md-WPI and heterodyne-detected FWM for molecule with two electronic levels

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CINA

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

$$V(t) = -\hat{\mu} \sum_{I=1}^{4} E_I(t) \quad ; \quad \hat{\mu} = \mu \left(|e\rangle\langle g| + |g\rangle\langle e| \right)$$

transition dipole moment, assumed real

$$E_I(t) = E_I \underbrace{f_I(t - t_I(\underline{r}))}_{\text{envelope function has duration } \sim \sigma_I} \cos(\Omega_I(t - t_I(\underline{r})) + \varphi_I)$$

$\underline{r}$ is the molecule's location

pulse arrival times : $t_I(\underline{r}) = t_I + \underline{n}_I \cdot \underline{r}/c$

propagation direction

$t_1 \le t_2 \le t_3$; t_4 may be greater than or equal to t_3 (as we shall assume initially) or much less than t_1 (as we will later assume in treating FWM measurements detected by spectral interferometry.

$$i\hbar \frac{\partial}{\partial t} |\Psi(t)\rangle = (H + V(t)) |\Psi(t)\rangle \quad ; \quad |\Psi(t \ll \text{all } t_I)\rangle = [t - t_1(\underline{r})] |g\rangle |\Psi_0\rangle$$

$$= |g\rangle [t - t_1(\underline{r})]_{gg} |\Psi_0\rangle ;$$

$$[t] = e^{-iHt/\hbar}$$

$$[t]_{gg} = \langle g | [t] | g \rangle = e^{-i\mathcal{H}_g t/\hbar} .$$

Interaction picture

$$|\tilde{\Psi}(t)\rangle = [-t + t_1(\tau)]\,|\Psi(t)\rangle \quad ; \quad |\tilde{\Psi}(t \ll \text{all } t_I)\rangle = |g\rangle|\psi_0\rangle$$

$$i\hbar \frac{\partial}{\partial t}|\tilde{\Psi}(t)\rangle = i\hbar\, \frac{\partial[-t+t_1(\tau)]}{\partial t}\,|\Psi(t)\rangle + i\hbar\,[-t+t_I(\tau)]\,\frac{\partial|\Psi(t)\rangle}{\partial t}$$

$$= [-t+t_1(\tau)]\big(-H + H + V(t)\big)|\Psi(t)\rangle$$

$$= \tilde{V}(t)\,|\tilde{\Psi}(t)\rangle \quad ;$$

$$\tilde{V}(t) = [-t + t_1(\tau)]\,V(t)\,[t - t_1(\tau)]$$

$$= -\sum_I E_I(t)\,[-t+t_1(\tau)]\,\hat{\mu}\,[t - t_1(\tau)]$$

$$= -\sum_I E_I(t)\,[-t_{I1}(\tau)][-t+t_I(\tau)]\,\hat{\mu}\,[t-t_I(\tau)][t_{I1}(\tau)]$$

$$\tilde{V}(t) \cong -|e\rangle\langle g|\,\frac{\mu}{2}\sum_I E_I\, f_I(t - t_I(\tau))\, e^{-i\Omega_I(t-t_I(\tau)) - i\varphi_I}\, [-t_{I1}(\tau)]_{ee}\,[-t+t_I(\tau)]_{ee}\,[t-t_I(\tau)]_{gg}\,[t_{I1}(\tau)]_{gg} + \text{H.c.}$$

rotating-wave approximation

Formal solution,

$$|\tilde{\Psi}(t)\rangle = |g\rangle|\psi_0\rangle + \frac{1}{i\hbar}\int_{-\infty}^{t} d\tau\, \tilde{V}(\tau)\,|\tilde{\Psi}(\tau)\rangle$$

$$= |g\rangle|\psi_0\rangle + \sum_I [-t_{I1}(\tau)]\,P_I(t;\tau)\,[t_{I1}(\tau)]\,|\tilde{\Psi}(\tau)\rangle \quad ;$$

