Non-linear response functions

We have made extended use of Eq. (1), but so far none of Eq. (2) and (3)

Eq. (3) describes the dynamics of the treated system

$$\frac{\partial}{\partial t}\hat{\rho}(t) = -\frac{i}{\hbar}\left[\underset{\text{or } M}{\hat{H}_S} + \underset{\text{or } SC}{\hat{H}_{E\text{-}M}(t)}, \hat{\rho}(t)\right]$$

We use $\hat{\rho}(t)$ instead of $|\psi(t)\rangle$ because the treatment is simpler and it is less difficult to talk about relaxation processes with $\hat{\rho}(t)$.

We introduce a <u>simplified notation</u>

We define a superoperator, an entity that acts on operators and changes them into different operators

e.g.
$$\frac{1}{\hbar}\left[\hat{H}, \hat{\rho}(t)\right] \equiv \mathcal{L}\hat{\rho}(t) \tag{54}$$

So we have

$$\boxed{\frac{\partial}{\partial t}\hat{\rho}(t) = -i\mathcal{L}_S\hat{\rho}(t) - i\mathcal{L}_{SC}(t)\hat{\rho}(t)} \tag{55}$$

Superoperator notation enables to use the tricks know from ordinary Hilbert space.

e.g. $\frac{\partial}{\partial t}|\Psi(t)\rangle = -\frac{i}{\hbar}\left(H_0 + H_I\right)|\Psi(t)\rangle$

$\Rightarrow \frac{\partial}{\partial t}|\Psi(t)\rangle^{(I)} = -\frac{i}{\hbar} H_I^{(I)}(t)\,|\Psi(t)\rangle^{(I)}$ where

$|\Psi(t)^{(I)}\rangle = U_0^+(t)\,|\Psi(t)\rangle$; $H_I^{(I)}(t) = U_0^+(t)\, H_I\, U_0(t)$

with

$U_0(t) = \exp\left\{-\frac{i}{\hbar} H_0 t\right\}$

Similarly for $\frac{\partial}{\partial t}\hat{\rho}(t) = -i\mathcal{L}_0\hat{\rho}(t) - i\mathcal{L}_I\hat{\rho}(t)$

$\Rightarrow \frac{\partial}{\partial t}\hat{\rho}^{(I)}(t) = -i\,\mathcal{L}_I^{(I)}(t)\,\hat{\rho}^{(I)}(t)$ where

$\hat{\rho}^{(I)}(t) = \mathcal{U}_0^+(t)\,\hat{\rho}(t)$

$\mathcal{L}_I^{(I)}(t) = \mathcal{U}_0^+(t)\,\mathcal{L}_I\,\mathcal{U}_0(t)$ and $\mathcal{U}_0(t) = \exp\left\{-i\mathcal{L}_0 t\right\}$

The property of $\mathcal{U}(t)$ is that $\frac{\partial}{\partial t}\mathcal{U}_0(t) = -i\mathcal{L}_0\,\mathcal{U}_0(t)$

Detailed investigation shows e.g. that

$$\mathcal{U}_0(t)\,\hat{\rho} = U_0(t)\,\hat{\rho}\,U_0^+(t)$$

For our purposes it is enough to know that we can do formally the same things with superoperators as with the operators.

Let us turn our attention to $H_{SC}(t)$ again

$$H_{SC}(t) = - \int d\vec{r}' \, \vec{\hat{P}}(\vec{r}') \, \vec{E}(t)$$

if only one molecule is concerned $\vec{\hat{P}}(\vec{r}') = \vec{\hat{\mu}} \, \delta(\vec{r}' - \vec{R})$

and thus $H_{SC}(t) = - \vec{\hat{\mu}} \cdot \vec{E}(t) = - \hat{\mu} \, \vec{n} \cdot \vec{E}(t) = - \hat{\mu} \, E(t)$

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

↖ this is the projection into the direction of the dipole

This leads to

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

The polarization density ~~at the location of the molecule~~

$$\boxed{\vec{P}(\vec{r}, t) = \sum_m \mathrm{Tr} \{ \hat{\mu}_m \hat{\rho}(t) \} \delta(\vec{r}' - \vec{R}_m)}$$

and we know that we need to expand it into the orders of $E(t)$.

