Hierarchy of representations:

Shroedinger → $\psi(t)$ Evolution of a pure state

Liouville – Von Neumann → $[H, \rho]$ Evolution of a statistic ensemble

Liouville → $L \, , \Gamma$ Evolution including damping

How to consider a time evolving system under a perturbation

$$i\hbar \frac{d|\psi_S(t)>}{dt} = H|\psi_S(t)>$$

Time dependent Shroedinger equation
Time dependence is in the wavefunction

$$\psi(\mathrm{r,t}) = \varphi(r)e^{-i\omega t}$$

$$\omega = \frac{E}{\hbar} \quad ; \quad H\varphi = E\varphi$$

N.B.: As any wave, ψ is a function of position and time. Time dependence is an oscillating constant term that does not change the probability ψ^2. Frequency of oscillation ω results from the solution of the stationary Shroedinger equation.

We can define a new operator to cancel out the time dependence on ψ and let the function propagates free over time:

$$\psi(\mathrm{t}) = e^{-iH_0(t-t_0)/\hbar}\,\psi(t_0)$$

$$U(t,t_0) = e^{-iH_0(t-t_0)/\hbar}$$

Free evolution operator

or propagator

The system doesn't change under the static hamiltonian H_0, it only translates in time.

Properties:

- Hermitian operator
- Composition property:
  $U(t,t_0) = U(t,t_1)U(t_1,t_0) \qquad t_0 \to t_1 \to t$
- Time reversibility:
  $U^{-1}(t_0,t) = U(t,t_0)$

$$< \hat{A}(t) > = < \psi(t) \big| \hat{A}s \big| \psi(t) >$$ Shroedinger

$$< \hat{A}(t) > = < \psi(0) \big| \underline{U^\dagger \hat{A}s\, U} \big| \psi(0) >$$

$$< \hat{A}(t) > = < \psi(0) \big| \hat{A}_H\,(t) \big| \psi(0) >$$ Heisenberg: time dependent operator

What if H is time dependent:

$$U(t, t_0) = exp\left[-\frac{i}{\hbar}\int_{t_0}^{t} \widehat{H}(t')dt'\right]$$

$$e^{-x} = 1 - x + \frac{1}{2!}x^2 - \frac{1}{3!}x^3 + \cdots$$

$$U(t, t_0) \\ = 1 - \frac{i}{\hbar}\int_{t_0}^{t} \widehat{H}(\tau)d\tau + \left(-\frac{i}{\hbar}\right)^2 \int_{t_0}^{t} d\tau \int_{t_0}^{\tau} d\tau' \widehat{H}(\tau)\widehat{H}(\tau') + \left(-\frac{i}{\hbar}\right)^3 \int_{t_0}^{t} d\tau \int_{t_0}^{\tau} d\tau' \int_{t_0}^{\tau''} d\tau'' \widehat{H}(\tau)\widehat{H}(\tau')\widehat{H}(\tau'') + \cdots$$

$$t > \tau > \tau' > \tau'' > \cdots > t_0$$

Time ordering:
factorial terms omitted because of time ordering
permutating terms not possible

Interaction with EM field: to describe an evolving system under a perturbation we need time evolution on both ψ *and* H:

Perturbation theory at 1st order

$$\psi(t) \qquad\qquad H(t) = H_0 + \underline{V(t)}$$

A small perturbation allows for conservation of the basis set |n> of the unperturbed hamiltonian

INTERACTION PICTURE:

to divide the stationary part of hamiltonian from following EM perturbations on the system, we define ψ_I:

$$|\psi_I(t)> = U_0^{\dagger}(t, t_0)\,|\psi_S(t_0)>$$

$U_0^{\dagger}(t, t_0) \rightarrow e^{i\omega t}$, $|\psi_S(t_0)> \rightarrow e^{-i\omega t}$

If we apply the free-propagator, we can rewrite ψ_S so that we are solidal to its constant oscillating part.