$$t_{IJ}(\tau) \equiv t_I(\tau) - t_J(\tau)$$

pulse propagator : $P_I(t;\tau) \equiv \frac{i}{\hbar}\int_{-\infty}^{t} d\tau\, E_I(\tau)[-\tau+t_I(\underline{\tau})]\hat{\mu}[\tau-t_I(\underline{\tau})]$

$$\cong i\,\frac{\mu E_I \sigma_I}{2\hbar}\left\{|e\rangle\langle g|\, e^{-i\varphi_I}\, p_I^{(eg)}(t;\tau) + |g\rangle\langle e|\, e^{i\varphi_I}\, p_I^{(ge)}(t;\tau)\right\};$$

reduced pulse propagator : $p_I^{(eg)}(t;\tau) = \frac{1}{\sigma_I}\int_{-\infty}^{t} d\tau\,[-\tau+t_I(\underline{\tau})]_{ee}\underbrace{[\tau-t_I(\underline{\tau})]_{gg}}_{e^{-i\Omega_I(\tau-t_I(\underline{\tau}))}}$;

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

Iterating the formal solution through third order and returning to the Schrödinger picture gives

$$|\Psi(t)\rangle \cong [t-t_1(\underline{\tau})]\Big\{1 + \sum_I [-t_{I1}(\underline{\tau})]\,P_I(t;\tau)\,[t_{I1}(\underline{\tau})]$$

$$+ \sum_{IJ} [-t_{I1}(\underline{\tau})]\,P_I(t;\tau)\,[t_{IJ}(\underline{\tau})]\,P_J(\tau;\tau')\,[t_{J1}(\underline{\tau})]$$

$$+ \sum_{IJK} [-t_{I1}(\underline{\tau})]\,P_I(t;\tau)[t_{IJ}(\underline{\tau})]\,P_J(\tau;\tau')[t_{JK}(\underline{\tau})]\,P_K(\tau';\tau'')\,[t_{K1}(\underline{\tau})]\Big\}|g\rangle|\psi_0\rangle$$

In order to calculate the FWM signal, we need the portion of the nuclear amplitude in the electronic ground state that are zeroth-order and bilinear in the laser fields

$$\langle g|\Psi(t)\rangle = \underbrace{|\psi_0(t)\rangle}_{\equiv [t-t_1(\underline{\tau})]_{gg}|\psi_0\rangle} + |\psi_{12}(t)\rangle + |\psi_{21}(t)\rangle + |\psi_{13}(t)\rangle + |\psi_{31}(t)\rangle$$

$$+ |\psi_{23}(t)\rangle + |\psi_{32}(t)\rangle ,$$

where, for example,

$$|\Psi_{12}(t)\rangle = -\frac{\mu^2 E_1 E_2 \sigma_1 \sigma_2}{4\hbar^2} e^{i\varphi_{21}} [t - t_2(\tau)]_{gg} P_2^{(ge)}(t;\tau) [t_{21}(\tau)]_{ee} P_1^{(eg)}(\tau;\tau') |\Psi_0\rangle .$$

The linear and trilinear nuclear amplitude in the excited electronic state is

$$\langle e|\Psi(t)\rangle = |\Psi_1(t)\rangle + |\Psi_2(t)\rangle + |\Psi_3(t)\rangle$$
$$+ |\Psi_{123}(t)\rangle + |\Psi_{132}(t)\rangle$$
$$+ |\Psi_{213}(t)\rangle + |\Psi_{231}(t)\rangle$$
$$+ |\Psi_{312}(t)\rangle + |\Psi_{321}(t)\rangle ,$$

where $$|\Psi_1(t)\rangle = i\frac{\mu E_1 \sigma_1}{2\hbar} e^{-i\varphi_1} [t - t_1(\tau)]_{ee} P_1^{(eg)}(t;\tau) |\Psi_0\rangle ,$$

$$|\Psi_{123}(t)\rangle = -i\frac{\mu^3 E_1 E_2 E_3 \sigma_1 \sigma_2 \sigma_3}{8\hbar^3} e^{i\varphi_{21} - i\varphi_3}$$
$$[t - t_3(\tau)]_{ee} P_3^{(eg)}(t;\tau) [t_{32}(\tau)]_{gg} P_2^{(ge)}(\tau;\tau') [t_{21}(\tau)]_{ee} P_1^{(eg)}(\tau';\tau'') |\Psi_0\rangle ,$$

and so forth.