Let us try the following

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

; where $\hat{\mathcal{A}}^{(I)}(t) = \mathcal{U}_S^{+}(t) \hat{\rho}(t)$

with $\mathcal{U}_S(t) = \exp\{ -i \mathcal{L}_S t \}$

This could be formally integrated

$$\boxed{\hat{\rho}^{(I)}(t) = \hat{\rho}^{(I)}(t_0) + i \int_{t_0}^{t} dt' \, \mathcal{V}^{(I)}(t') \, E(t') \, \hat{\rho}^{(I)}(t')}$$

The formal solution could be inserted into itself iteratively

$\Rightarrow$

$$\rho^{(I)}(t) = \rho^{(I)}(t_0) + i\int_{t_0}^{t} dt' \,\gamma^{(I)}(t') E(t') \rho^{(I)}(t_0) + (i)^2 \int_{t_0}^{t} dt' \int_{t_0}^{t'} dt'' \,\gamma^{(I)}(t') \gamma^{(I)}(t'')$$

$$\times E(t') E(t'') \rho^{(I)}(t_0) + (i)^3 \int_{t_0}^{t} dt' \int_{t_0}^{t'} dt'' \int_{t_0}^{t''} dt''' \,\gamma^{(I)}(t') \gamma^{(I)}(t'') \gamma^{(I)}(t''') E(t') E(t'') E(t''') \rho^{(I)}(t_0)$$

$$+ \dots$$

$$\mathcal{U}(t_0) = \mathbb{1} \quad \Rightarrow \rho^{(I)}(t_0) = \rho(t_0)$$

and we get

$$\rho(t) = \mathcal{U}(t) \rho(t_0) + i \int_{t_0}^{t} dt' \,\mathcal{U}(t) \gamma^{(I)}(t') E(t') \rho(t_0)$$

$$+ (i)^2 \int_{t_0}^{t} dt' \int_{t_0}^{t'} dt'' \,\mathcal{U}(t) \gamma^{(I)}(t') \gamma^{(I)}(t'') E(t') E(t'') \rho(t_0)$$

$$+ (i)^3 \int_{t_0}^{t} dt' \int_{t_0}^{t'} dt'' \int_{t_0}^{t''} dt''' \,\mathcal{U}(t) \gamma^{(I)}(t') \gamma^{(I)}(t'') \gamma^{(I)}(t''') \rho(t_0) E(t') E(t'') E(t''') + \dots$$

It looks very good, it only needs a bit of cosmetics

We expand all $\gamma^{(I)}(t)$ into $\mathcal{U}^{+}(t)\, \gamma\, \mathcal{U}(t)$ and let us consider 1. order and 3. order separately.

1. order

$$\cancel{\mathcal{U}(t')\rho t}$$

$$i\int_{t_0}^{t} dt'\,\mathcal{U}(t)\,\mathcal{U}^{+}(t')\,\mathcal{V}\,\mathcal{U}(t')\,\rho(t_0)\,E(t') =$$

$$= i\int_{t_0}^{t} dt'\,\mathcal{U}(t-t')\,\mathcal{V}\,\overset{\mathcal{U}(t')}{\cancel{\ }}\rho(t_0)\,E(t') = -i\int_{t-t_0}^{0} dt''\,\mathcal{U}(t'')\,\mathcal{V}\,\mathcal{U}(t-t'')\,\rho(t_0)\,E(t-t'')$$

$$t'' = t - t' \quad , t' = t - t''$$
$$dt'' = -dt'$$
$$t''(t_0) = t - t_0$$
$$t''(t) = 0$$

$$= i\int_{0}^{t-t_0} dt''\,\mathcal{U}(t'')\,\mathcal{V}\,\mathcal{U}(t-t'')\,\rho(t_0)\,E(t-t'')$$

we send $t_0 \to -\infty$

$$= i\int_{0}^{\infty} dt''\,\mathcal{U}(t'')\,\mathcal{V}\,\mathcal{U}(t-t'')\,\rho(-\infty)\,E(t-t'')$$

equilibrium before the action of the field

$$\mathcal{U}(t-t'')\,\rho(-\infty) = \rho(-\infty)$$

$$= i\int_{0}^{\infty} dt''\,\mathcal{U}(t'')\,\mathcal{V}\,\rho(-\infty)\,E(t-t'')$$

$$\vec{P}(\vec{r},t) = i\int_{0}^{\infty} dt''\,\mathrm{Tr}\left\{\vec{\mu}\,\mathcal{U}(t'')\,\mathcal{V}\,\rho(-\infty)\right\}E(t-t'')$$

$$\Rightarrow \boxed{S^{(1)}(t) = \frac{i}{\hbar}\,\mathrm{Tr}\left\{\vec{\mu}\,\mathcal{U}(t)\,[\mu,\rho(-\infty)]\right\}}$$

