Final run-through on transient absorption; nested pulse-propagators, origin of the phase-flip, fluorescence-detected wave-packet interferometry approach to TA

28 Feb 15

CINA

We need only the g- and e-states

$$H = |g\rangle \mathcal{H}_g \langle g| + |e\rangle \mathcal{H}_e \langle e|$$

$$H(t) = H + v(t) \quad ; \quad v(t) = -\hat{m}\, E(t)$$

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

$$E(t) = E_u(t) + E_r(t)$$

$$E_u(t) = E_u f(t) \cos(\Omega t + \varphi_u)$$

$$E_r(t) = E_r f(t - t_d) \cos(\Omega(t - t_d) + \varphi_r)$$

$$i\hbar \frac{\partial}{\partial t} |\Psi(t)\rangle = H(t)|\Psi(t)\rangle \text{ , with } |\Psi(t \ll 0)\rangle = e^{-iHt/\hbar} |g\rangle|\psi_0\rangle$$

$$= |g\rangle e^{-i\mathcal{H}_g t/\hbar} |\psi_0\rangle$$

$$= |g\rangle e^{-i\epsilon_0 t/\hbar} |\psi_0\rangle$$

using

$H_g|\psi_0\rangle = \epsilon_0 |\psi_0\rangle$;

$|\psi_0\rangle$ is any eigenket of $\mathcal{H}_g$

Interaction picture

$$|\tilde{\Psi}(t)\rangle = e^{iHt/\hbar} |\Psi(t)\rangle$$

$$i\hbar \frac{\partial}{\partial t} |\tilde{\Psi}(t)\rangle = e^{iHt/\hbar} \left(-H + H + v(t)\right) |\Psi(t)\rangle$$

$$= \tilde{v}(t)\, |\tilde{\Psi}(t)\rangle ,$$

where

$$\tilde{v}(t) = e^{iHt/\hbar}\, v(t)\, e^{-iHt/\hbar} ,$$

and the initial condition is

$$|\tilde{\Psi}(t \ll 0)\rangle = |g\rangle|\psi_0\rangle .$$

More explicitly,

$$\tilde{\mathcal{V}}(t) = -m\, e^{i\mathcal{H}_e t/\hbar} |e\rangle\langle g| e^{-i\mathcal{H}_g t/\hbar} E(t) + \text{H.c.}$$

$$\cong -m\, e^{i\mathcal{H}_e t/\hbar} |e\rangle\langle g| e^{-i\mathcal{H}_g t/\hbar} \cdot \left[\frac{E_u}{2} f(t)\, e^{-i\Omega t - i\varphi_u} + \frac{E_r}{2} f(t-t_d)\, e^{-i\Omega(t-t_d) - i\varphi_r}\right] + \text{H.c.}$$

In the second line, we have neglected the terms involving

$$e^{i\mathcal{H}_e t/\hbar} |e\rangle\langle g| e^{-i\mathcal{H}_g t/\hbar + i\Omega t}$$

and its Hermitian conjugate; these terms oscillate as $e^{\pm i(\epsilon/\hbar + \Omega)t}$ — at frequencies much higher than the electronic amplitude-transfer rates $\frac{E_{u,r}\, m}{2\hbar}$ and are ineffectual at driving the electronic transition.

The spectrally resolved transient transmission signal is the increase in the electromagnetic energy of the probe within a narrow frequency range due to the presence of the pump pulse:

$$\Delta\mathcal{U}(\bar{\omega}) \cong \frac{1}{2\pi}\int d^3R\; E_r'(\underset{\sim}{R}, t)\, \mathcal{E}_{u^2 r}'(\underset{\sim}{R}, t)$$

$$= \frac{1}{2\pi}\int d^3R\; E_r'(\underset{\sim}{R}, t)\, \mathcal{E}_{u2r}(\underset{\sim}{R}, t)\ .$$

save for later

$E_r'(\underset{\sim}{R}, t)$ is the portion of the probe field having frequency components in the narrow range $\bar{\omega} - \frac{\delta\omega}{2} < |\omega| < \bar{\omega} + \frac{\delta\omega}{2}$. The observation time t is assumed to be large enough that $t \cdot \delta\omega >> 1$. The spectrally filtered probe, with duration $\sim 2\pi/\delta\omega$, therefore exists only in the forward-propagated region. Since that trailing edge of the filtered probe lies at $\sim c\left(t - \frac{1}{2}\frac{2\pi}{\delta\omega}\right) >> \frac{c}{2}\frac{2\pi}{\delta\omega} = \pi c \frac{\lambda}{2\pi c}\left|\frac{\lambda}{\delta\lambda}\right| >> \lambda$, the region of spatial overlap between E_r' and the radiated signal field — proportional to the square of the field amplitude of the pump and linear in the

incident probe field-amplitude
lies entirely in the molecule's far-field region.
This feature simplifies the calculation of $\Delta\mathcal{U}(\bar\omega)$, as in this regime, the signal field takes the form

$$\mathcal{E}_{u^2r}(\underline{R},t) = -\frac{1}{c^2R}\,\ddot{m}_{u^2r}\left(t-\frac{R}{c}\right).$$