The nuclear wavepackets $|\Psi_{132}\rangle$ and $|\Psi_{231}\rangle$ both carry the uncontrolled optical phase-factor $e^{-i\varphi_1 - i\varphi_2}$, which averages to zero over many laser shots, and therefore make no experimentally meaningful contribution to the trilinear dipole moment. Similarly, the $|\Psi_{31}\rangle$ and $|\Psi_{32}\rangle$ contributions to $\langle g|\Psi(t)\rangle$ (p. 3) would meet up with $\langle\psi_2|$ and $\langle\psi_1|$, respectively, in calculating the trilinear dipole moment. The resulting terms would carry an uncontrolled phase-factor $e^{-i\varphi_2-i\varphi_1}$, and would therefore average to zero.

We arrive at a compact expression for the trilinear dipole moment in terms of eight contributing wave-packet overlaps:

$$\mu_{123}(t) = 2\mu\,\mathrm{Re}\Big\{ \langle\psi_0(t)|\psi_{123}(t)\rangle + \langle\psi_0(t)|\psi_{321}(t)\rangle + \langle\psi_{21}(t)|\psi_3(t)\rangle + \langle\psi_{23}(t)|\psi_1(t)\rangle \Big\}$$
$$+\,2\mu\,\mathrm{Re}\Big\{ \langle\psi_0(t)|\psi_{213}(t)\rangle + \langle\psi_0(t)|\psi_{312}(t)\rangle + \langle\psi_{13}(t)|\psi_2(t)\rangle + \langle\psi_{12}(t)|\psi_3(t)\rangle \Big\}.$$

Here we have, for example,

$$\langle\psi_0(t)|\psi_{123}(t)\rangle = -i\,\frac{\mu^3 E_1E_2E_3\sigma_1\sigma_2\sigma_3}{8\hbar^3}\,e^{i\varphi_{21}-i\varphi_3}$$
$$\langle\psi_0|[-t+t_1(\tau)]_{gg}[t-t_3(\tau)]_{ee}\,P_3^{(eg)}(t;\tau)[t_{32}(\tau)]_{gg}\,P_2^{(ge)}(\tau;\tau')[t_{21}(\tau)]_{ee}\,P_1^{(eg)}(\tau';\tau'')|\psi_0\rangle$$

and

$$\langle \Psi_0(t) | \Psi_{213}(t) \rangle = -i \frac{\mu^3 E_1 E_2 E_3 \sigma_1 \sigma_2 \sigma_3}{8\hbar^3} e^{-i\varphi_{21} - i\varphi_3}$$

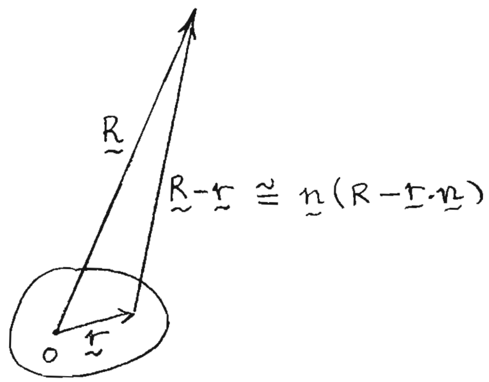
$$\langle \Psi_0 | [-t + t_1(\tau)]_{gg} [t - t_3(\tau)]_{ee} \, p_3^{(eg)}(t;\tau) [t_{31}(\tau)]_{gg} \, p_1^{(ge)}(\tau;\tau') [-t_{21}(\tau)]_{ee} \, p_2^{(eg)}(\tau';\tau'') [t_{21}(\tau)]_{gg} | \Psi_0 \rangle .$$

Notice that the nuclear wave-packet overlaps constituting $\mu_{123}(t)$ have been grouped by their optical phase-factors, $e^{i\varphi_{21} - i\varphi_3}$ or $e^{-i\varphi_{21} - i\varphi_3}$.

