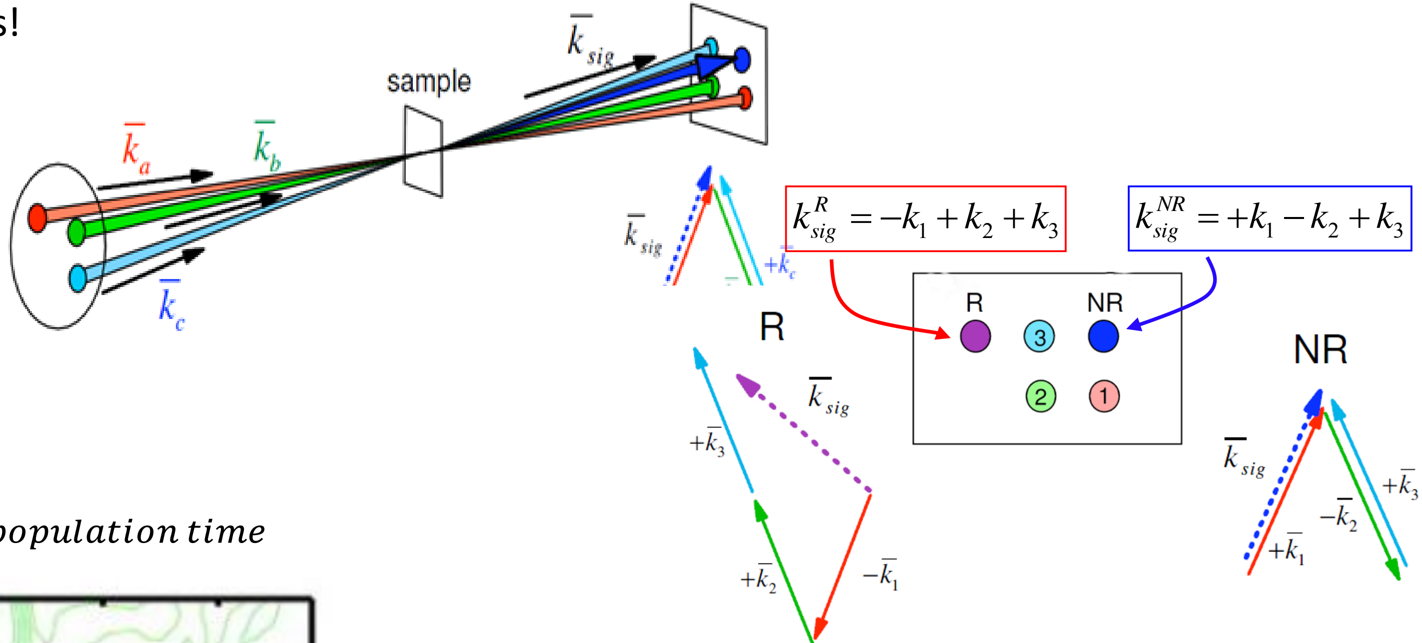
Non-rephasing



$+\langle \mu_t \mu_3 \mu_2 \mu_1 \rho_0 \rangle \Rightarrow R_1$
E_{sig}
$|0 \rangle\langle 0|$
E_3
$|1 \rangle\langle 0|$
E^*_2
$|0 \rangle\langle 0|$
E_1
$|1 \rangle\langle 0|$
$|0 \rangle\langle 0|$
$k_{sig} = k_1 - k_2 + k_3$
Non-rephasing
$+\langle \mu_t \mu_3 \rho_0 \mu_1 \mu_2 \rangle \Rightarrow R_2$
E_{sig}
$|0 \rangle\langle 0|$
$|1 \rangle\langle 0|$
E_3
$|0 \rangle\langle 0|$
E_2
$|0 \rangle\langle 1|$
E^*_1
$|0 \rangle\langle 0|$
$k_{sig} = -k_1 + k_2 + k_3$
Rephasing
$+\langle \mu_t \mu_2 \rho_0 \mu_1 \mu_3 \rangle \Rightarrow R_3$
E_{sig}
$|0 \rangle\langle 0|$
E_3
$|1 \rangle\langle 0|$
E_2
$|1 \rangle\langle 1|$
$|0 \rangle\langle 1|$
E^*_1
$|0 \rangle\langle 0|$
$k_{sig} = -k_1 + k_2 + k_3$
Rephasing
$+\langle \mu_t \mu_1 \rho_0 \mu_2 \mu_3 \rangle \Rightarrow R_4$
E_{sig}
$|0 \rangle\langle 0|$
E_3
$|1 \rangle\langle 0|$
$|1 \rangle\langle 1|$
E^*_2
E_1
$|1 \rangle\langle 0|$
$|0 \rangle\langle 0|$
$k_{sig} = k_1 - k_2 + k_3$
Non-rephasing

