Time-dependent perturbation theory

Response-functions

Quantum system – molecule

$$\hat{\varrho}(t)$$ ← density matrix

Polarization:

$$\vec{P}(t) = tr\{\hat{\vec{\mu}}\,\hat{\varrho}(t)\}$$

– we ignore here dependence on $\vec{r}$

Equation of motion

$$\boxed{\frac{\partial}{\partial t}\hat{\varrho}(t) = -i\mathcal{L}\hat{\varrho}(t) - \mathcal{D}(t)\hat{\varrho}(t) + i\mathcal{V}E(t)\,\hat{\varrho}(t)}$$

classical field

$$\mathcal{V}\hat{A} = \frac{1}{\hbar}[\hat{\mu}, \hat{A}]$$

$$\hat{\mu} = \hat{\vec{\mu}}\cdot\vec{e}$$ ← polarization vector of electric field

$$\vec{E}(t) = \vec{e}\,E(t)$$ ← scalar field

We apply perturbation theory with respect to $E(t)$

Three steps towards time-dependent PT

1) Interaction picture

$$\mathcal{K} = \mathcal{L} - i\mathcal{D}$$

$$-i\mathcal{K} = -i\mathcal{L} + (i)^2\mathcal{D} = -i\mathcal{L} - \mathcal{D}$$

EM:

$$\frac{\partial}{\partial t}\hat{\rho}(t) = -i\mathcal{K}\hat{\rho}(t) + i\mathcal{V}\hat{\rho}(t)E(t)$$

$$\hat{\rho}^{(I)}(t) = \mathcal{U}_0(-t)\hat{\rho}(t) \qquad \boxed{\mathcal{U}_0(t) = e^{-i\mathcal{K}t}}$$

$$\mathcal{V}^{(I)}(t) = \mathcal{U}_0(-t)\mathcal{V}\mathcal{U}_0(t)$$

$$\boxed{\frac{\partial}{\partial t}\hat{\rho}^{(I)}(t) = i\mathcal{V}^{(I)}(t)\hat{\rho}^{(I)}(t)E(t)} \equiv \boxed{i\mathcal{V}(t)\hat{\rho}^{(I)}(t)E(t)}$$

2) Integration from t_0

$$\boxed{\hat{\rho}^{(I)}(t) = \hat{\rho}^{(I)}(t_0) + i\int_{t_0}^{t} d\tau\, \mathcal{V}^{(I)}(\tau)\hat{\rho}^{(I)}(\tau)E(\tau)}$$

we can have $t_0 = 0$

$$\mathcal{U}_0(t) \longrightarrow \mathcal{U}_0(t-t_0)$$

3) Iteration

$$\hat{\rho}^{(I)}(t) = \underbrace{\hat{\rho}^{(I)}(t_0)}_{\boxed{\equiv \hat{\rho}(t_0)}} + i\int_{t_0}^{t} d\tau\, \mathcal{V}^{(I)}(\tau)\underbrace{\hat{\rho}^{(I)}(t_0)}_{\equiv \hat{\rho}(t_0)}E(\tau)$$

$$+(i)^2 \int_{t_0}^{t} d\tau \int_{t_0}^{\tau} d\tau' \, \gamma(\tau)\, \gamma(\tau')\, \hat{\rho}^{(I)}(\tau') E(\tau) E(\tau')$$

in the next iteration

$\hat{\rho}^{(I)}(\tau') \to \hat{\rho}(t_0)$

$$\rho^{(I)}(t) = \Big(1 + i \int_{t_0}^{t} d\tau\, \gamma(\tau) E(\tau) + (i)^2 \int_{t_0}^{t} d\tau \int_{t_0}^{\tau} d\tau' \, \gamma(\tau) \gamma(\tau') E(\tau) E(\tau') + \dots \Big) \hat{\rho}(t_0)$$