The FWM signal can be detected by allowing the E-field radiated by the trilinear dipole moment to interfere with a delayed external "local oscillator" (pulse 4), which does not pass through the sample. At a field-point $\underline{R} = R\underline{n}$ far from the sample, the trilinear radiated field is

$$E_{123}(t) \cong \frac{\rho \Omega^2}{c^2 R} \int_V d^3r \; \mu_{123}\left(t - \frac{R}{c} + \frac{\underline{r}\cdot\underline{n}}{c}\right) ,$$

where ρ is the density of chromophores in the illuminated sample volume V and Ω is a representative resonant optical frequency.



The signal is

$$\Delta U = \frac{1}{4\pi}\int d^3R\left\{\left(E_4(t)+E_{123}(t)\right)^2 - E_4^2(t)\right\}$$

$$\cong \frac{1}{2\pi}\int d^3R\; E_4(t)E_{123}(t),$$

where the integral is over a volume containing the local-oscillator light pulse at time t. We pick a time $t = R_0/c + t_4$, when the local oscillator is centered at $\underline{R}_0 = R_0\underline{n}_4$ and let $\Delta\underline{R} = \underline{R} - \underline{R}_0$. Then

$$\Delta U = \frac{\rho\Omega^2}{2\pi c^2 R}\int d^3(\Delta R)\, E_4(R_0/c + t_4)\int_V d^3r\; u_{123}\left(\frac{R_0}{c} + t_4 - \frac{R}{c} + \frac{r\cdot n}{c}\right).$$

We imagine that the "sample" is a laser-illuminated disk of diameter d and thickness h lying perpendicular to the laboratory z-axis $\left(V = \pi\left(\frac{d}{2}\right)^2 h\right)$. All four laser beams propagate at very small angles with respect to the z-axis (and with respect to each other) so that the geometrical shifts in pulse arrival time $n_{IJ}\cdot r/c \approx \delta\theta_{IJ}\, d/c$ are negligible on any relevant timescale of nuclear motion.

The integral over the far-field displacement variable $\underset{\sim}{\Delta R}$ is carried out in a different coordinate system, whose ΔZ-axis is along the direction $\underline{n}_4$, whose ΔX-axis lies in the plane containing $\underline{R}_0 = R_0 \underline{n}_4$ and the laboratory z-axis, and whose ΔY-axis is perpendicular to the other two (see below). We then have

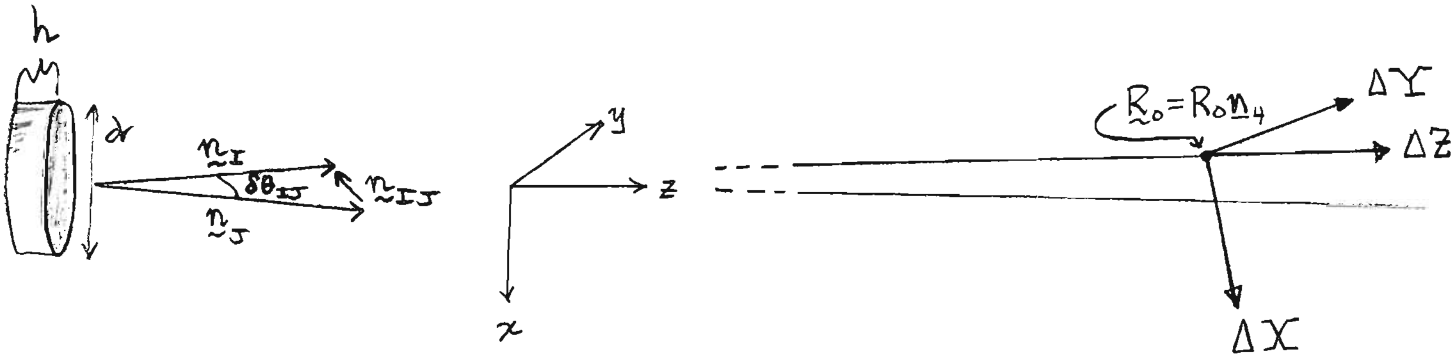
$$E_4\left(\frac{R_0}{c}+t_4\right) = E_4 f_4\left(\frac{R_0}{c}+t_4-t_4-\frac{\underline{n}_4\cdot\underline{R}}{c}\right)\cos\left(\Omega_4\left(\frac{R_0}{c}+t_4-t_4-\frac{\underline{n}_4\cdot\underline{R}}{c}\right)+\varphi_4\right)$$

