Pulsed experiments

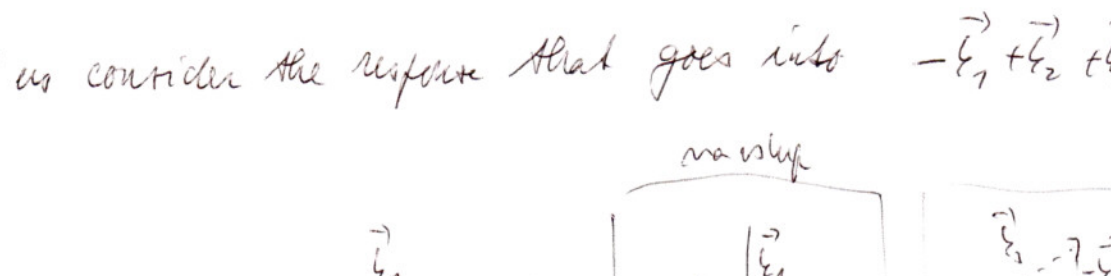
We need to calculate polarization $\vec{P}(\vec{r},t)$, but it is given as a complicated convolution

$$\vec{P}(\vec{r},t) = \int_0^\infty dt_3 \int_0^\infty dt_2 \int_0^\infty dt_1 \, S^{(3)}(t_3,t_2,t_1)\, E(t-t_3)\, E(t-t_2-t_3)\, E(t-t_1-t_2-t_3)$$

Let us assume a 4-wave mixing experiment, where the incomming field is

$$E(\vec{r},t) = A_1(t+T+\tau)\, e^{-i\omega_1(t+T+\tau)+i\vec{k}_1\cdot\vec{r}} + A_2(t+T)\, e^{-i\omega_2(t+T)+i\vec{k}_2\cdot\vec{r}}$$

$$+ A_3(t)\, e^{-i\omega_3 t + i\vec{k}_3\cdot\vec{r}} + c.c.$$



Let us consider the response that goes into $-\vec{k}_1+\vec{k}_2+\vec{k}_3$ direction

From 3 fields we have $6 \times 6 \times 6$ terms and we need to choose those that have the $-\vec{k}_1+\vec{k}_2+\vec{k}_3$ phase factor.

$$\begin{array}{ccc} 2 & 3 & 1 \\ 3 & 2 & 1 \\ 3 & 1 & 2 \\ 1 & 3 & 2 \\ 2 & 1 & 3 \\ 1 & 2 & 3 \end{array}$$

$$E(t-t_3)\,E(t-t_2-t_3)\,E(t-t_1-t_2-t_3)^{-\vec{k}_1+\vec{k}_2+\vec{k}_3} \approx$$

$$A_1^*(t+T+\tau-t_3)\,e^{i\omega(t+T+\tau-t_3)}\,A_2(t+T-t_2-t_3)\,e^{-i\omega(t+T-t_2-t_3)}$$

$$\times A_3(t-t_1-t_2-t_3)\,e^{-i\omega(t-t_1-t_2-t_3)}$$

$$+ A_1^*(t+T+\tau-t_2-t_3)\,e^{i\omega(t+T+\tau-t_2-t_3)}\,A_2(t+T-t_3)\,e^{-i\omega(t+T-t_3)}$$

$$\times A_3(t-t_1-t_2-t_3)\,e^{-i\omega(t-t_1-t_2-t_3)}$$

$$+ A_1^*(t+T+\tau-t_3)\,e^{i\omega(t+T+\tau-t_3)}\,A_2(t+T-t_1-t_2-t_3)\,e^{-i\omega(t+T-t_1-t_2-t_3)}$$

$$\times A_3(t-t_2-t_3)\,e^{-i\omega(t-t_2-t_3)}$$

$$+ A_1^*(t+T+\tau-t_2-t_3)\,e^{i\omega(t+T+\tau-t_2-t_2)}\,A_2(t+T-t_1-t_2-t_3)\,e^{-i\omega(t+T-t_1-t_2-t_3)}$$

$$\times A_3(t-t_3)\,e^{-i\omega(t-t_3)}$$

$$+ A_1^*(t+T+\tau-t_1-t_2-t_3)\,e^{i\omega(t+T+\tau-t_1-t_2-t_3)}\,A_2(t+T-t_2-t_3)\,e^{-i\omega(t+T-t_2-t_3)}$$