$\tau \longrightarrow \tau^{(1)}$

$\tau' \longrightarrow \tau^{(2)}$

$\tau^{(1)} > \tau^{(2)}$ ... time ordering

$$\hat{\rho}^{(I)}(t) = \Big(1 + i \int_{t_0}^{t} d\tau^{(1)} \gamma(\tau^{(1)}) E(\tau^{(1)}) + (i)^2 \int_{t_0}^{t} d\tau^{(1)} \int_{t_0}^{\tau^{(1)}} d\tau^{(2)} \gamma(\tau^{(1)}) \gamma(\tau^{(2)}) \times E(\tau^{(1)}) E(\tau^{(2)}) \dots \Big) \times \hat{\rho}(t_0)$$

Note! There are no factorials.

$$\hat{\rho}^{(I)}(t) = \underbrace{\overrightarrow{\exp} \left\{ i \int_{t_0}^{t} d\tau \, \gamma(\tau) E(\tau) \right\}} \hat{\rho}(t_0)$$

time-ordered exponential

symbolize the whole series

n-th order of the exponential

$$\hat{I}_n^{(I)}(t) = (i)^n \int_{t_0}^{t} d\tau^{(1)} \dots \int_{t_0}^{\tau^{(n-1)}} d\tau^{(n)}\, \mathcal{V}(\tau^{(1)})\mathcal{V}(\tau^{(2)}) \dots \mathcal{V}(\tau^{(n)})$$
$$\times E(\tau^{(1)})E(\tau^{(1)}) \dots E(\tau^{(n)})$$

$$\hat{I}_n(t) = \mathcal{U}_0(t-t_0)\, \hat{I}_n^{(I)}(t)$$

n-th order of the polarization

$$\vec{P}(t) = \vec{P}^{(0)}(t) + \vec{P}^{(1)}(t) + \vec{P}^{(2)}(t) + \dots$$

$$\boxed{\vec{P}^{(n)}(t) = tr\{\hat{\vec{\mu}}\, \hat{\rho}^{(n)}(t)\}}$$

$$\mathcal{V}(t) = \mathcal{U}_0(-t)\mathcal{V}\,\mathcal{U}_0(t)$$

$$\vec{P}^{(n)}(t) = tr\{\hat{\vec{\mu}}\, (i)^n \int_{t_0}^{t} d\tau^{(1)} \dots \int_{t_0}^{\tau^{(n-1)}} d\tau^{(n)}\, \underline{\mathcal{U}_0(t-t_0)\, \mathcal{U}_0(-(\tau^{(n)}-t_0))}\, \mathcal{V}$$
$$\times \mathcal{U}_0(\tau^{(1)}-t_0)\, \mathcal{U}_0(-(\tau^{(2)}-t_0))\, \mathcal{V}\, \mathcal{U}_0(\tau^{(2)}-t_0) \dots \mathcal{V}\, \mathcal{U}(\tau^{(n)}-t_0)$$
$$\times \hat{\rho}(t_0)\} E(\tau^{(1)})\, E(\tau^{(2)}) \dots E(\tau^{(n)})$$

3rd order polarization

$$\vec{P}^{(3)}(t) = (i)^3 \int_{t_0}^{t} d\tau^{(3)} \int_{t_0}^{\tau^{(3)}} d\tau^{(2)} \int_{t_0}^{\tau^{(2)}} d\tau^{(1)}\, tr\Big\{ \vec{\mu}\, \mathcal{U}_0(t-\tau^{(3)})\, \mathcal{V}\, \mathcal{U}_0(\tau^{(3)}-\tau^{(2)})\, \mathcal{V}$$

$$\times\, \mathcal{U}_0(\tau^{(2)}-\tau^{(1)})\, \mathcal{V}\mathcal{U}_0(\tau^{(1)}-t_0)\, \hat{\rho}(t_0) \Big\}$$

$$\times\, E(\tau^{(3)})\, E(\tau^{(2)})\, E(\tau^{(1)})$$

$$\tau_3 = t - \tau^{(3)} \qquad d\tau_3 = -d\tau^{(3)} \qquad \tau^{(3)} = t - \tau_3$$

$$\tau_3(t_0) = t - t_0$$

$$\tau_3(t) = 0$$

$$\int_{t_0}^{t} d\tau^{(3)} \to \int_{t-t_0}^{0} (-d\tau_3) \to \int_{0}^{t-t_0} d\tau_3$$