$$= E_4 f_4\left(-\frac{\Delta Z}{c}\right)\cos\left(-\frac{\Omega_4 \Delta Z}{c}+\varphi_4\right)\Big)$$

and

$$\mu_{123}\left(\frac{R_0}{c}+t_4-\frac{R}{c}+\frac{\underset{\sim}{r}\cdot\underset{\sim}{n}}{c}\right) = \mu_{123}\left(t_4-\frac{\Delta Z}{c}+\frac{\underset{\sim}{n}\cdot\underset{\sim}{r}}{c}-\frac{\Delta X^2+\Delta Y^2-2\Delta Z^2}{2cR_0}\right)$$

$$\frac{1}{c}\sqrt{(R_0+\Delta Z)^2+(\Delta X)^2+(\Delta Y)^2} \cong \frac{R_0}{c}\left(1+\frac{\Delta Z}{R_0}+\frac{(\Delta X)^2+(\Delta Y)^2-2(\Delta Z)^2}{2c R_0}\right)$$



With reference to p. 5, we see that the integral of μ_{123} over the sample volume in $\Delta\mathcal{U}$ (p. 7) involves, for example, the expression

$$\int_V d^3r \left[-t_{41} + \frac{\Delta Z}{c} + \frac{\Delta R^2 - 3\Delta Z^2}{2cR_0} + \frac{(\underline{n}_1 - \underline{n})\cdot\underline{r}}{c}\right]_{gg} \left[t_{43} - \frac{\Delta Z}{c} - \frac{\Delta R^2 - 3\Delta Z^2}{2cR_0} - \frac{(\underline{n}_3 - \underline{n})\cdot\underline{r}}{c}\right]_{ee}$$

$$p_3^{(eg)}\left(t_4 - \frac{\Delta Z}{c} + \frac{\Delta R^2 - 3\Delta Z^2}{2cR_0} + \frac{\underline{n}\cdot\underline{r}}{c}; \tau\right)\left[t_{32} + \frac{\underline{n}_{32}\cdot\underline{r}}{c}\right]_{gg} p_2^{(ge)}(\tau;\tau')\left[t_{21} + \frac{\underline{n}_{21}\cdot\underline{r}}{c}\right]_{ee} p_1^{(eg)}(\tau';\tau'')$$

$$u = \tau - \underline{n}_3\cdot\underline{r}/c \qquad u' = \tau' - \underline{n}_2\cdot\underline{r}/c \qquad u'' = \tau'' - \underline{n}_1\cdot\underline{r}/c$$

$$\cong \left[-t_{41} + \frac{\Delta Z}{c}\right]_{gg}\left[t_{43} - \frac{\Delta Z}{c}\right]_{ee} e^{i\Omega\frac{\Delta R^2 - 3\Delta Z^2}{2cR_0}} \int_V d^3r\, e^{i\frac{\Omega}{c}(\underline{n}_3 - \underline{n})\cdot\underline{r}}$$

$$p_3^{(eg)}\left(t_4 - \frac{\Delta Z}{c}; u\right)[t_{32}]_{gg}\, p_2^{(ge)}(u;u')\,[t_{21}]_{ee}\, e^{-i\frac{\Omega}{c}\underline{n}_{21}\cdot\underline{r}}\, p_1^{(eg)}(u';u'')$$