$$\times A_3(t-t_3)\,e^{-i\omega(t-t_3)}$$

$$+ A_1^*(t+T+\tau-t_1-t_2-t_3)\,e^{i\omega(t+T+\tau-t_1-t_2-t_3)}\,A_2(t+T-t_3)\,e^{-i\omega(t+T-t_3)}$$

$$\times A_3(t-t_2-t_3)\,e^{-i\omega(t-t_2-t_3)}$$

Collect phase factors

1) $$e^{i\omega(\cancel{t}+T+\tau-\cancel{t}-\cancel{T}-t)+i\omega(-\cancel{t_3}+t_2+\cancel{t_3}+t_1+t_2+t_3)}$$

$$= e^{i\omega(\tau-t)+i\omega(t_1+2t_2+t_3)} \qquad (DC)$$

2) $$e^{i\omega(\cancel{t}+\cancel{T}+\tau-\cancel{t}-\cancel{T}-t)+i\omega(-\cancel{t_2}-\cancel{t_3}+\cancel{t_3}+t_1+\cancel{t_2}+t_3)}$$

$$= e^{i\omega(\tau-t)+i\omega(t_1+t_3)} \qquad (NR)$$

3) $$e^{i\omega(\cancel{t}+\cancel{T}+\tau-\cancel{t}-\cancel{T}-t)+i\omega(-\cancel{t_3}+t_1+t_2+t_3+t_2+\cancel{t_3})}$$

$$= e^{i\omega(\tau-t)+i\omega(t_1+2t_2+t_3)} \qquad (DC)$$

4) $$e^{i\omega(\tau-t)+i\omega(-\cancel{t_2}-\cancel{t_3}+t_1+\cancel{t_2}+\cancel{t_3}+t_3)} = e^{i\omega(\tau-t)+i\omega(t_1+t_3)} \quad (NR)$$

5) $$e^{i\omega(\tau-t)+i\omega(-t_1-\cancel{t_2}-\cancel{t_3}+\cancel{t_2}+\cancel{t_3}+t_3)} = e^{i\omega(\tau-t)+i\omega(t_3-t_1)} \quad (R)$$

6) $$e^{i\omega(\tau-t)+i\omega(-t_1-\cancel{t_2}-\cancel{t_3}+\cancel{t_3}+\cancel{t_2}+t_3)} = e^{i\omega(\tau-t)+i\omega(t_3-t_1)} \quad (R)$$

all together:

$$P(\vec{r},t) = e^{-i\omega(t-\tau)} \int_0^\infty dt_3 \int_0^\infty dt_2 \int_0^\infty dt_1 \, S^{(3)}(t_3,t_2,t_1)$$

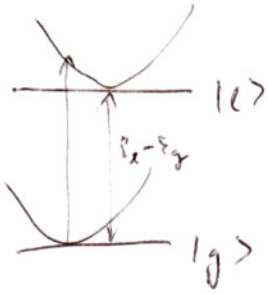
$$\times \Big\{ \Big[A_1^*(t+T+\tau-t_1-t_2-t_3)\, A_2(t+T-t_3)\, A_3(t-t_2-t_3)$$

$$+ A_1^*(t+T+\tau-t_1-t_2-t_3)\, A_2(t+T-t_2-t_3)\, A_3(t-t_3) \Big] e^{i\omega(t_3-t_1)}$$

$$+ \Big[\; (NR) \; \Big] e^{i\omega(t_3+t_2)} + \Big[\; (DC) \; \Big] e^{i\omega(t_1+2t_2+t_3)} \Big\}$$

Next step is to look at what phase factors come from the response functions. For this we however need to specify $\hat{\mu}$ and $U(t)$ operators.