$$\mathcal{U}_0(t-\tau^{(3)}) \to \mathcal{U}_0(\tau_3)$$

$$\tau_2 = \tau^{(3)} - \tau^{(2)} = t - \tau_3 - \tau^{(2)} \qquad d\tau_2 = -d\tau^{(2)} \qquad \tau^{(2)} = t - \tau_3 - \tau_2$$

$$\tau_2(t_0) = t - \tau_3 - t_0$$

$$\tau_2(\tau^{(3)}) = 0$$

$$\int_{t_0}^{\tau^{(3)}} d\tau^{(2)} \to \int_{t-\tau_3-t_0}^{0} (-d\tau_2) \longrightarrow \int_{0}^{t-\tau_3-t_0} d\tau_2$$

$$\mathcal{U}_0(\tau^{(3)}-\tau^{(2)}) \longrightarrow \mathcal{U}_0(\tau_2)$$

$$\tau_1 = \tau^{(2)} - \tau^{(1)} \qquad d\tau_1 = -d\tau^{(1)}$$

$$\tau^{(1)} = t - \tau_3 - \tau_2 - \tau_1 \qquad \tau_1(t_0) = \tau^{(2)} - \tau_1$$

$$\tau_1(\tau^{(2)}) = 0$$

$$\vec{P}^{(3)}(t) = (i)^{n} \int_0^{t-t_0} d\tau_3 \int_0^{t-\tau_3-t_0} d\tau_2 \int_0^{t-\tau_3-\tau_2-t_0} d\tau_1$$

$$\times \, tr\left\{ \vec{\mu}\, \mathcal{U}_0(\tau_3)\, V\, \mathcal{U}_0(\tau_2)\, V\, \mathcal{U}_0(\tau_1)\, V\, \mathcal{U}_0(t-\tau_3-\tau_2-\tau_1-t_0)\, \hat{\rho}(t_0) \right\}$$

$$\times \, E(t-\tau_3)\, E(t-\tau_3-\tau_2)\, E(t-\tau_3-\tau_2-\tau_1)$$

Two important steps

1) $\mathcal{U}_0(t-t_0)\,\hat{\rho}(t_0) = \hat{\rho}(t_0) \longleftarrow$ when $\hat{\rho}(t_0)$ describes equilibrium

$$\mathcal{U}_0(t-\tau_3-\tau_2-\tau_1-t_0)\,\hat{\rho}(t_0) \equiv \hat{\rho}(t_0)$$