Response functions are in general tensors because they relate $\vec{E}$ with $\vec{P}$. We will drop all the discussions of different polarizations – they have to be discussed case by case

$\Rightarrow$

$$S^{(1)}(t) = \frac{i}{\hbar} \mathrm{Tr}\left\{\hat{\mu}\, \mathcal{U}(t)\, \hat{\mu}\, \rho(-\infty)\right\} - \frac{i}{\hbar} \mathrm{Tr}\left\{\hat{\mu}\, \mathcal{U}(t)\, \rho(-\infty)\, \hat{\mu}\right\}$$

We said that $\mathcal{U}(t) A = U(t) A U^{\dagger}(t)$

$\Rightarrow$

$$S^{(1)}(t) = \frac{i}{\hbar} \mathrm{Tr}\left\{\hat{\mu}\, U(t)\, \hat{\mu}\, \rho(-\infty)\, U^{\dagger}(t)\right\} - \frac{i}{\hbar} \mathrm{Tr}\left\{\hat{\mu}\, U(t)\, \rho(-\infty)\, \hat{\mu}\, U^{\dagger}(t)\right\}$$

Let us use the cyclic property of Tr and define

$$\boxed{J_1(t) = \mathrm{Tr}\left\{ U^{\dagger}(t)\, \hat{\mu}\, U(t)\, \hat{\mu}\, \rho(-\infty)\right\}}$$

We can check that the second term is $-\frac{i}{\hbar} J_1^{*}(t)$

$$\Rightarrow \boxed{S^{(1)}(t) = \Theta(t)\, \frac{i}{\hbar} \left(J_1(t) - J_1^{*}(t)\right)}$$

↑ we added a step function to ensure that t is always positive.

To treat third order is slightly more complicated, but not impossible.

~~We define:~~

$$\cancel{S^{(3)}(t_3,t_2,t_1) = (i)^3\, \mathrm{Tr}\{\hat{\mu}}$$

First let us change variable again

$$(i)^3 \int_{t_0}^{t} dt' \int_{t_0}^{t'} dt'' \int_{t_0}^{t''} dt'''\, \mathcal{U}(t-t')\,\mathcal{V}\,\mathcal{U}(t'-t'')\,\mathcal{V}\,\mathcal{U}(t''-t''')\,\mathcal{V}\,\mathcal{U}(t''')\,\rho(t_0)$$

$$\times\, E(t')\,E(t'')\,E(t''')$$

$$t_3 = t - t' \qquad dt_3 = -dt', \quad t_3(t_0) = t - t_0, \quad t_3(t) = 0$$

$$t_2 = t' - t'' \qquad t' = t - t_3$$

$$t_1 = t'' - t''' \qquad t'' = t' - t_2 = t - t_2 - t_3 \qquad t_0 \to \infty$$

$$t''' = t'' - t_1 = t - t_1 - t_2 - t_3$$

$$(i)^3 \int_0^{\infty} dt_3 \int_0^{\infty} dt_2 \int_0^{\infty} dt_1\, \mathcal{U}(t_3)\,\mathcal{V}\,\mathcal{U}(t_2)\,\mathcal{V}\,\mathcal{U}(t_1)\,\rho(-\infty)$$

$$\times\, E(t-t_3)\,E(t-t_2-t_3)\,E(t-t_1-t_2-t_3)$$

We define

$$\boxed{S^{(3)}(t_3,t_2,t_1) = (i)^3\, \Theta(t_3)\,\Theta(t_2)\,\Theta(t_1)\, \mathrm{Tr}\left\{\hat{\mu}\,\mathcal{U}(t_3)\,\mathcal{V}\,\mathcal{U}(t_2)\,\mathcal{V}\,\mathcal{U}(t_1)\,\mathcal{V}\,\rho(-\infty)\right\}}$$

Similarly, $S^{(3)}$ hides several terms that origin from the commutators.