$$= \delta_V(\underline{k} - \underline{k}_3 - \underline{k}_2 + \underline{k}_1)\left[-t_{41} + \frac{\Delta Z}{c}\right]_{gg}\left[t_{43} - \frac{\Delta Z}{c}\right]_{ee} e^{i\Omega\frac{\Delta R^2 - 3\Delta Z^2}{2cR_0}}$$

$$p_3^{(eg)}\left(t_4 - \frac{\Delta Z}{c}; u\right)[t_{32}]_{gg}\, p_2^{(ge)}(u;u')\,[t_{21}]_{ee}\, p_1^{(eg)}(u';u'') \quad . \qquad \bigstar$$

All the pulse propagators and time-evolution operators are now reckoned at the sample origin, $\underline{r} = 0$. The function $\delta_V(\underline{k}) = \int d^3r\, e^{-i\underline{k}\cdot\underline{r}}$ (note $\delta_V(\underline{0}) = V$) enforces wave-vector matching.

The range of relevant ΔZ values is limited by the duration of pulse-4 to $|\Delta Z| \lesssim c\sigma_4$. As a result

$$\Omega \frac{\Delta Z^2}{2cR_0} \lesssim \frac{\Omega\sigma_4}{2}\frac{c\sigma_4}{R_0} \approx (\#\text{optical periods})\frac{\text{spatial pulselength}}{R_0}.$$

This quantity can be held to values much smaller than unity by taking the reference distance R_0 larger than the spatial pulse length by a sufficiently large factor. Under this circumstance the factor

$$e^{i\Omega\frac{\Delta R^2 - 3\Delta Z^2}{2cR_0}} \cong e^{i\Omega\frac{\Delta X^2+\Delta Y^2}{2cR_0}}$$

depends only on displacements transverse to the propagation direction of local-oscillator beam.

When we substitute the expression ★ (p. 9) into ΔU (p. 7), it makes a contribution

$$\Delta U_\star = \frac{\rho\Omega^2}{2\pi c^2 R} E_4 \int d^3(\Delta R)\, f_4\left(-\frac{\Delta Z}{c}\right)\cos\left(-\Omega_4\frac{\Delta Z}{c}+\varphi_4\right)$$

$$2\mu\,\mathrm{Re}\left\{-i\frac{\mu^3 E_1E_2E_3\sigma_1\sigma_2\sigma_3}{8\hbar^3}\, e^{i\varphi_{21}-i\varphi_3}\,\delta_V(\underline{k}-\underline{k}_3+\underline{k}_2-\underline{k}_1)\, e^{i\Omega\frac{\Delta X^2+\Delta Y^2}{2cR_0}}\right.$$

$$\left.\langle\psi_0|\left[-t_{41}+\frac{\Delta Z}{c}\right]_{gg}\left[t_{43}-\frac{\Delta Z}{c}\right]_{ee} p_3^{(eg)}\left(t_4-\frac{\Delta Z}{c};u\right)[t_{32}]_{gg}\, p_2^{(ge)}(u;u')[t_{21}]_{ee}\, p_1^{(eg)}(u';u'')|\psi_0\rangle\right\}$$

Both of the functions $\delta_V(\underline{k}-\underline{k}_3+\underline{k}_2-\underline{k}_1)$ and $e^{i\Omega\frac{\Delta X^2+\Delta Y^2}{2cR_0}}$ restrict the range of ΔX and ΔY, hence the angular range within which significant interference can occur between the trilinear signal field and the local oscillator. δ_V restricts the components of $\underline{k}$ transverse to $\underline{k}_3-\underline{k}_2+\underline{k}_1$ within a range $\sim 2\pi/d$; the angular range of $\underline{k}$ (and $\underline{R}=\underline{R}_0+\Delta\underline{R}$) is thereby restricted to $\sim 2\pi c/(d\,\Omega) = \lambda/d$. The exponential function, on the other hand, restricts the components of $\underline{R}$ transverse to $\underline{R}_0$ within a range $\sim\sqrt{cR_0/\Omega} \cong \sqrt{\lambda R_0}$