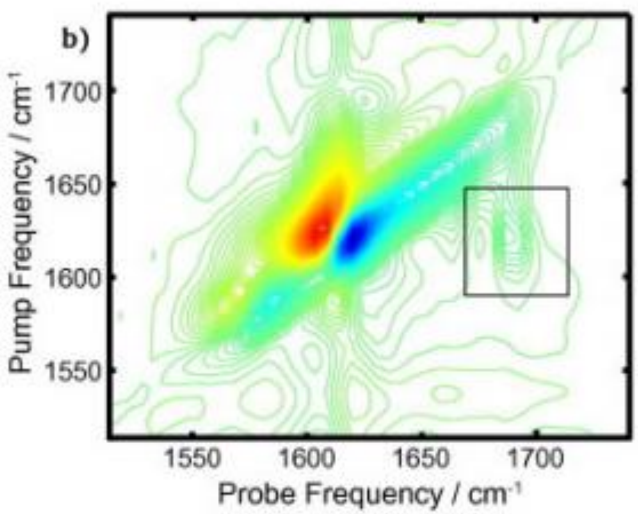
4-wave-mixing experiments: 2D spectra intime domain

Full control on relative electric fields time delays!



$T_{\text{fix}} = \tau_{2\ population\ time}$

$FT\ \tau_3$

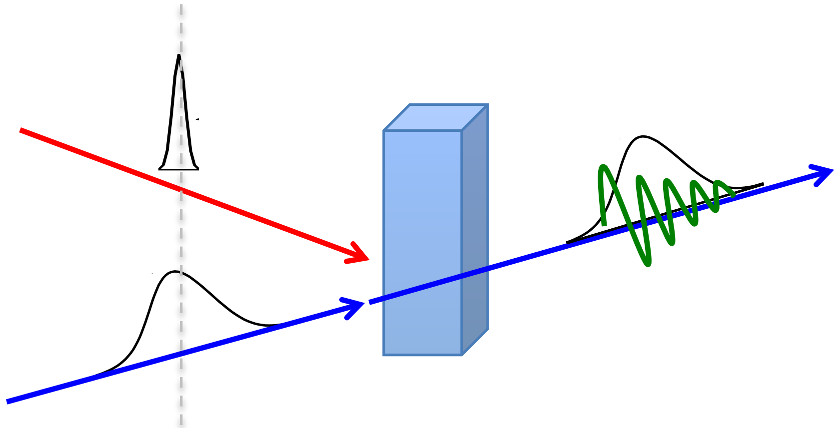


$FT\ \tau_1$

If E_1 E_2 E_3 carry the same frequency, the rephasing signal is weak due to a non-perfect phase matching condition!