In the abstract, contributions to m_{u^2r} could arise from any of the six matrix elements

$$\langle 0|\hat{m}|\uparrow_u\downarrow_u\uparrow_r\rangle, \quad \cancel{\langle 0|\hat{m}|\uparrow_u\downarrow_r\uparrow_u\rangle}, \quad \langle 0|\hat{m}|\uparrow_r\downarrow_u\uparrow_u\rangle,$$

GSB $\sim e^{-2ig_u}$ GSB′

$$\langle\uparrow_u|\hat{m}|\uparrow_u\downarrow_r\rangle, \quad \cancel{\langle\uparrow_u|\hat{m}|\uparrow_r\downarrow_u\rangle}, \quad \langle\uparrow_r|\hat{m}|\uparrow_u\downarrow_u\rangle,$$

SE $\sim e^{2ig_u}$ SE′

and their complex conjugates. But, as is easily seen, the two stricken terms carry factors involving the experimentally uncontrolled <u>absolute</u> optical phase of the pump pulse; they average to zero, relative to the other terms, over the many laser shots needed to accumulate a transient transmission signal.

The terms labelled GSB (ground-state bleach) and SE (stimulated emission) have unequivocal physical interpretations. The primed version of each of these differs only by the interchange of a probe and one pump interaction (which is to say that, from the molecule's point of view, they don't differ at all).

Since the probe field must act on the system after at least one pump interaction in GSB and SE, these terms vanish for negative delays (probe before pump) greater than about their common pulse duration (~σ). Because probe action must precede pump action in GSB′, this signal contribution must vanish for $t_d \gtrsim \sigma$. The same turns out to be true of SE′, but this is not immediately obvious from the source-dipole matrix element.

The upshot of the analysis to this point is that calculation of the transient-transmission dipole requires the zeroth-order state $|0\rangle$, the first-order states $|\uparrow_u\rangle$ and $|\downarrow_r\rangle$, the second-order states $|\uparrow_u\downarrow_r\rangle$ and $|\uparrow_u\downarrow_u\rangle$, and the third-order states $|\uparrow_u\downarrow_u\uparrow_r\rangle$ and $|\uparrow_r\downarrow_u\uparrow_u\rangle$. Expressions for the required state-kets follow directly from the perturbative solution of the interaction-picture equation of motion (p. 1) transformed to the Schrödinger picture:

$$|\Psi(t)\rangle = e^{-iHt/\hbar}\left\{ 1 - \frac{i}{\hbar}\int_{-\infty}^{t} d\tau\, \tilde{v}(\tau) - \frac{1}{\hbar^2}\int_{-\infty}^{t} d\tau \int_{-\infty}^{\tau} d\bar{\tau}\, \tilde{v}(\tau)\tilde{v}(\bar{\tau}) + \frac{i}{\hbar^3}\int_{-\infty}^{t} d\tau \int_{-\infty}^{\tau} d\bar{\tau} \int_{-\infty}^{\bar{\tau}} d\bar{\bar{\tau}}\, \tilde{v}(\tau)\tilde{v}(\bar{\tau})\tilde{v}(\bar{\bar{\tau}}) \right\} |0\rangle|\Psi_0\rangle .$$

Hence

$$|0\rangle = e^{-iHt/\hbar}\,|g\rangle|\Psi_g\rangle = |g\rangle|\Psi_0\rangle e^{-i\epsilon_0 t/\hbar}$$

$$|\uparrow_\upsilon\rangle = |e\rangle \frac{i m E_\upsilon}{2\hbar}\int_{-\infty}^{t} d\tau\, f(\tau)\, e^{-i\mathcal{H}_e(t-\tau)/\hbar}\, e^{-i\mathcal{H}_g \tau/\hbar}\, e^{-i\Omega\tau - i\varphi_\upsilon}$$

$$= |e\rangle e^{-i\varphi_\upsilon}\, i F_\upsilon\, e^{-i\mathcal{H}_e t/\hbar}\, p^{(eg)}(t;\tau)|\Psi_0\rangle ,$$

where $p^{(eg)}(t;\tau) = \int_{-\infty}^{t} \frac{d\tau}{\sigma} f(\tau)\, e^{i\mathcal{H}_e\tau/\hbar}\, e^{-i\mathcal{H}_g\tau/\hbar - i\Omega\tau}$

and $F_\upsilon = \dfrac{m E_\upsilon \sigma}{2\hbar}$. OK agrees w/ $\boxed{\text{6 Aug 14}}$

$$|\uparrow_r\rangle = |e\rangle \frac{i m E_r}{2\hbar}\, e^{-i\mathcal{H}_e t/\hbar}\int_{-\infty}^{t} d\tau\, f(\tau - t_d)\, e^{i\mathcal{H}_e\tau/\hbar}\, e^{-i\mathcal{H}_g\tau/\hbar}\, e^{-i\Omega(\tau - t_d) - i\varphi_r}|\Psi_0\rangle$$

$$= |e\rangle e^{-i\varphi_r}\, i F_r\, e^{-i\mathcal{H}_e(t-t_d)/\hbar}\, p^{(eg)}(t - t_d;\tau)\, e^{-i\mathcal{H}_g t_d/\hbar}|\Psi_0\rangle$$

