Linear and non-linear spectroscopies

Wavefunction of the ground state ψ_0

(or more generally the state of the system before the interaction with the field)

We are interested to understand what will be the wavenction $\psi(t)$ after the interaction with the field.

$$H = \underbrace{H_0}_{\substack{\text{field}\\ \text{free}}} + \underbrace{H_I(t)}_{\substack{\text{time-dependent}\\ \text{interaction part}}}$$

Time-dependent perturbation theory:

$$\psi^{(0)}(t) = e^{-\frac{i}{\hbar}H_0(t-t_0)}\,\psi^{(0)}(t_0)$$

$$\psi^{(1)}(t) = \frac{1}{i\hbar}\int_{t_0}^{t} dt'\; e^{-\frac{i}{\hbar}H_0(t-t')}\,H_I(t')\,e^{-\frac{i}{\hbar}H_0(t'-t_0)}\,\psi^{(0)}(t_0)$$

$$\psi^{(2)}(t) = \frac{1}{(i\hbar)^2}\int_{t_0}^{t} dt' \int_{t_0}^{t'} dt''\; e^{-\frac{i}{\hbar}H_0(t-t')}\,H_I(t')\,e^{-\frac{i}{\hbar}H_0(t'-t'')}\,H_I(t'')\,\times$$
$$\times\, e^{-\frac{i}{\hbar}H_0(t''-t_0)}\,\psi^{(0)}(t_0)$$

To understand better the application of perturbation theory to spectroscopy we use the following notation

$$H_0 = \begin{pmatrix} H_a & 0 \\ 0 & H_b \end{pmatrix}, \quad \psi^{(0)}(t_0) = \begin{pmatrix} \psi_a \\ 0 \end{pmatrix},$$

the system is represented by two „parts" and before the interaction with the field, it is in the „a" part.

the interaction $H_I = \begin{pmatrix} 0 & \tilde{H}_I \\ \tilde{H}_I^* & 0 \end{pmatrix}$, so the interaction initiates transitions from „a" quantum states to „b"

Then $\psi^{(1)}(t)$ can be explicitly written as:

$$\psi^{(1)}(t) = \begin{pmatrix} 0 \\ \frac{1}{i\hbar}\int_{t_0}^{t} \underbrace{e^{-\frac{i}{\hbar}H_b(t-t')} \overbrace{\tilde{H}_I(t') \underbrace{e^{-\frac{i}{\hbar}H_a(t'-t_0)} \psi_a(t_0)}_{①}}^{②}}_{③} dt' \end{pmatrix}$$

① propagation of the system in initial field free state ψ_a

② interaction with the field which causes transitions from H_a system to H_b

③ propagation of the resulting state in H_b Hamiltonian.

Therefore in the 1st order perturbation theory, the field takes (in general time-dependent state) ψ_a and places it to the excited states described by H_a.

$\psi^{(2)}(t)$ second order response can be used to understand the action of the second field on top of $\psi^{(1)}(t)$ → pump-probe spectroscopy

We can split the system:

$$H_0 = \begin{pmatrix} H_a & 0 & 0 \\ 0 & H_b & 0 \\ 0 & 0 & H_c \end{pmatrix}$$

$$\psi^{(0)}(t_0) = \begin{pmatrix} \psi_a \\ 0 \\ 0 \end{pmatrix}$$

$$H_I = \begin{pmatrix} 0 & H_{pump} & 0 \\ H^*_{pump} & 0 & H_{probe} \\ 0 & H^*_{probe} & 0 \end{pmatrix}$$

$$\psi^{(2)}(t) = \begin{pmatrix} 0 \\ 0 \\ \left(\frac{1}{i\hbar}\right)^2 \int_{t_0}^{t} dt' \int_{t_0}^{t'} dt'' \, e^{-\frac{i}{\hbar} H_c (t-t')} H_{probe} \, e^{-\frac{i}{\hbar} H_b (t'-t'')} H_{pump} \times \\ e^{-\frac{i}{\hbar} H_a (t''-t_0)} \psi_a(t_0) \end{pmatrix}$$

1) After applying the pump pulse, ~~system is the~~ populations transfer to H_b states and evolve there.

2) After some delay, probe pulse takes the time-dependent state and puts it to the H_c Hamiltonian.

The resulting wavefunction

$$\Psi(t) = \Psi^{(0)}(t) + \Psi^{(1)}(t) + \Psi^{(2)}(t) + \dots$$ gives

access to different properties of the system:

$\langle \Psi^{(1)}(t) | \Psi^{(1)}(t) \rangle$ - populations of excited states after 1 photon transitions (fluorescence signal)

$\langle \Psi^{(2)}(t) | \Psi^{(2)}(t) \rangle$ - populations of resulting states after two-photon process (e.g. ionization yield in pump excitation probe ionization)

and various coherences $\langle \Psi^{(0)}(t) | \Psi^{(1)}(t) \rangle$

$\langle \Psi^{(0)}(t) | \Psi^{(3)}(t) \rangle$ etc. or more precisely transitions connecting initial and final states.

