Transient absorption spectroscopy

"Conventional formula":

$$\sigma(\omega) \sim \omega \sum_n |\langle\psi_n|\hat{\mu}|\psi_i\rangle|^2 \delta(\omega + \omega_i - \omega_n),$$

where ω is the incident light frequency,
ω_i and ω_n are the energies of initial and final states,
$\langle\psi_n|\hat{\mu}|\psi_i\rangle$ are transition dipole moments.

Time dependent formulation:

$$\sigma(\omega) \sim \omega \frac{\mathrm{Im}[\tilde{P}^*(\omega)\tilde{E}(\omega)]}{|\tilde{E}(\omega)|^2} \qquad \tilde{E}(\omega) = \mathcal{F}[E(t)] \qquad \tilde{P}(\omega) = \mathcal{F}[P(t)]$$

TD approach allows one to: 1) take explicit form of the field into account

2) treat more complicated situations when both the initial and final states are time-dependent

Main problem with the TD approach is how to compute $P(t)$?

$$P(t) = \langle\psi(t)|\hat{\mu}|\psi(t)\rangle \qquad i\hbar\frac{\partial\psi(t)}{\partial t} = \hat{H}\psi(t)$$

$$\hat{H}(t) = \hat{H}_0 - \hat{\vec{\mu}}\cdot\vec{E}(t)$$

Perturbation theory for $\psi(t)$:

$$|\psi(t)\rangle = \underbrace{\hat{U}(t)|\psi(0)\rangle}_{\psi^{(0)}(t)} + \underbrace{i\int_{t_0}^{t} dt'\, \hat{U}(t-t')\hat{\mu}E(t')\hat{U}(t')|\psi(0)\rangle}_{\psi^{(1)}(t)} + \ldots$$

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

$$P^{(0)}(t) = \langle \psi^{(0)}(t) | \hat{\mu} | \psi^{(0)}(t) \rangle$$

a) if $\psi(0)$ at initial moment of time is an eigenstate of the system, than $P^{(0)}$ is permanent dipole moment

b) if $\psi(0)$ is superposition of states, so the field-free state is time-dependent, than $P^{(0)}(t)$ describes harmonic emission.

$$P^{(1)}(t) = i \langle \psi(0) | \hat{u}^{+}(t) \hat{\mu} \int_{t_0}^{t} dt' \, \hat{u}(t-t') \hat{\mu} \, E(t') \hat{u}(t') | \psi(0) \rangle + c.c.$$

$$H_0 | \psi_k \rangle = \varepsilon_k | \psi_k \rangle$$

$$\hat{u}(t) | \psi(0) \rangle = \sum_K C_K e^{-i\varepsilon_k t} | \psi_k \rangle$$

I) the case of stationary initial state

$$|\psi(0)\rangle = |\psi_k\rangle$$

$$\hat{u}(t) | \psi(0) \rangle = e^{-i\varepsilon_i t} | \psi_i \rangle$$

$$P^{(1)}(t) = i \langle \psi_i | e^{i\varepsilon_i t} \hat{\mu} \int_{t_0}^{t} dt' \, \hat{u}(t-t') \hat{\mu} \, E(t') \, e^{-i\varepsilon_i t'} | \psi_i \rangle + c.c. =$$

$$= i \int_{t_0}^{t} dt' \, E(t') \, e^{i\varepsilon_i (t-t')} \langle \psi_i | \hat{\mu} \, \hat{u}(t-t') \hat{\mu} | \psi_i \rangle + c.c.$$

$$\sum_n |\psi_n\rangle\langle\psi_n| \equiv 1$$

$$P^{(1)}(t) = i \int_{t_0}^{t} dt'\, E(t')\, e^{i\varepsilon_i (t-t')} \langle \psi_i | \hat{\mu}\, \hat{u}(t-t') \sum_n |\psi_n\rangle\langle\psi_n|\mu|\psi_i\rangle + c.c.$$

$$= \quad \text{—''—} \quad \sum_n \langle \psi_i | \hat{\mu}\, e^{-i\varepsilon_n (t-t')} |\psi_n\rangle\langle\psi_n|\mu|\psi_i\rangle + c.c.$$

$$= i \sum_n \langle \psi_i|\hat{\mu}|\psi_n\rangle\langle\psi_n|\mu|\psi_i\rangle \int_{t_0}^{t} dt'\, E(t')\, e^{i\varepsilon_i (t-t')}\, e^{-i\varepsilon_n (t-t')} =$$

$$= i \sum_n |\langle \psi_i|\mu|\psi_n\rangle|^2 \underbrace{\int_{t_0}^{t} dt'\, E(t')\, e^{i(\varepsilon_i - \varepsilon_n)(t-t')}}_{I(t)}$$

We are interested in computing $\mathcal{F}[P^{(1)}(t)]$, so we need to compute $\mathcal{F}[I(t)]$

~~Let's assume that field $E(t)$ is infinitely short:~~

$$\cancel{E(t) = E_0\, \delta(t-t')}$$

~~assuming $t_0 \to -\infty$, $t \to \infty$, we can compute:~~

$$\cancel{\mathcal{F}\left[\int_{-\infty}^{+\infty} E_0\, \delta(t-t')\, e^{i(\varepsilon_i - \varepsilon_n)(t-t')}\, dt'\right]}$$

~~We can use the property of the Fourier transform~~

$$\cancel{\mathcal{F}[f(t)\, e^{iat}] = \tilde{f}(\omega - a)}$$

$$\cancel{\mathcal{F}[I(t)] = \tilde{E}(\omega + \varepsilon_i + \varepsilon_n)}$$

Assuming $t_0 \to -\infty$ $t \to \infty$, we obtain:

$$I(t) = \int_{-\infty}^{+\infty} dt' \underbrace{E(t')}_{f(t')} \underbrace{e^{i(\varepsilon_i - \varepsilon_n)(t-t')}}_{g(t'-t)}$$ – this is convolution of two functions

$$\mathcal{F}[(f * g)(t)] = \mathcal{F}[f(t)]\mathcal{F}[g(t)]$$

$$\mathcal{F}[I(t)] = \mathcal{F}[E(t')]\,\mathcal{F}[e^{i(\varepsilon_n - \varepsilon_i)(\cancel{t})}]$$

$$\mathcal{F}[E(t')] \to \tilde{E}(\omega) \qquad \mathcal{F}[e^{i(\varepsilon_n - \varepsilon_i)t}] \to \delta(\omega - (\varepsilon_n - \varepsilon_i))$$

Thus we obtain

$$P^{(1)}(\omega) = i \sum_n |\langle \psi_i | \hat{\mu} | \psi_n \rangle|^2 \tilde{E}(\omega)\, \delta(\omega - (\varepsilon_n - \varepsilon_i))$$

So substituting $P^{(1)}(\omega)$ to $\sigma(\omega)$, we obtain

$$\sigma(\omega) \sim \omega \sum_n |\langle \psi_i | \hat{\mu} | \psi_n \rangle|^2 \delta(\omega - (\varepsilon_n - \varepsilon_i))$$ –

same expression as in the case of stationary transitions between states.