OK

$$= |e\rangle e^{-i\varphi_r}\, i F_r\, e^{-i\mathcal{H}_e(t-t_d)/\hbar}\, p^{(eg)}(t - t_d;\tau)|\Psi_0\rangle e^{-i\epsilon_0 t_d/\hbar} ,$$

where

$$F_r = \frac{m E_r \sigma}{2\hbar} .$$

$$|\uparrow_v \downarrow_r\rangle = -|g\rangle \frac{m^2 E_r E_v}{4\hbar^2} e^{-i\mathcal{H}_g t/\hbar} \int_{-\infty}^{t} d\tau \int_{-\infty}^{\tau} d\bar{\tau}\, f(\tau - t_d) f(\bar{\tau})$$

$$\times e^{i\mathcal{H}_g \tau/\hbar} e^{-i\mathcal{H}_e \tau/\hbar} e^{i\mathcal{H}_e \bar{\tau}/\hbar} e^{-i\mathcal{H}_g \bar{\tau}/\hbar} e^{i\Omega(\tau - t_d) - i\Omega\bar{\tau}} e^{i\varphi_r - i\varphi_v} |\Psi_0\rangle$$

$$= -|g\rangle e^{-i\varphi_v + i\varphi_r} F_v F_r e^{-i\mathcal{H}_g (t - t_d)/\hbar} p^{(ge)}(t - t_d; \tau)$$

$$\times e^{-i\mathcal{H}_e t_d/\hbar} p^{(eg)}(\tau + t_d; \bar{\tau}) |\Psi_0\rangle ,$$

OK, agrees

where

$$p^{(ge)}(t;\tau) = \int_{-\infty}^{t} \frac{d\tau}{\sigma} f(\tau) e^{i\mathcal{H}_g \tau/\hbar} e^{-i\mathcal{H}_e \tau/\hbar} e^{i\Omega\tau}$$

$$= \left(p^{(eg)}(t;\tau)\right)^{+} .$$

$\Updownarrow$ SWITCH ORDER

agrees

$$|\uparrow_v \downarrow_v\rangle = -|g\rangle F_v^2 e^{-i\mathcal{H}_g t/\hbar} p^{(ge)}(t;\tau) p^{(eg)}(\tau;\bar{\tau}) |\Psi_0\rangle .$$

$$|\uparrow_v \downarrow_v \uparrow_r\rangle = -|e\rangle e^{-i\varphi_r} i F_v^2 F_r e^{-i\mathcal{H}_e (t - t_d)/\hbar} p^{(eg)}(t - t_d; \tau)$$

$$e^{-i\mathcal{H}_g t_d/\hbar} p^{(ge)}(\tau + t_d; \bar{\tau}) p^{(eg)}(\bar{\tau}; \bar{\bar{\tau}}) |\Psi_0\rangle .$$ ✓

$$|\uparrow_r \downarrow_v \uparrow_v\rangle = -|e\rangle i F_v^2 F_r e^{-i\varphi_r} e^{-i\mathcal{H}_e t/\hbar} p^{(eg)}(t;\tau) p^{(ge)}(\tau;\bar{\tau})$$

$$\times e^{+i\mathcal{H}_e t_d/\hbar} p^{(eg)}(\bar{\tau} - t_d; \bar{\bar{\tau}}) |\Psi_0\rangle e^{-i\epsilon_0 t_d/\hbar} .$$ ✓

With these expressions for the relevant zeroth- through third-order states, we can write the four required contributions to $m_{U^2 r}$ as

$$m_{GSB} = e^{i\epsilon_0 t/\hbar}\left(-i m F_U^2 F_r e^{-i\varphi_r}\right) \times \langle\psi_0| e^{-iH_e(t-t_d)/\hbar}\, p^{(eg)}(t-t_d;\tau)\, e^{-iH_g t_d/\hbar}\, p^{(ge)}(\tau+t_d;\bar{\tau})\, p^{(eg)}(\bar{\tau};\bar{\bar{\tau}})|\psi_0\rangle + c.c.$$

$$m_{SE} = i F_U^2 F_r m e^{i\varphi_r} \langle\psi_0| p^{(ge)}(t;\tau')\, e^{iH_e t/\hbar}\, e^{-iH_g(t-t_d)/\hbar}\, p^{(ge)}(t-t_d;\tau)\, e^{-iH_e t_d/\hbar}\, p^{(eg)}(\tau+t_d;\bar{\tau})|\psi_0\rangle + c.c.$$

$$m_{GSB'} = -i F_U^2 F_r m e^{-i\varphi_r} \langle\psi_0| e^{-iH_e t/\hbar}\, p^{(eg)}(t;\tau)\, p^{(ge)}(\tau;\bar{\tau}) \times e^{iH_e t_d/\hbar}\, p^{(eg)}(\bar{\tau}-t_d;\bar{\bar{\tau}})|\psi_0\rangle\, e^{i\epsilon_0(t-t_d)/\hbar} + c.c.$$