$|\psi_I(t)> \rightarrow$ Time dependence is only due to the perturbating part V(t)

Time evolution in the interaction picture:

$$i\hbar \frac{d|\psi_S>}{dt} = H(t)|\psi_S>$$

$$i\hbar \frac{d}{dt}(U_0(t,t_0)|\psi_I>) = [H_0 + V(t)]\, U_0(t,t_0)|\psi_I>$$

$$\frac{dU_0}{dt}|\psi_I> + \frac{d|\psi_I>}{dt}U_0 = -\frac{i}{\hbar}[H_0 + V(t)]\, U_0|\psi_I>$$

$$U_0(t,t_0) = e^{-iH_0(t-t_0)/\hbar}$$

$$-\frac{i}{\hbar}H_0U_0|\psi_I> + \frac{d|\psi_I>}{dt}U_0 = -\frac{i}{\hbar}[H_0 + V(t)]\, U_0|\psi_I>$$

$$\frac{d|\psi_I>}{dt} = -\frac{i}{\hbar}\underline{U_0^\dagger V(t) U_0}|\psi_I>$$

$$i\hbar \frac{d|\psi_I>}{dt} = VI(t)\;|\psi_I>$$

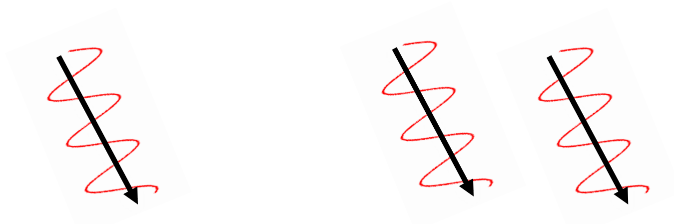
Formally indentical to shroedinger time dependent equation

V(t)

$$U(t,t_0) = U_0(t,t_0) + \sum_{n=1}^{\infty}\left(-\frac{i}{\hbar}\right)^n \int_{t_0}^{t} d\tau_n \int_{t_0}^{\tau_n} d\tau_{n-1} \dots \int_{t_0}^{\tau_2} d\tau_1 U_0(t,\tau_n)V(\tau_n)U_0(\tau_n\tau_{n-1})V(\tau_{n-1}) \dots$$

H_0

$$\dots U_0\,(\tau_2,\tau_1)V(\tau_1)U_0(\tau_1,t_0)$$



$$t_0 \rightarrow \tau_1 \rightarrow \tau_2 \rightarrow \cdots \rightarrow \tau_{n-1} \rightarrow \tau_n \rightarrow t$$

V_i = EM field interactions

During the free-evolution propagator U_0 the system rearranges and relaxes.

That evolution operator can be applied on a pure state ψ as well as on a statistics ensemble ρ.

ψ:

$$|\psi(t)>=|\psi(t_0)>+\sum_{n=1}^{\infty}\left(-\frac{i}{\hbar}\right)^n \int_{t_0}^{t} d\tau_n \int_{t_0}^{\tau_n} d\tau_{n-1} \ldots \int_{t_0}^{\tau_2} d\tau_1 U_0(t,\tau_n)V(\tau_n)U_0(\tau_n\tau_{n-1})V(\tau_{n-1})\ldots$$

$$\ldots U_0\,(\tau_2,\tau_1)V(\tau_1)U_0(\tau_1,t_0)|\psi(t_0)>$$

ρ:

$$|\psi(t)><\psi(t)|=U_0(t,t_0)\,|\psi_I(t)><\psi_I(t)|U^{\dagger}{}_0\,(t,t_0)$$

$$\rho(t)=U_0(t,t_0)\cdot\rho_I(t)\cdot U^{\dagger}{}_0\,(t,t_0)$$

$$\frac{\partial\hat{\rho}_I}{\partial t}=-\frac{i}{\hbar}[\widehat{H_I},\hat{\rho}_I]$$