The system takes photons from the applied field.
The absorption cross section can be understood as

$$\sigma(\omega) = \frac{\Delta H(\omega) \text{ - absorbed energy}}{I_0(\omega) \text{ - incident energy}} \quad \Big(\underbrace{\text{for photon energy } \omega \text{ and per unit area}}_{\text{intensity of the incident light}} \Big)$$

Thus we have $$\sigma(\omega) = \frac{\Delta H(\omega)}{\frac{1}{2} c |\tilde{E}(\omega)|^2},$$ how to calculate $\Delta H(\omega)$?

To understand $\Delta H(\omega)$ - the absorbed energy for given photon energy ω, we consider change of system energy in time:

$$\frac{dE}{dt} = \frac{d}{dt}\langle \psi(t)|\hat{H}|\psi(t)\rangle =$$

$$= \langle \dot{\psi}(t)|H|\psi(t)\rangle + \langle\psi(t)|\frac{dH}{dt}|\psi(t)\rangle + \langle\psi(t)|\hat{H}|\dot{\psi}(t)\rangle =$$

$$= i\hbar\underbrace{\left(\langle\dot{\psi}(t)|\psi(t)\rangle - \langle\psi(t)|\dot{\psi}(t)\rangle\right)}_{0} + \langle\psi(t)|\frac{d}{dt}\hat{H}(t)|\psi(t)\rangle \overset{*}{=}$$

$$H(t) = H_0 + H_I(t)$$

$$\overset{*}{=} \boxed{\langle\psi(t)|\frac{d}{dt}H_I|\psi(t)\rangle}$$

Let us consider dipole interaction, so $H_I(t) = -\hat{\mu}\cdot\vec{\mathcal{E}}(t)$

Than we have

polarization function

$$\overset{*}{=} -\langle\psi(t)|\hat{\vec{\mu}}|\psi(t)\rangle\cdot\frac{d}{dt}\vec{\mathcal{E}}(t) = -\vec{P}(t)\cdot\frac{d}{dt}\vec{\mathcal{E}}(t)$$

Change of energy of the system during the interaction with the field:

$$\Delta H = \int_{-\infty}^{+\infty}\frac{d}{dt}E(t) = -\int_{-\infty}^{+\infty}P(t)\frac{d}{dt}\mathcal{E}(t)\,dt \overset{*}{=} \text{(See next page)}$$

Parseval's theorem:

$$f(t) \xleftrightarrow{FT} F(\omega)$$

$$g(t) \xleftrightarrow{FT} G(\omega)$$

$$\int_{-\infty}^{+\infty} f(t)\, g^*(t)\, dt = \frac{1}{2\pi} \int_{-\infty}^{+\infty} F(\omega)\, G^*(\omega)\, d\omega$$

Proof:

$$\int_{-\infty}^{+\infty} f(t)\, g^*(t)\, dt = \int_{-\infty}^{+\infty} f(t) \left[\frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} G(\omega)\, e^{i\omega t}\, d\omega \right]^* dt =$$

$$= \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} G^*(\omega) \underbrace{\left[\int_{-\infty}^{+\infty} f(t)\, e^{-i\omega t}\, dt \right]}_{F(\omega)} d\omega = \frac{1}{2\pi} \int_{-\infty}^{+\infty} F(\omega)\, G^*(\omega)\, d\omega$$

thus we have

$$\Delta H \overset{*}{=} - \int_{-\infty}^{+\infty} P(t) \frac{d}{dt} \mathcal{E}(t)\, dt = -\frac{1}{2\pi} \int_{-\infty}^{+\infty} \tilde{P}(\omega)\, \tilde{\dot{\mathcal{E}}}(\omega)\, d\omega =$$

$$= - \int_{-\infty}^{+\infty} \tilde{P}(\omega)\, i\, \omega\, \tilde{\mathcal{E}}(\omega)\, d\omega = -i \int_{-\infty}^{+\infty} \omega\, \tilde{P}(\omega)\, \tilde{\mathcal{E}}(\omega)\, d\omega$$

P(t) is purely real, ~~so $\tilde{P}(\omega)$ is imaginary, thus we~~

[illegible]

$$\Delta H = -4\pi\, \mathrm{Im} \int_{-\infty}^{+\infty} \omega\, \tilde{P}^*(\omega)\, \tilde{\mathcal{E}}(\omega)\, d\omega$$

Finally we obtain

$$\sigma(\omega) = -\frac{4\pi\omega}{c} \frac{\mathrm{Im}\{\tilde{P}^*(\omega)\, \tilde{\mathcal{E}}(\omega)\}}{|\tilde{\mathcal{E}}(\omega)|^2} .$$