$$m_{SE'} = i m F_U^2 F_r e^{i\varphi_r} e^{i\epsilon_0 t_d/\hbar} \langle\psi_0| p^{(ge)}(t-t_d;\tau')\, e^{iH_e(t-t_d)/\hbar} \times e^{-iH_g t/\hbar}\, p^{(ge)}(t;\tau)\, p^{(eg)}(\tau;\bar{\tau})|\psi_0\rangle + c.c.$$

all four look good by comparison w/ p. 17 of $\boxed{\text{6Aug14}}$

We specialize to pulses of sufficient brevity that nuclear dynamics can be ignored for the duration $\sim \sigma$ of the incident pulses. In this case, all the reduced pulse-propagators become complex numbers and commute with the nuclear time evolution operators. Specifically

$$p^{(eg)}(t;\tau) = \int_{-\infty}^{t} \frac{d\tau}{\sigma} f(\tau)\, e^{i\mathcal{H}_e\tau/\hbar}\, e^{-i\mathcal{H}_g\tau/\hbar}\, e^{-i\Omega\tau}$$

$$\cong \int_{-\infty}^{t} \frac{d\tau}{\sigma} f(\tau)\, e^{i(\mathcal{H}_e-\mathcal{H}_g)\tau/\hbar}\, e^{-i\Omega\tau}$$

ignoring $\frac{\tau^2}{\hbar^2}[\mathcal{H}_e, \mathcal{H}_g] \sim \frac{\sigma^2}{\hbar^2}[\mathcal{H}_e, \mathcal{H}_g]$

$$\cong \int_{-\infty}^{t} \frac{d\tau}{\sigma} f(\tau)\, e^{i(\Omega_{eg}-\Omega)\tau} \equiv p(t) .$$

where $\Omega_{eg} \cong (\mathcal{H}_e - \mathcal{H}_g)/\hbar$ is some constant estimate of the electronic transition frequency.

For the pulse envelope, we take

$$f(t) = g(t/\sigma)\, P(t/\sigma),$$

where $P(x) = \Theta(x+1) - \Theta(x-1)$ is a pedestal function.

Accordingly,

$$p(t) = \int_{-1}^{t/\sigma} dx\; P(x)\, g(x)\, e^{-i\nu x} ,$$

where $\nu = (\Omega - \Omega_{eg})\sigma$ is a dimensionless resonance offset.

Hence

$$p(t) = \int_{-1}^{t/\sigma} dx\, [\theta(x+1) - \theta(x-1)]\, g(x)\, e^{-i\nu x} .$$

We seek to remove the x-dependent step functions from the integrands, so that only integrals of algebraic functions must be evaluated.

$$\int_{-1}^{x_t} dx\; \phi(x)\, \theta(x - x_0) = \int_{-1}^{x_0} dx\, \phi(x)\, \theta(x - x_0) + \int_{x_0}^{x_t} dx\, \phi(x)\, \theta(x - x_0)$$

$$= \theta(x_t - x_0) \int_{x_0}^{x_t} dx\; \phi(x) \;-\; \theta(-1 - x_0) \int_{x_0}^{-1} dx\; \phi(x) ,$$

Integration by parts yields the same expression; see p. 11

whence

$$p(t) = \theta\left(\tfrac{t}{\sigma}+1\right) \int_{-1}^{t/\sigma} dx\; g(x)\, e^{-i\nu x} \;-\; \theta\left(\tfrac{t}{\sigma}-1\right) \int_{1}^{t/\sigma} dx\; g(x)\, e^{-i\nu x}$$

$$\boxed{p(t) = \theta\left(\tfrac{t}{\sigma}+1\right)\left[G\left(\tfrac{t}{\sigma}\right) - G(-1)\right] - \theta\left(\tfrac{t}{\sigma}-1\right)\left[G\left(\tfrac{t}{\sigma}\right) - G(1)\right]} ,$$

where

$$G(x) = \int dx\; g(x)\, e^{-i\nu x} .$$

Mathematica plot for $\nu = 0$ case looks good

We also need

$$p(t,\tau_1) \equiv p^{(ge)}(t,\tau)\, p^{(eg)}(\tau+\tau_1,\bar{\tau})$$

$$= \int_{-\sigma}^{t} \frac{d\tau}{\sigma} f(\tau)\, e^{i(\Omega-\Omega_{eg})\tau} \cdot p(\tau+\tau_1)$$

$$= \int_{-1}^{t/\sigma} dx\, e^{i\nu x} g(x) \left[\theta(x+1) - \theta(x-1)\right]$$

$x_1 \equiv \tau_1/\sigma$

$$\times \left\{ \theta(x+x_1+1)\left[G(x+x_1) - G(-1)\right] - \theta(x+x_1-1)\left[G(x+x_1) - G(1)\right] \right\}$$

$$\theta(x+1)\theta(x+x_1+1) = \theta(x_1)\theta(x+1) + \theta(-x_1)\theta(x+x_1+1)$$

$$\theta(x-1)\theta(x+x_1+1) = \theta(x-1)\theta(x+x_1+2-1)$$

$$= \theta(x_1+2)\theta(x-1) + \theta(-x_1-2)\theta(x+x_1+1)$$

$$\theta(x+1)\theta(x+x_1-1) = \theta(x+1)\theta(x+x_1-2+1)$$

$$= \theta(x_1-2)\theta(x+1) + \theta(-x_1+2)\theta(x+x_1-1)$$

$$\theta(x-1)\theta(x+x_1-1) = \theta(x_1)\theta(x-1) + \theta(-x_1)\theta(x+x_1-1)$$