$$\rho(t)=\rho(t_0)+\sum_{n=1}^{\infty}\left(-\frac{i}{\hbar}\right)^n \int_{t_0}^{t} d\tau_n \int_{t_0}^{\tau_n} d\tau_{n-1} \ldots \int_{t_0}^{\tau_2} d\tau_1 U_0(t,t_0)\cdot\left[V_I(\tau_n),\ldots[V_I(\tau_1),\rho(t_0)]\right]\cdot U_0^{\dagger}(t,t_0)$$

$$V_I=\mu_I\cdot E$$

$$P(t) = Tr\{\mu\rho\}$$ Expectation value of the macroscopic polarization

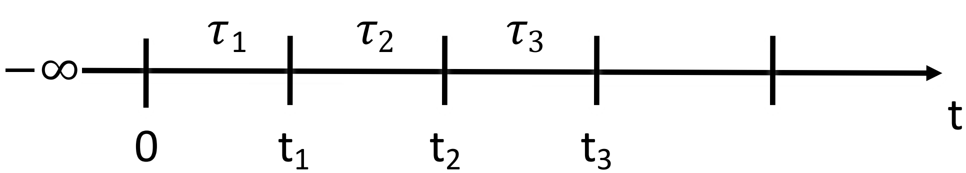
Infinite time evolution: $t_0 = -\infty$

$\Sigma \longrightarrow \int$

$$P^{(n)}(t) = \left(-\frac{i}{\hbar}\right)^n \int_{-\infty}^{t} d\tau_n \int_{-\infty}^{\tau_n} d\tau_{n-1} \ldots \int_{-\infty}^{\tau_2} d\tau_1 E(\tau_n) E(\tau_{n-1}) \ldots$$

$$\ldots E(\tau_1) \langle \mu_t [\mu(\tau_n), \ldots [\mu(\tau_1), \rho(-\infty)]] \rangle$$

$Tr\{\mu_t \rho_t\}$



Notice: μ is still in the interaction picture,
It contains free-evolutions

The non-linear response function $S^{(n)}$ is the convolution of N electric fields with the non-liner response $R^{(n)}$ of the system:

$$S^{(n)}(t) = E_n E_{n-1} \ldots E_1 \otimes R^{(n)}(t)$$

$$R^{(n)}(t) = \langle \mu_t [\mu_n, \ldots [\mu_1, \rho(-\infty)]] \rangle$$

Take notice:

$$\bar{P}(t) = P^{(0)}(t) + P^{(1)}(t) + P^{(2)}(t) + P^{(3)}(t) + \cdots$$ Time domain

before perturbation

$$\bar{P}(\omega) = \chi E + \chi^2 EE + \chi^3 EEE + \cdots$$ Frequency domain

Analyzing the system response function $R^{(n)}(t)$:

$$R^{(n)}(t) = \langle \mu_t [\mu_n, \ldots [\mu_1, \rho(-\infty)]] \rangle$$

t = observation time

$\rho(-\infty) = \rho_0$

Linear term:

$$R^{(1)}(t) = \langle \mu_t [\mu_1, \rho_0] \rangle$$

$$= \langle \mu_t \mu_1 \rho_0 \rangle - \langle \mu_t \rho_0 \mu_1 \rangle$$

$$= \langle \mu_t \mu_1 \rho_0 \rangle - \langle \rho_0 \mu_1 \mu_t \rangle$$ invariance of the trace to permutations

$$= \langle \mu_t \mu_1 \rho_0 \rangle - \langle \mu_t \mu_1 \rho_0 \rangle^*$$

$$= R_1 - R_1^*$$

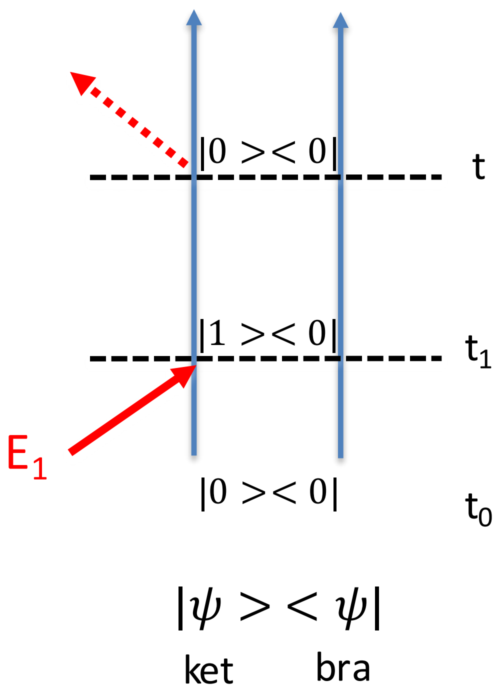
$$R_1 - R_{1c.c.} = \langle \mu_t \mu_1 \rho_0 \rangle - \langle \mu_t \mu_1 \rho_0 \rangle^*$$