2D spectra in frequency domain

Fabry-Perot etalon
Narrow band pump
Loss in time resolution

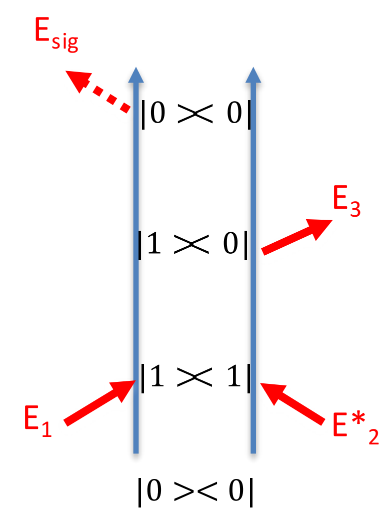


Broadband probe

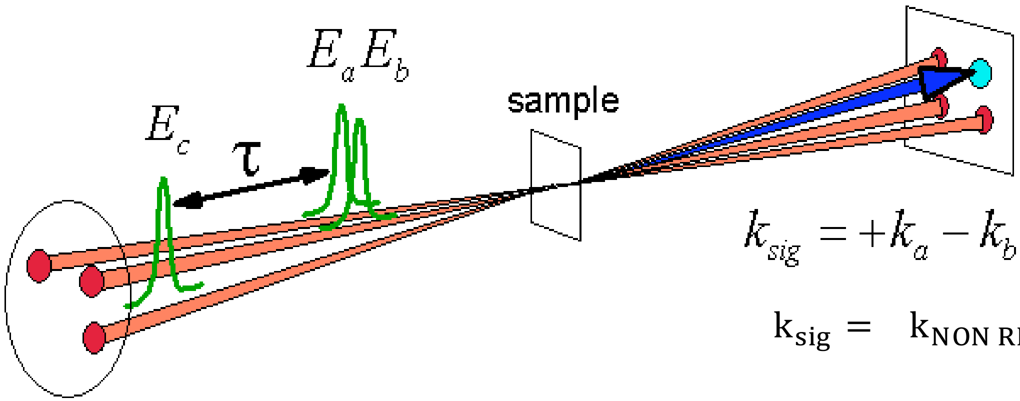
$$k_{sig\ REPH} = -k_1 + k_2 + k_3$$
$$+$$
$$k_{sig\ NON-REPH} = k_1 - k_2 + k_3$$

$$k_{sig} = k_{REPH} + k_{NON\ REPH} = 2k_3$$

- First due interaction are in space and time overlapped
- Within the signal is not possible to distinguish between rephasing and non rephasing parts
- The signal is emitted along the direction of the probe:
  Self-heterodyne detection: probe beam acts as a carrier wave for the weak signal from the system.
  You do not need an extra local oscillator (necessary for time domain experiments).



Transient grating



$$k_{sig} = +k_a - k_b + k_c$$

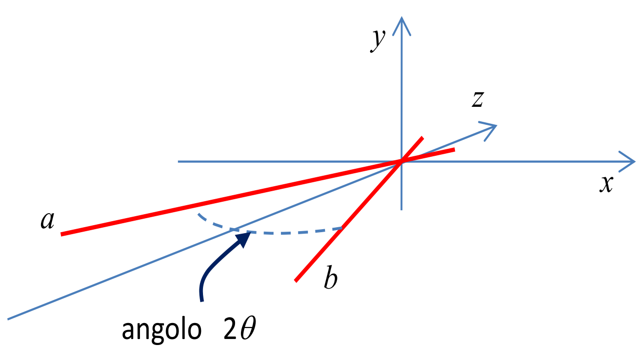
$$\mathrm{k_{sig}} = \mathrm{k_{NON\ REPH}}$$

The first 2 fields are overlapped in time but not in space: they create a grating on the sample spot which decays along with time (impulsive limit).