Hence

$$p(t,\tau_1) = \int_{-1}^{t/\sigma} dx\, e^{i\nu x} g(x) \Big\{ \Big[\theta(x_1)\theta(x+1) + \theta(-x_1)\theta(x+x_1+1)$$

$$- \theta(x_1+2)\theta(x-1) - \theta(-x_1-2)\theta(x+x_1+1)\Big]\left[G(x+x_1) - G(-1)\right]$$

$$+ \Big[-\theta(x_1-2)\theta(x+1) - \theta(-x_1+2)\theta(x+x_1-1)$$

$$+ \theta(x_1)\theta(x-1) + \theta(-x_1)\theta(x+x_1-1)\Big]\left[G(x+x_1) - G(1)\right] \Big\}$$

looks good to here

Let's use integration by parts to find again the expression on p. 9:

$$\int_{-1}^{x_t} dx\, \phi(x)\, \theta(x - x_0) = \theta(x_t - x_0) V(x_t) - \theta(-1 - x_0) V(-1) - \int_{-1}^{x_t} dx\, \delta(x - x_0) V(x)$$

$$U = \theta(x - x_0) \qquad dV = \phi(x)\, dx$$

$$dU = \delta(x - x_0)\, dx \qquad V(x) = \int dx\, \phi(x)$$

$$= \theta(x_t - x_0) V(x_t) - \theta(-1 - x_0) V(-1) - \underbrace{[\theta(x_0 + 1) - \theta(x_0 - x_t)]}_{= -\theta(-1 - x_0) + \theta(x_t - x_0)} V(x_0)$$

$$= \theta(x_t - x_0)[V(x_t) - V(x_0)] - \theta(-1 - x_0)[V(-1) - V(x_0)],$$

just as we found before.

We define

$$H(x, x_1) = \int dx\, e^{i\nu x} g(x) [G(x + x_1) - G(-1)]$$

and

$$J(x, x_1) = \int dx\, e^{i\nu x} g(x) [G(x + x_1) - G(1)] .$$

We then obtain (with $x_t \equiv t/\sigma$)

$$
\begin{aligned}
p(t,\tau_1) = {} & \theta(x_1)\,\theta(x_t+1)\,[H(x_t,x_1) - H(-1,x_1)] \\
& + \theta(-x_1)\,\theta(x_t+x_1+1)\,[H(x_t,x_1) - H(-x_1-1,x_1)] \\
& - \theta(-x_1)\,\underbrace{\cancel{\theta(-1+x_1+1)}}_{0}\,[H(-1,x_1) - H(-x_1-1,x_1)] \\
& - \theta(x_1+2)\,\theta(x_t-1)\,[H(x_t,x_1) - H(1,x_1)] \\
& + \theta(x_1+2)\,\underbrace{\cancel{\theta(-1-1)}}_{0}\,[H(-1,x_1) - H(1,x_1)] \\
& - \theta(-x_1-2)\,\theta(x_t+x_1+1)\,[H(x_t,x_1) - H(-x_1-1,x_1)] \\
& + \theta(-x_1-2)\,\underbrace{\cancel{\theta(x_1)}}_{0}\,[H(-1,x_1) - H(-x_1-1,x_1)] \\
& - \theta(x_1-2)\,\theta(x_t+1)\,[J(x_t,x_1) - J(-1,x_1)] \\
& + \theta(x_1-2)\,\underbrace{\cancel{\theta(-1+1)}}_{0}\,[J(-1,x_1) - J(-1,x_1)] \\
& - \theta(-x_1+2)\,\theta(x_t+x_1-1)\,[J(x_t,x_1) - J(-x_1+1,x_1)] \\
& + \theta(-x_1+2)\,\underbrace{\cancel{\theta(-1+x_1-1)}}_{0}\,[J(-1,x_1) - J(-x_1+1,x_1)] \\
& + \theta(x_1)\,\theta(x_t-1)\,[J(x_t,x_1) - J(1,x_1)] \\
& - \theta(x_1)\,\underbrace{\cancel{\theta(-1-1)}}_{0}\,[J(-1,x_1) - J(1,x_1)] \\
& + \theta(-x_1)\,\theta(x_t+x_1-1)\,[J(x_t,x_1) - J(-x_1+1,x_1)] \\
& - \theta(-x_1)\,\underbrace{\cancel{\theta(-1+x_1-1)}}_{0}\,[J(-1,x_1) - J(-x_1+1,x_1)] .
\end{aligned}
$$