$$Tr\{\mu_t \mu_1 |\psi><\psi|\}$$

Feynman diagrams:

- Two linear terms in the response function
- One operates on the bra and one on the ket
- Both define the same process

Only the process with the emission from the ket is considered !!

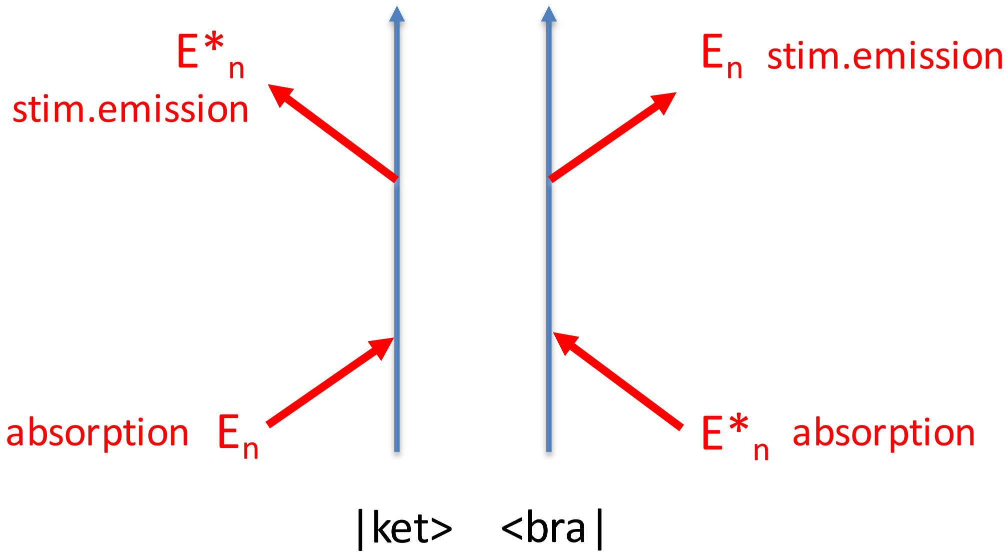


- Time evolution is represented by vertical arrows from bottom to top
- side arrows represent interactions with the electric field
- The last arrow rises from the system and represents the signal: it restores a population state
- Between interactions there is free evolution of the system described by super-operator $\hat{G}(t) = UAU^{\dagger}$

$E_1 = e^{ikr+i\omega t}$ Each field interacts only for a specific wave vector $\vec{k}$ and frequency ω

Phase matching condition

Resonance condition



$$E_n = e^{ikr+i\omega t} \qquad +k, +\omega$$

$$E^*{}_n = e^{-ikr-i\omega t} \qquad -k, -\omega$$

The pump – probe
Feynman and ladder diagrams:

Third order term:

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

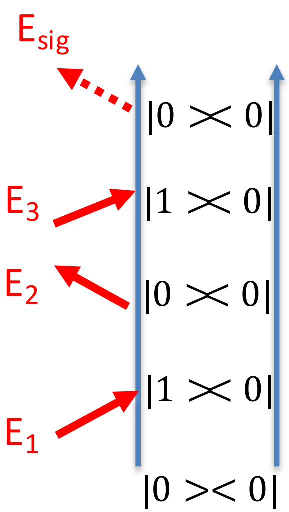
2^n *terms* and 2^{n-1} *independent terms*

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

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

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

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



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

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