Let us consider a system with 2 electronic levels $|g\rangle$ and $|e\rangle$



$$\hat{H}_s = \hat{H}_g(PQ)\,|g\rangle\langle g| + \hat{H}_e(PQ)\,|e\rangle\langle e|$$

$$= \left[\varepsilon_g + T(P) + V_g(Q)\right]|g\rangle\langle g| + \left[\varepsilon_e + T(P) + V_e(Q)\right]|e\rangle\langle e|$$

$$= \varepsilon_g|g\rangle\langle g| + \varepsilon_e|e\rangle\langle e| + \left[T(P) + V_g(Q)\right]\Big(\underbrace{|g\rangle\langle g| + |e\rangle\langle e|}_{\mathbb{1}}\Big)$$

$$+ \Big(V_e(Q) - V_g(Q)\Big)|e\rangle\langle e|$$

$$= \underbrace{\varepsilon_g|g\rangle\langle g| + \left[\varepsilon_e + \langle V_e(Q) - V_g(Q)\rangle\right]|e\rangle\langle e|}_{\hat{H}_{el}} + \overbrace{T(P) + V_g(Q)}^{\hat{H}_B}$$

$$+ \underbrace{\Big(V_e(Q) - V_g(Q) - \langle V_e(Q) - V_g(Q)\rangle\Big)|e\rangle\langle e|}_{\hat{H}_{int}}$$

$$\hat{H} = \hat{H}_B(P,Q)\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \begin{pmatrix} \varepsilon_g & 0 \\ 0 & \bar{\varepsilon}_e \end{pmatrix} + \Delta V(Q)\begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}$$

$$\hat{\mu} = d\,|e\rangle\langle g| + d^*\,|g\rangle\langle e| = \begin{pmatrix} 0 & d \\ d^* & 0 \end{pmatrix}$$

We assume that $\hat{\mu}$ does not depend on anything else than electronic degrees of freedom - Condon approximation.

Hamiltonian is diagonal and so even the evolution operator $U(t)$ is diagonal and has a form

$$U(t) = U_g(t)|g\rangle\langle g| + U_e(t)|e\rangle\langle e|$$

Now we can write down the pathways more explicitly

$$R_1(t_3,t_2,t_1) = Tr\{U^+(t_1)\hat{\mu}\,U(t_1)\,U^+(t_1+t_2)\hat{\mu}\,U(t_1+t_2)\,U^+(t_1+t_2+t_3)\hat{\mu}\,U(t_1+t_2+t_3)$$

$$\times\hat{\mu}\,\rho(-\infty)\}$$

$$= Tr\{U^+(t_1)\hat{\mu}\,U^+(t_2)\hat{\mu}\,U^+(t_3)\hat{\mu}\,U(t_1+t_2+t_3)\hat{\mu}\,\rho(-\infty)\}$$

$$= Tr_Q\{\langle g|U_g^+(t_1)|g\rangle\langle g|d^*|g\rangle\langle e|U_e^+(t_2)|e\rangle\langle e|d|e\rangle\langle g|U_g^+(t_3)|g\rangle\langle g|$$

$$d^*|g\rangle\langle e|U_e(t_1+t_2+t_3)|e\rangle\langle e|d|e\rangle\langle g|\rho_{eq}|g\rangle\langle g|\;|g\rangle$$

$$+\;0\;\}$$

[if we used $|e\rangle$ to close the Tr we would get $=0$

$$= |d|^4\,Tr_Q\{U_g^+(t_1)\,U_e^+(t_2)\,U_g^+(t_3)\,U_e(t_1+t_2+t_3)\,\rho_{eq}\}$$

Now take a look at evolution operators

$$U_g(t) = exp\left\{-\frac{i}{\hbar}\left(\varepsilon_g + \hat{H}_B(P,Q)\right)t\right\} = e^{-\frac{i}{\hbar}\varepsilon_g t}\,\tilde{U}_g(t)$$

$$U_e(t) = exp\left\{-\frac{i}{\hbar}\left(\varepsilon_e + \hat{H}_B(P,Q) + \Delta V(Q)\right)t\right\} = e^{-\frac{i}{\hbar}\varepsilon_e t}\,\underbrace{exp\left\{-\frac{i}{\hbar}\left(\hat{H}_B(Q,P) + \Delta V(Q)\right)t\right\}}_{\tilde{U}_e(t)}$$

$$R_1(t_3,t_2,t_1) = |d|^4 \, Tr_Q \{ \tilde{U}_g^+(t_1) \, \tilde{U}_e^+(t_2) \, \tilde{U}_g^+(t_3) \, \tilde{U}_e(t_1+t_2+t_3) \, \rho_{eq} \}$$

$$\times e^{+\frac{i}{\hbar}\varepsilon_g t_1 + \frac{i}{\hbar}\varepsilon_e t_2 + \frac{i}{\hbar}\varepsilon_g t_3 - \frac{i}{\hbar}\varepsilon_e (t_1+t_2+t_3)}$$

$$= |d|^4 \underbrace{e^{-i\omega_{eg} t_1 - i\omega_{eg} t_3}}_{e^{-i\omega_{eg}(t_1+t_3)}} Tr_Q \{ \tilde{U}_g^+(t_1) \tilde{U}_e^+(t_2) \tilde{U}_g^+(t_3) \tilde{U}_e(t_1+t_2+t_3) \rho_{eq} \}$$