- An equivalent transient grating signal is emitted along the *rephasing* and the *non-rephasing* directions. In the forth direction of the square only the NR part is recorded (box car geometry).

$$\overrightarrow{E_1} \cdot \overrightarrow{E_2} = E_1 E_2 \exp(-i(\omega_1 - \omega_2)t + \underline{i(k_1 - k_2)r)}$$

Oscillating field in space



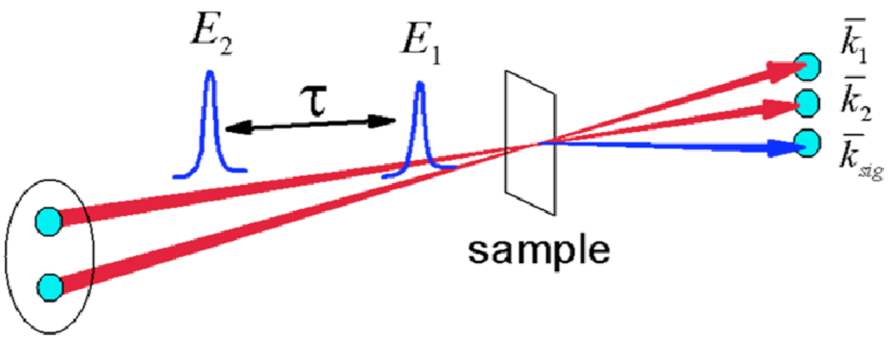
$$(k_1 - k_2) = \frac{2\pi}{d}$$

New k vector

$$d = \frac{\lambda}{2\eta \sin\theta}$$

Grating line space

Photon echo



$$\mathrm{k}_{sig} = -k_1 + k_2 + k_3$$

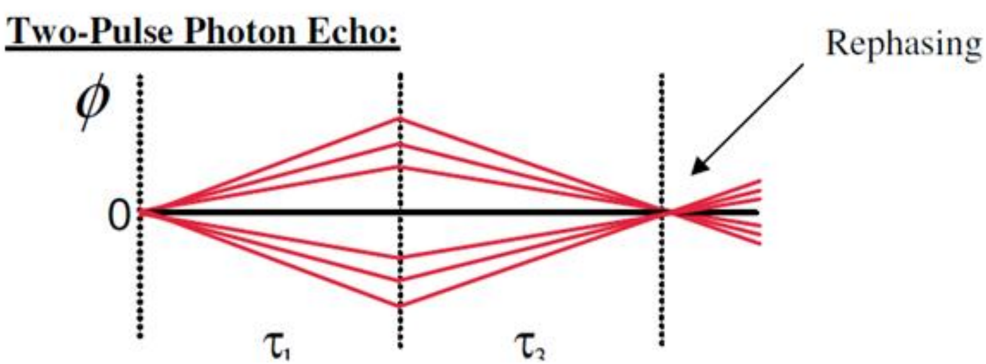
$$\mathrm{k}_{sig} = -k_1 + k_{23}$$ Rephasing signal

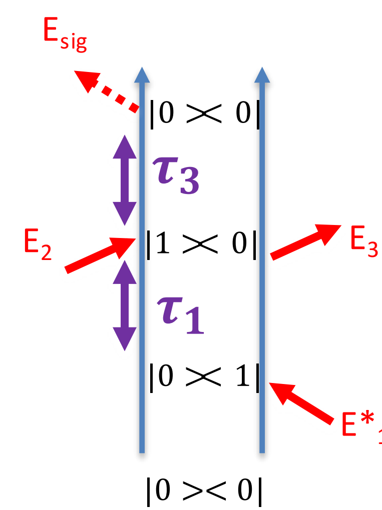
E_2 and E_3 are overlapped in space and time