Leaving out the terms that vanish gives

$$
\begin{aligned}
p(t,\tau_1) = {} & \theta(x_1)\theta(x_t+1)[H(x_t,x_1)-H(-1,x_1)] \quad \checkmark \\
& +\theta(-x_1)\theta(x_t+x_1+1)[H(x_t,x_1)-H(-x_1-1,x_1)] \quad \checkmark \\
& -\theta(x_1+2)\theta(x_t-1)[H(x_t,x_1)-H(1,x_1)] \quad \checkmark \\
& -\theta(-x_1-2)\theta(x_t+x_1+1)[H(x_t,x_1)-H(-x_1-1,x_1)] \quad \checkmark \\
& -\theta(x_1-2)\theta(x_t+1)[J(x_t,x_1)-J(-1,x_1)] \quad \text{ok} \\
& -\theta(-x_1+2)\theta(x_t+x_1-1)[J(x_t,x_1)-J(-x_1+1,x_1)] \quad \text{ok} \\
& +\theta(x_1)\theta(x_t-1)[J(x_t,x_1)-J(1,x_1)] \quad \text{ok} \\
& +\theta(-x_1)\theta(x_t+x_1-1)[J(x_t,x_1)-J(-x_1+1,x_1)] \quad \text{ok} \; .
\end{aligned}
$$

all looks good

While the expression above is correct as written, and an analogous one could be derived for

$$
\mathbf{ppp}(t,\tau_1,\tau_2) \equiv p^{(eg)}(t;\tau)\,p^{(ge)}(\tau+\tau_1;\bar{\tau})\,p^{(eg)}(\bar{\tau}+\tau_2;\bar{\bar{\tau}})
$$

$$
= \int_{-1}^{x_t} dx\, e^{-i\nu x}\, g(x)\, pp(x+x_1, x_2) \; .
$$

But trials have shown that using symbolic integration under Mathematica to evaluate the double pulse propagator

$$
p(t,\tau_1) = \int_{-1}^{x_t} dx\, e^{i\nu x}\, g(x)\, p(x+x_1)
$$

(with a specific algebraic envelope function $g(x)$)

yields a conditional expression for the definite integral on the RHS that is equivalent to the one obtained above, but which evaluates markedly faster when numerical values for t and τ_1 are inserted.

Accordingly, we adopt an analogous approach for the triple pulse-propagator (rather than evaluating it "by hand") and symbolically integrate

$$\int_{-1}^{x_t} dx\, e^{-i\nu x}\, g(x)\, pp(x+x_1, x_2)$$

using Mathematica's conditional expression for pp for the chosen envelope function g.

The resulting expressions for ppp are lengthy, and are much more easily generated than reproduced, but nonetheless evaluate very rapidly when numerical values are assigned to t, τ_1, and τ_2. [The GSB and GSB′ dipoles make use of triple pulse-propagators. It is worth noting that in GSB, $\tau_1 = t_d$ and $\tau_2 = 0$, while in GSB′, $\tau_1 = 0$ and $\tau_2 = -t_d$. Since neither case involves nonzero τ_1 and τ_2, it might be helpful to generate separate expressions for ppp in each case (functions of two variables) rather than relying on the common general expression (a function of three variables).

Using the single, double, and triple pulse propagators (p. 7, p. 13, and p. 13, respectively) that obtain in the present, short-pulse limit, we may write

$$m_{GSB} = -imF_U^2F_r e^{-i\varphi_r} e^{i\epsilon_0(t-t_d)/\hbar} \langle\Psi_0|e^{-i\mathcal{H}_e(t-t_d)/\hbar}|\Psi_0\rangle$$

$$\times\, ppp(t-t_d, t_d, 0) + c.c.$$

ok, repeats from 6 Aug 14

$$m_{SE} = imF_U^2F_r e^{i\varphi_r} \langle\Psi_0|e^{i\mathcal{H}_e t/\hbar} e^{-i\mathcal{H}_g(t-t_d)/\hbar} e^{-i\mathcal{H}_e t_d/\hbar}|\Psi_0\rangle$$

$$\times\, p^*(t)pp(t-t_d, t_d) + c.c.$$

ok, repeats

$$m_{GSB'} = -imF_U^2F_r e^{-i\varphi_r} e^{i\epsilon_0(t-t_d)/\hbar} \langle\Psi_0|e^{-i\mathcal{H}_e(t-t_d)/\hbar}|\Psi_0\rangle$$

$$\times\, ppp(t, 0, -t_d) + c.c.$$

repeats

$$m_{SE'} = imF_U^2F_r e^{i\varphi_r} e^{-i\epsilon_0(t-t_d)/\hbar} \langle\Psi_0|e^{i\mathcal{H}_e(t-t_d)/\hbar}|\Psi_0\rangle$$

$$\times\, p^*(t-t_d)\, pp(t,0) + c.c.$$

repeats

In the vibrationally abrupt limit, the GSB, GSB′, and SE′ dipoles are seen to be determined by the Heller absorption kernel. The GSB and SE dipoles vanish for $t_d \lesssim -\sigma$, and the GSB′ dipole does so for $t_d \gtrsim \sigma$.

Before setting up the signal calculation itself, we first further develop the expression for $\Delta U(\bar{\omega})$ given on p. 2, obtaining both time- and frequency-based one-dimensional integrals for the transient absorption signal. We also explicitly justify the use – in the second signal formula on page 2 – of the spectrally <u>unfiltered</u> field radiated by the molecular source.