(NR)

$$R_2(t_3,t_2,t_1) = |d|^4 \, Tr_Q \{ \tilde{U}_e^+(t_1+t_2) \, \tilde{U}_g^+(t_3) \, \tilde{U}_e(t_2+t_3) \, \tilde{U}_g(t_1) \, \rho_{eq} \}$$

$$\times e^{\frac{i}{\hbar}\varepsilon_e (t_1+t_2)} e^{\frac{i}{\hbar}\varepsilon_g t_3} e^{-\frac{i}{\hbar}\varepsilon_e (t_2+t_3)} e^{-\frac{i}{\hbar}\varepsilon_g t_1}$$

(R)

$$= |d|^4 e^{-i\omega_{eg}(t_3-t_1)} Tr_Q \{ \tilde{U}_e^+(t_1+t_2) \tilde{U}_g^+(t_3) \tilde{U}_e(t_2+t_3) \tilde{U}_g(t_1) \rho_{eq} \}$$

(R)

$$R_3(t_3,t_2,t_1) = |d|^4 e^{-i\omega_{eg}(t_3-t_1)} Tr_Q \{ \tilde{U}_e^+(t_1) \tilde{U}_g^+(t_2+t_3) \tilde{U}_e(t_3) \tilde{U}_g(t_1+t_2) \rho_{eq} \}$$

(NR)

$$R_4(t_3,t_2,t_1) = |d|^4 e^{-i\omega_{eg}(t_1+t_3)} Tr_Q \{ \tilde{U}_g(t_1+t_2+t_3) \tilde{U}_e^+(t_3) \tilde{U}_g(t_2) \tilde{U}_e(t_1) \rho_{eq} \}$$

Response functions could also be grouped ~~into~~ according to a phase factors. We get (apart of the sign) the same phase factors as with the field – rephasing (R) and non-rephasing (NR). There are non (DC) terms, but in a multilevel system they would appear, too.

Now we can go back into Eq. ( ) and insert

$$S^{(1)}(t_3,t_2,t_1) = \sum_n R_n(t_3,t_2,t_1) - R_n^*(t_3,t_2,t_1)$$

into the expression for $\vec{P}(\vec{r},t)$.

It is always an integration of slow envelopes and fast phase factors. We assume $\omega \approx \omega_{eg}$ – close to resonance

$$S^{(1)}(t_3,t_2,t_1)\ [DC]\ e^{i\omega(t_1+2t_2+t_3)}$$ ← this gives a negligible contribution because it is integrated with $e^{i2t_2\omega}$

$$\approx 0$$

$$S^{(1)}(t_3,t_2,t_1)\ [R]\ e^{i\omega(t_3-t_1)}$$

- the contribution $(NR)\ e^{-i\omega_{eg}(t_3+t_1)} \approx e^{-i2\omega t_1}$ gives ≈ 0 due to fast oscillation
- the contribution $(R)\ e^{-i\omega_{eg}(t_3-t_1)} \approx$ const gives measurable contribution

$$S^{(1)}(t_3,t_2,t_1)\ [NR]\ e^{i\omega(t_3+t_1)}$$

- gives only measurable contribution if $(NR)\ e^{-i\omega_{eg}(t_3+t_1)}$ is taken

altogether we can write →

$$\vec{P}(\vec{r},t) = \left(\frac{i}{\hbar}\right)^3 \int_0^\infty dt_3 \int_0^\infty dt_2 \int_0^\infty dt_1 \; e^{-i\omega(t-\tau)}$$

$$\times\Big\{\left[\bar{R}_2(t_3,t_2,t_1) + \bar{R}_3(t_3,t_2,t_1)\right]\Big(A_1^*(t+T+\tau-t_1-t_2-t_3)$$