To illustrate this, let us discuss a term corresponding to right part of first two commutator (from left) and the left part of the last commutator

$$-R(t_3,t_2,t_1) = +\left(\frac{i}{\hbar}\right)^3 \mathrm{Tr}\left\{\hat{\mu}\,\mathcal{U}(t_3)\,\hat{\mu}\,\mathcal{U}(t_2)\,\hat{\mu}\,\mathcal{U}(t_1)\,\rho(-\infty)\,\hat{\mu}\right\}$$

let us expand $\mathcal{U}(t)$:

$$-R(t_3,t_2,t_1) = \left(\frac{i}{\hbar}\right)^3 \mathrm{Tr}\left\{\hat{\mu}\,U(t_3)\,\hat{\mu}\,U(t_2)\,\hat{\mu}\,U(t_1)\,\rho(-\infty)\,\hat{\mu}\,U^\dagger(t_1)\,U^\dagger(t_2)\,U^\dagger(t_3)\right\}$$

$$= \left(\frac{i}{\hbar}\right)^3 \mathrm{Tr}\left\{\hat{\mu}\,U^\dagger(t_1+t_2+t_3)\,\hat{\mu}\,U(t_3)\,\hat{\mu}\,U(t_2)\,\hat{\mu}\,U(t_1)\,\rho(-\infty)\right\}$$

turn everything into „interaction picture"

$$= \left(\frac{i}{\hbar}\right)^3 \mathrm{Tr}\left\{\hat{\mu}\,U^\dagger(t_1+t_2+t_3)\,\hat{\mu}\,U(t_3+t_2+t_1)\,U^\dagger(t_2+t_1)\,\hat{\mu}\,U(t_2+t_1)\,U^\dagger(t_1)\,\hat{\mu}\,U(t_1)\,\rho(-\infty)\right\}$$

$$\boxed{\hat{\mu}(t) = U^\dagger(t)\,\hat{\mu}\,U(t)}$$ definition

$$= \left(\frac{i}{\hbar}\right)^3 \mathrm{Tr}\left\{\hat{\mu}(0)\,\hat{\mu}(t_3+t_2+t_1)\,\hat{\mu}(t_2+t_1)\,\hat{\mu}(t_1)\,\rho(-\infty)\right\}$$

If all terms are analyzed, we arrive at the following

$\longrightarrow$

$$S^{(3)}(t_3,t_2,t_1) = \left(\frac{i}{\hbar}\right)^3 \Theta(t_1)\Theta(t_2)\Theta(t_3) \sum_{\alpha=1}^{4}\left[R_\alpha(t_3,t_2,t_1) - R_\alpha^*(t_3,t_2,t_1)\right]$$

where

$$R_1(t_3,t_2,t_1) = Tr\left\{\hat{\mu}(t_1)\hat{\mu}(t_1+t_2)\hat{\mu}(t_1+t_2+t_3)\hat{\mu}(0)\rho(-\infty)\right\}$$

$$R_2(t_3,t_2,t_1) = Tr\left\{\hat{\mu}(0)\hat{\mu}(t_1+t_2)\hat{\mu}(t_1+t_2+t_3)\hat{\mu}(t_1)\rho(-\infty)\right\}$$

$$R_3(t_3,t_2,t_1) = Tr\left\{\hat{\mu}(0)\hat{\mu}(t_1)\hat{\mu}(t_1+t_2+t_3)\hat{\mu}(t_1+t_2)\rho(-\infty)\right\}$$

$$R_4(t_3,t_2,t_1) = Tr\left\{\hat{\mu}(t_1+t_2+t_3)\hat{\mu}(t_1+t_2)\hat{\mu}(t_1)\hat{\mu}(0)\rho(-\infty)\right\}$$

Comments:

- These expressions are general for any molecular systems for which the interaction with the field can be described as

$$H_{int} = -\hat{\mu}E(t)$$

- Specific form of $\hat{\mu}$ was not set yet
- Neither was the specific form of $\hat{H}$ specified

For microscopic theory we have to specify $\hat{\mu}$ and $\hat{H}_S$