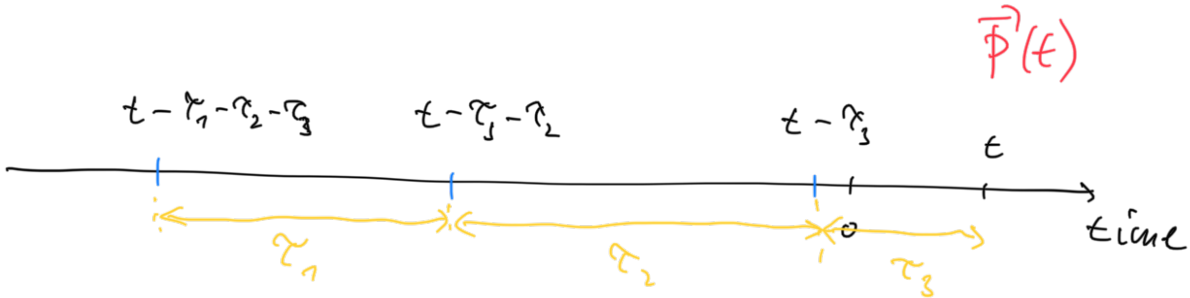
2) $t_0 \longrightarrow -\infty$

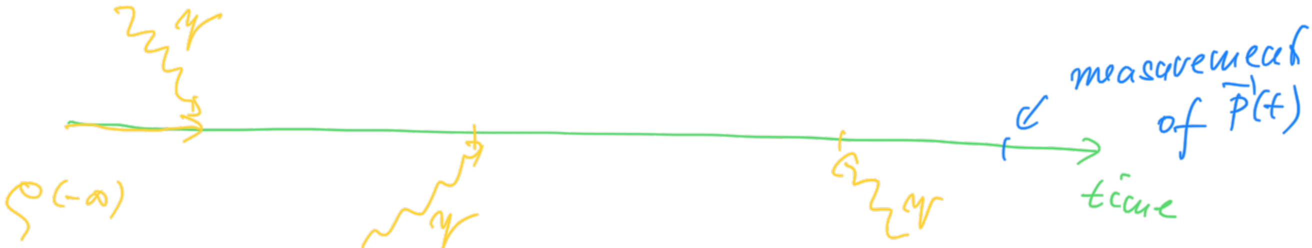
$$\vec{P}^{(3)}(t) = (i)^{n} \int_0^{\infty} d\tau_3 \int_0^{\infty} d\tau_2 \int_0^{\infty} \tau_1 \; tr\left\{ \vec{\mu}\, \mathcal{U}_0(\tau_3)\, V\, \mathcal{U}_0(\tau_2)\, V\, \mathcal{U}_0(\tau_1)\, V\, \hat{\rho}(-\infty) \right\}$$

$$\times \, E(t-\tau_3)\, E(t-\tau_3-\tau_2)\, E(t-\tau_3-\tau_2-\tau_1)$$

Structure of the response function

In time:



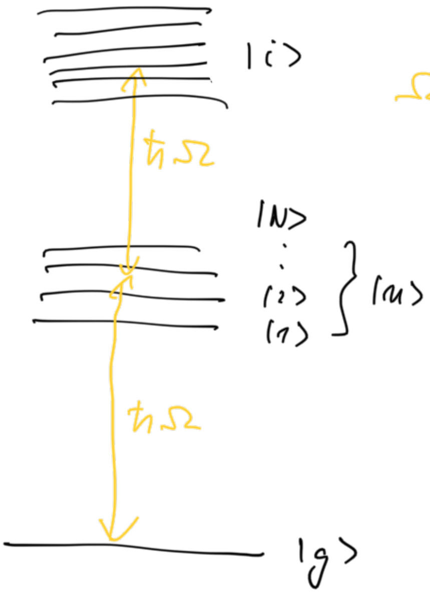


We integrate over all time intervals τ_1, τ_2, τ_3 at which the fields can interact.

Structure in the Liouville space

$$\hat{\rho}(-\infty) \xrightarrow{\text{no evolution}} \mathcal{V}\hat{\rho}(-\infty) \xrightarrow{\tau_1} \mathcal{V}\,\mathcal{U}_0(\tau_1)\,\mathcal{V}\hat{\rho}(-\infty) \ldots$$

What is the structure of the superoperator $\mathcal{V}$?



$\Omega \sim \omega$ ← frequency of light

$$\boxed{\begin{aligned}\hat{\vec{\mu}} &= \sum_n \left(\vec{d}_{ng}|n\rangle\langle g| + \vec{d}_{gn}|g\rangle\langle n|\right)\\ &+ \sum_{n,i}\left(\vec{d}_{in}|i\rangle\langle n| + \vec{d}_{ni}|n\rangle\langle i|\right)\end{aligned}}$$

$$\mathcal{V}\ldots = \frac{1}{\hbar}\left[\hat{\mu}, \ldots\right] = \frac{1}{\hbar}\left(\hat{\mu}\ldots - \ldots\hat{\mu}\right)$$

$$\hat{\rho}(-\infty) = |g\rangle\langle g| \quad \leftarrow \quad k_B T \ll \hbar\Omega$$

1. interaction

$$\mathcal{V}|g\rangle\langle g| = \frac{1}{\hbar}\left(\hat{\mu}|g\rangle\langle g| - |g\rangle\langle g|\hat{\mu}\right)$$

$$= \frac{1}{\hbar}\sum_n \left(d_{ng}\underbrace{|n\rangle\langle g|} - d_{gn}\underbrace{|g\rangle\langle n|}\right)$$

1. evolution

→ evolution of off-diagonal elements of ρ

~ coherences

$$\mathcal{U}_0(\tau_1)\mathcal{V}\rho(-\infty) = \sum_n d_{ng}\,\mathcal{U}_0(\tau_1)|n\rangle\langle g| + \dots$$

$$= \sum_{\varepsilon e}\sum_n d_{ng}\,\mathcal{U}^{(0)}_{\varepsilon e ng}(\tau_1)$$