The filtered probe field appearing in

$$\Delta U(\bar{\omega}) = \frac{1}{2\pi}\int_{\text{all space}} d^3R \, E_r'(\underset{\sim}{R},t)\, \mathcal{E}_{v2_r}'(\underset{\sim}{R},t)$$

is confined to the spatial slab

$$c\left(t - t_d - \frac{1}{2}\frac{2\pi}{\delta\omega}\right) < Z < c\left(t - t_d + \frac{1}{2}\frac{2\pi}{\delta\omega}\right).$$

Since $(t - t_d)\,\delta\omega \gg 1$, it follows that within this slab, $Z \gg c\frac{2\pi}{\delta\omega} \gg c\frac{2\pi}{\bar{\omega}}$; The filtered probe field dwells entirely in the molecule's far zone. The filtered probe at any point in space can be written in terms of its spectral components at the molecular location:

$$E_r'(\underset{\sim}{R},t) = \int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\, e^{-i\omega t}\, \tilde{E}_r'(\underset{\sim}{R},\omega)$$

$$= \int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\, e^{-i\omega t}\int_{-\infty}^{\infty} dt'\, e^{i\omega t'}\, \underbrace{E_r'(\underset{\sim}{R},t)}_{E_r'(\underset{\sim}{0},\, t - Z/c)}$$

$$= \int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\, e^{-i\omega(t - Z/c)}\, \tilde{E}_r'(\underset{\sim}{0},\omega)$$

The spectrally filtered signal field is

$$\mathcal{E}'_{v^2r}(\underset{\sim}{R},t) = -\frac{1}{c^2R}\ddot{m}'(t-R/c)$$

$$= -\frac{1}{c^2R}\int_{-\infty}^{\infty}\frac{d\omega'}{2\pi}e^{-i\omega' t}\cdot\int_{-\infty}^{\infty}dt'\, e^{i\omega' t'}\ddot{m}'(t'-\tfrac{R}{c})$$

the v^2r subscript is implicit

The t'-integral can be evaluated by parts:

$$e^{i\omega' t'}\frac{d^2}{dt'^2}m'(t'-\tfrac{R}{c}) = \frac{d}{dt'}e^{i\omega' t'}\frac{d}{dt'}m'(t'-\tfrac{R}{c}) - i\omega' e^{i\omega' t'}\frac{d}{dt'}m'(t'-\tfrac{R}{c})$$

$$= \frac{d^2}{dt'^2}e^{i\omega' t'}m'(t'-\tfrac{R}{c}) - 2i\omega'\frac{d}{dt'}e^{i\omega' t'}m'(t-\tfrac{R}{c}) - \omega'^2 e^{i\omega' t'}m'(t'-\tfrac{R}{c})$$

The first two terms integrate to zero because the filtered signal dipole and its time derivative vanish at plus and minus infinity. So we end up with

$$\mathcal{E}'_{v^2r}(\underset{\sim}{R},t) = \frac{1}{c^2R}\int_{-\infty}^{\infty}\frac{d\omega'}{2\pi}e^{-i\omega' t}\omega'^2\int_{-\infty}^{\infty}dt'\, e^{i\omega' t'}m'(t'-\tfrac{R}{c})$$

$$= \frac{1}{c^2R}\int_{-\infty}^{\infty}\frac{d\omega'}{2\pi}e^{-i\omega'(t-R/c)}\omega'^2\tilde{m}'(\omega')$$

$$= \frac{1}{c^2R}\int_{-\infty}^{\infty}\frac{d\omega'}{2\pi}e^{i\omega'(t-R/c)}\omega'^2\tilde{m}'(-\omega')$$

because the field is real

Inserting the two Fourier expansions in the transient-absorption signal formula gives

$$\Delta \mathcal{U}(\bar{\omega}) = \frac{1}{2\pi c^2}\int d^3R \,\frac{1}{R}\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\, e^{-i\omega(t-z/c)} \cdot \tilde{E}_r'(\underline{0},\omega)\int_{-\infty}^{\infty}\frac{d\omega'}{2\pi} \times e^{i\omega'(t-R/c)}\,\omega'^2\,\tilde{m}'(-\omega')$$

$$= \frac{1}{c^2}\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\, e^{-i\omega t}\,\tilde{E}_r'(\underline{0},\omega)\int_{-\infty}^{\infty}\frac{d\omega'}{2\pi}\, e^{i\omega' t}\,\omega'^2 \times \int_0^{\infty} R\,dR\, e^{-i\omega' R/c}\underbrace{\int_0^{\pi}\sin\theta\, d\theta\, e^{\frac{i\omega R}{c}\cos\theta}}$$

$$-\frac{c}{i\omega R}\, e^{\frac{i\omega R}{c}\cos\theta}\Big|_0^{\pi} = \frac{ic}{\omega R}\left(e^{-\frac{i\omega R}{c}} - e^{i\omega R/c}\right)$$

$$= \frac{i}{c}\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\,\frac{1}{\omega}\, e^{-i\omega t}\,\tilde{E}_r'(\underline{0},\omega)\int_{-\infty}^{\infty}\frac{d\omega'}{2\pi}\, e^{i\omega' t}\,\omega'^2\,\tilde{m}'(-\omega') \times \int_0^{\infty} dR\left(e^{-i(\omega'+\omega)R/c} - e^{-i(\omega'-\omega)R/c}\right)$$

The first term in parenthesis can be neglected because the filtered probe field does not exist in the negative-Z region; for the same reason, the lower integration limit for the second term can be extended to $R = -\infty$.