$$\times A_2(t+T-t_2-t_3)\,A_3(t-t_3) + A_1^*(t+T+\tau-t_1-t_2-t_3)$$

$$\times A_3(t\cancel{+T}-t_2-t_3)\,A_2(t+T-t_3)\Big)\; e^{i(\omega-\omega_{eg})(t_3-t_1)}$$

$$+\left[\bar{R}_1(t_3,t_2,t_1) + \bar{R}_4(t_3,t_2,t_1)\right]\Big(A_1^*(t+T+\tau-t_2-t_3)$$

$$\times A_2(t+T-t_3)\,A_3(t-t_1-t_2-t_3) + A_1^*(t+T+\tau-t_2-t_3)$$

$$\times A_2(t+T-t_1-t_2-t_3)\,A_3(t-t_3)\Big)\; e^{i(\omega-\omega_{eg})(t_3+t_1)} \Big\}$$

$$\bar{R}_1(t_3,t_2,t_1) = |d|^4\, Tr_Q\left\{\tilde{U}_g^+(t_1)\,\tilde{U}_e^+(t_2)\,\tilde{U}_g^+(t_3)\,\tilde{U}_e(t_1+t_2+t_3)\,\rho_{eq}\right\}$$

$$\bar{R}_2(t_3,t_2,t_1) = \;\dots \quad \text{etc.}$$

With these expressions we can calculate a signal going into the $-\vec{k}_1+\vec{k}_2+\vec{k}_3$ direction. It is all too complicated – let us assume we send the pulses in an order k_1, k_2, k_3 so that $T>0$ and $\tau>0$ and let us assume $A(t) \equiv \delta(t)$

$$A_1^*(t+T+\tau-t_1-t_2-t_3)\,A_2(t+T-t_2-t_3)\,A_3(t-t_3) = \delta(t+T+\tau-t_1-t_2-t_3)$$
$$\times\,\delta(t+T-t_2-t_3)\,\delta(t-t_3)$$

$$\Rightarrow \quad t_3 = t$$
$$t_2 = T$$
$$t_1 = \tau$$

$$A_1^*(t+T+\tau-t_1-t_2-t_3)\,A_3(t-t_2-t_3)\,A_2(t+T-t_3) =$$

$$= \delta(t+T+\tau-t_1-t_2-t_3)\,\delta(t-t_2-t_3)\,\delta(t+T-t_3)$$

$$\Rightarrow \quad t_3 = t+T$$
$$t_2 = t-t_3 = t-t-T = -T$$
$$t_1 = t+T+\tau-t_2-t_3 = \cancel{t}+T+\tau+\cancel{T}-(\cancel{t}+\cancel{T}) = T+\tau$$

t_2 is negative and therefore no non-zero contribution exists.

$$\delta(t+T+\tau-t_2-t_3)\,\delta(t+T-t_3)\,\delta(t-t_1-t_2-t_3)$$

$$\Rightarrow \quad t_3 = t+T$$
$$t_2 = t+T+\tau-t-T = \tau$$
$$t_1 = t-t_2-t_3 = t-\tau-t-T = -\tau-T < 0$$

$$\delta(t+T+\tau-t_2-t_3)\,\delta(t+T-t_1-t_2-t_3)\,\delta(t-t_3)$$

$$\Rightarrow \quad t_3 = t$$
$$t_2 = t+T+\tau-t_3 = T+\tau$$
$$t_1 = t+T-t_2-t_3 = \cancel{t}+\cancel{T}-\cancel{T}-\tau-\cancel{t} = -\tau < 0$$

The only surviving contribution is the one of the response functions R_2 and R_3

$$\vec{P}(\vec{r},t) = \left(\frac{i}{\hbar}\right)^3 e^{-i\omega(t-\tau)}\left[\bar{R}_2(t,T,\tau)+\bar{R}_3(t,T,\tau)\right] e^{i(\omega-\omega_{eg})(t-\tau)}$$

$$= -\frac{i}{\hbar^3}\, e^{-i\omega_{eg}(t-\tau)}\left[\bar{R}_2(t,T,\tau)+\bar{R}_3(t,T,\tau)\right]$$

$$\vec{E}_s(t) \approx i\omega \vec{P}(t) =$$

$$= \omega\, e^{-i\omega_{eg}(t-\tau)} \left[\bar{R}_2(t, T, \tau) + \bar{R}_3(t, T, \tau) \right]$$

For an impulsive experiment we will need to express R_2 and R_3 in more detail.