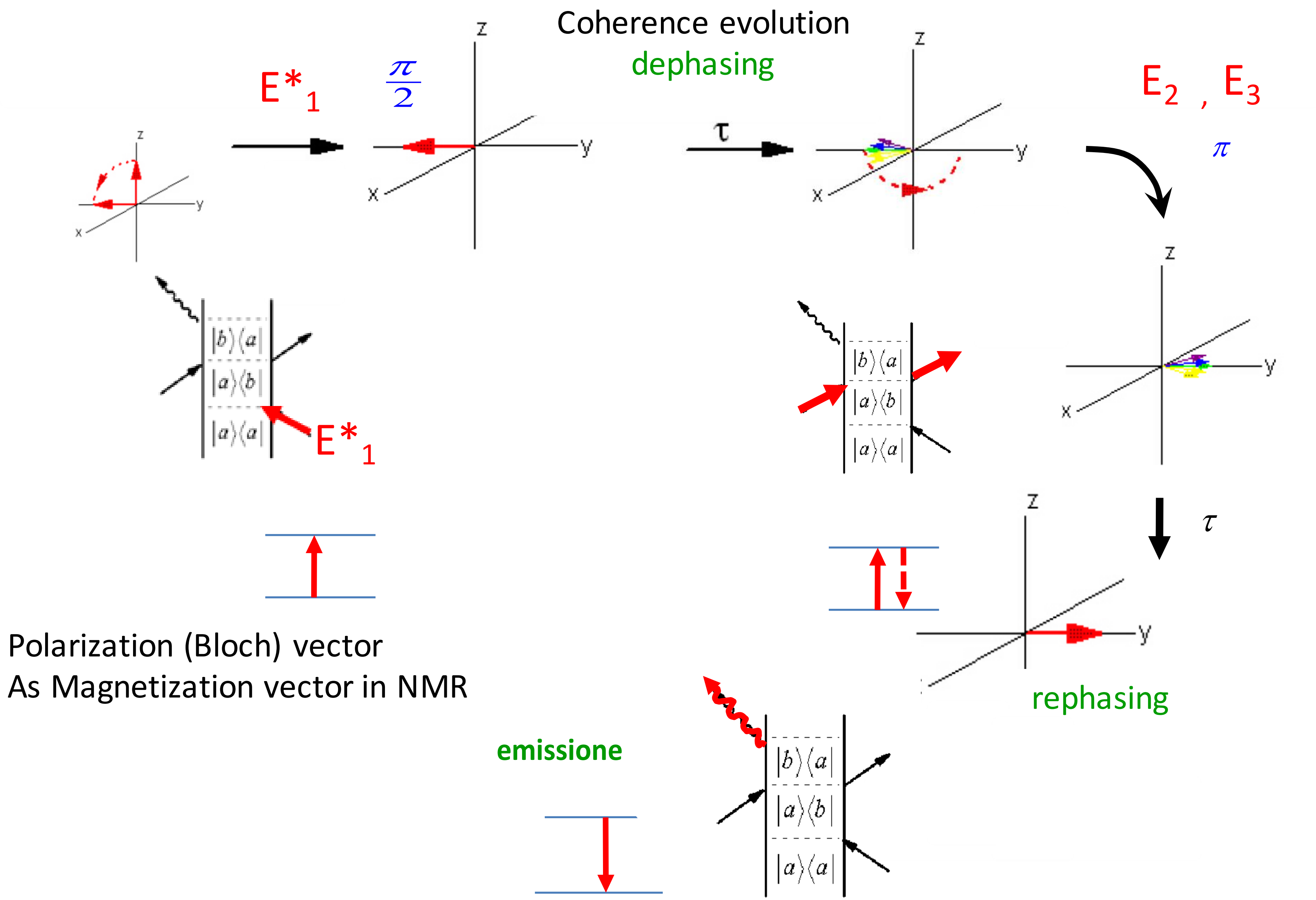
$$C(t) = p_{00}\mu_{01}^4 e^{-i\omega_{01}(\tau_3-\tau_1)\underline{-\Gamma_{10}(\tau_3-\tau_1)}\underline{-(\tau_3-\tau_1)^2\Delta^2/2}}$$

Divide homo/inhomogeneous broadening

Echo signal emitted at $\tau_3 = \tau_1$







Coherence evolution
dephasing
E*1
π/2
τ
E2 , E3
π
τ
rephasing
emissione
|b⟩⟨a|
|a⟩⟨b|
|a⟩⟨a|
E*1
Polarization (Bloch) vector
As Magnetization vector in NMR