So we get

$$\Delta\mathcal{U}(\bar{\omega}) = -i\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\,\frac{1}{\omega}\,e^{-i\omega t}\,\tilde{E}'_r(\underline{0},\omega)\int_{-\infty}^{\infty}d\omega'\,e^{i\omega' t}\,\omega'^2\,\tilde{m}'(-\omega') \times\delta(\omega'-\omega)$$

$$\boxed{\Delta\mathcal{U}(\bar{\omega}) = -i\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\,\omega\,\tilde{E}'_r(\underline{0},\omega)\,\tilde{m}'_{\nu 2r}(-\omega)}\;^{*}\;.$$

OK, repeats

As only "matching" frequency components of $\tilde{E}'$ and $\tilde{m}'$ appear together in the integrand, it's clear that both needn't be primed. In particular, the calculated signal would be unchanged if $\tilde{m}'$ were replaced with $\tilde{m}$ in this formula, or, equivalently, if $\mathcal{E}'_{\nu 2r}$ were replaced by $\mathcal{E}_{\nu 2r}$ in the starting equation on p. 2.

We could build time-integral expression for $\Delta\mathcal{U}(\bar{\omega})$ directly from the starting equation, but instead derive it from the frequency-integral version (with $\tilde{m}'$ replaced by $\tilde{m}$):

$$\Delta\mathcal{U}(\bar{\omega}) = -i\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\,\omega\int_{-\infty}^{\infty}dt\,e^{i\omega t}\,E'_r(\underline{0},t)\int_{-\infty}^{\infty}dt'\,e^{-i\omega t'}\,m(t')$$

$$= -\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\int_{-\infty}^{\infty}dt\left[\frac{d}{dt}\,e^{i\omega t}\,E'_r(\underline{0},t) - e^{i\omega t}\,\dot{E}'_r(\underline{0},t)\right]\int_{-\infty}^{\infty}dt'\,e^{-i\omega t'}\,m(t')$$

$$\boxed{\Delta\mathcal{U}(\bar{\omega}) = \int_{-\infty}^{\infty}dt\;\dot{E}'_r(\underline{0},t)\,m_{\nu 2r}(t)}\;.$$

OK, repeats

* Notice that the integral in this equation must be purely imaginary, as can easily be verified. It is also worth noting that this frequency-integral expression is independent of the observation-time t, as we asserted that $\Delta\mathcal{U}(\bar{\omega})$ must be.

Given the carrier-wave/envelope form of the ultrashort probe pulse given on p. 1, we can obtain Fourier (frequency) components as

$$\tilde{E}_r(\underset{\sim}{0}, \omega) = \int_{t_d-\sigma}^{t_d+\sigma} dt\, e^{i\omega t}\, E_r\, g[(t-t_d)/\sigma] \cos[\Omega(t-t_d)+\varphi_r] .$$

For positive frequencies we have

$$\tilde{E}_r(\underset{\sim}{0}, \omega>0) \cong \frac{E_r}{2} e^{i\omega t_d - i\varphi_r} \int_{t_d-\sigma}^{t_d+\sigma} dt\, e^{i(\omega-\Omega)(t-t_d)} g[(t-t_d)/\sigma]$$

$$= \frac{E_r \sigma}{2} e^{i\omega t_d - i\varphi_r} \tilde{g}[\sigma(\omega-\Omega)],$$

or, repeats

where

$$\tilde{g}[y] = \int_{-1}^{1} dx\, e^{iyx} g[x] ;$$

$$\tilde{E}_r(\underset{\sim}{0}, -\omega) = \tilde{E}_r^*(\underset{\sim}{0}, \omega) .$$

Next we seek a carrier-wave/envelope expression for the spectrally filtered probe pulse.

$$E_r'(\underset{\sim}{0}, t) = \int_{\bar{\omega}-\delta\omega/2}^{\bar{\omega}+\delta\omega/2} \frac{d\omega}{2\pi} e^{-i\omega t} \frac{E_r \sigma}{2} e^{i\omega t_d - i\varphi_r} \tilde{g}[\sigma(\omega-\Omega)] + c.c.$$

$$\omega' = \omega - \bar{\omega} \; ; \quad \omega = \omega' + \bar{\omega}$$

$$d\omega = d\omega'$$

$$= \frac{E_r \sigma}{2} e^{-i\bar{\omega}(t-t_d) - i\varphi_r} \int_{-\delta\omega/2}^{\delta\omega/2} \frac{d\omega'}{2\pi} e^{-i\omega'(t-t_d)} \tilde{g}[\sigma(\omega'+\bar{\omega}-\Omega)] + c.c.$$