~ secular approximation

$$\approx \sum_n d_{ng}\,\mathcal{U}^{(0)}_{ngng}(\tau_1)$$

Response function of a two-level system

$|e\rangle$

$|g\rangle$

$$S^{(3)}(\tau_3,\tau_2,\tau_1) =$$

$$= (i)^3\,\mathrm{tr}\{\hat{\mu}\,\mathcal{U}_0(\tau_3)\mathcal{V}\,\mathcal{U}_0(\tau_2)\mathcal{V}\,\mathcal{U}_0(\tau_1)\mathcal{V}\rho(-\infty)\}$$

$$\rho(-\infty) = |g\rangle\langle g|$$

$$\hat{\mu} = d\,(|e\rangle\langle g| + |g\rangle\langle e|) = d\,\hat{m}$$

$$\mathcal{M} = [\hat{m}, \dots]$$

$$S^{(3)}(\tau_3,\tau_2,\tau_1) = \left(\frac{i}{\hbar}\right)^3 d^4\,\mathrm{tr}\{\hat{m}\,\mathcal{U}_0(\tau_3)\mathcal{M}\,\mathcal{U}_0(\tau_2)\mathcal{M}\,\mathcal{U}_0(\tau_1)\mathcal{M}\,|g\rangle\langle g|\}$$

Expression under the $\underline{\underline{\mathrm{Tr}}}$

$$m\,|g\rangle\langle g| = |e\rangle\langle g| - |g\rangle\langle e|$$

$$\mathcal{U}_0(\tau_1)\, m\,|g\rangle\langle g| = G_{eg}(\tau_1)\,|e\rangle\langle g| - G_{eg}^*(\tau_1)\,|g\rangle\langle e| \qquad (2)$$

$$G_{eg}(\tau_1) = e^{-i\omega_{eg}\tau_1 - \Gamma_{eg}\tau_1} \qquad G_{eg}^*(\tau_1) = e^{+i\omega_{eg}\tau_1 - \Gamma_{eg}\tau_1}$$

$$m\,\mathcal{U}_0(\tau_1)\, m\,|g\rangle\langle g| = G_{eg}(\tau_1)\big(|g\rangle\langle g| - |e\rangle\langle e|\big) - G_{eg}^*(\tau_1)\big(|e\rangle\langle e| - |g\rangle\langle g|\big) \qquad (4)$$

Next step: evolution $\mathcal{U}_0(\tau_2) \Rightarrow \quad G_{ee}(\tau_2) = G_{gg}(\tau_2) = 1$

$$m\,\mathcal{U}_0(\tau_2)\, m\,\mathcal{U}_0(\tau_1)\, m\,|g\rangle\langle g| = \qquad (8)$$

$$= G_{eg}(\tau_1)\big(|e\rangle\langle g| - |g\rangle\langle e| - |g\rangle\langle e| + |e\rangle\langle g|\big)$$
$$- G_{eg}^*(\tau_2)\big(|g\rangle\langle e| - |e\rangle\langle g| - |e\rangle\langle g| + |g\rangle\langle e|\big)$$

$$\mathcal{U}_0(\tau_3)\, m\,\mathcal{U}_0(\tau_2)\, m\,\mathcal{U}_0(\tau_1)\, m\,|g\rangle\langle g| =$$

$$= G_{eg}(\tau_3)\,G_{eg}(\tau_1)\,|g\rangle\langle g| - G_{eg}^*(\tau_3)\,G_{eg}(\tau_1)\,|e\rangle\langle e|$$
$$- G_{eg}^*(\tau_3)\,G_{eg}(\tau_1)\,|e\rangle\langle e| + G_{eg}(\tau_3)\,G_{eg}(\tau_1)\,|g\rangle\langle g|$$
$$+ \ldots$$

Trace tr over the whole expression

$$\mathrm{tr}\{|g\rangle\langle g|\} = \mathrm{tr}\{|e\rangle\langle e|\} = 1$$

8 different terms to classify!