The angular range of field points where significant signal-oscillator interference can occur is thereby restricted to $\sim\sqrt{\lambda/R_0}$. If the (arbitrarily selected) reference point $\underline{R}_0$ is far enough from the sample, and $\underline{k}_4$ is chosen well within the angular range λ/d of $\underline{k}_3-\underline{k}_2+\underline{k}_1$, then

$$\delta_V(\underline{k}-\underline{k}_3+\underline{k}_2-\underline{k}_1)\,e^{i\Omega\frac{\Delta X^2+\Delta Y^2}{2cR_0}} \cong \delta_V(\underline{k}_4-\underline{k}_3+\underline{k}_2-\underline{k}_1)\,e^{i\Omega\frac{\Delta X^2+\Delta Y^2}{2cR_0}}.$$

Integration over the transverse components of $\Delta\underline{R}$ therefore gives a factor

$$\int d(\Delta X)\int d(\Delta Y)\; e^{i\Omega\frac{\Delta X^2+\Delta Y^2}{2cR_0}} = \frac{2cR_0}{i\Omega}\pi .$$

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Upon applying the rotating-wave approximation to pulse-4, we have to contend with

$$\frac{e^{i\varphi_4}}{2}\int_{-\infty}^{\infty} d(\Delta Z)\, f_4\!\left(-\frac{\Delta Z}{c}\right) e^{-i\Omega_4 \Delta Z/c} \left[-t_{41}+\frac{\Delta Z}{c}\right]_{gg}\left[t_{43}-\frac{\Delta Z}{c}\right]_{ee} p_3^{(eg)}\!\left(t_4-\frac{\Delta Z}{c};u\right)$$

let $\quad v = t_4 - \frac{\Delta Z}{c}\quad , \quad d(\Delta Z) = -c\,dv$

$$\to \frac{e^{i\varphi_4}}{2}\, c\int_{-\infty}^{\infty} dv\, f_4(v-t_4)\, e^{i\Omega_4(v-t_4)}\, \underbrace{[t_1-v]_{gg}}_{[-t_{41}]_{gg}[t_4-v]_{gg}}\ \underbrace{[-t_3+v]_{ee}}_{[-t_4+v]_{ee}[t_{43}]_{ee}}\ p_3^{(eg)}(v;u)$$

$$= \frac{c\sigma_4}{2} e^{i\varphi_4}\, [-t_{41}]_{gg}\, p_4^{(ge)}(\infty;v)\, [t_{43}]_{ee}\, p_3^{(eg)}(v;u)\ .$$

correction 12 Jul 2011

We finally arrive at

$$\Delta U_\star = -2\hbar\Omega p\, \delta_v(k_4-k_3+k_2-k_1)\ \frac{\mu^4 E_1E_2E_3E_4\sigma_1\sigma_2\sigma_3\sigma_4}{16\hbar^4}$$

$$\to \mathrm{Re}\left\{ e^{i\varphi_{21}+i\varphi_{43}} \langle\psi_0|[-t_{41}]_{gg}\, p_4^{(ge)}(\infty;u)[t_{43}]_{ee}\, p_3^{(eg)}(u;u')[t_{32}]_{gg}\, p_2^{(ge)}(u';u'')[t_{21}]_{ee}\, p_1^{(eg)}(u'';u''')|\psi_0\rangle \right\}.$$

OK, repeats

The other contributions to ΔU follow similarly.

Omitting for brevity the (obvious) inter-pulse free-evolution operators, we can then write the FWM signal (from pp. 7 & 5) as

$$\Delta U = \Delta U_{++} + \Delta U_{-+}\,, \quad \text{with}$$

"flip angle" $\theta_I = \dfrac{\mu E_I \sigma_I}{2\hbar}$

$$\Delta U_{++} = -2\hbar\Omega\rho\,\delta_V(\underline{k}_2-\underline{k}_1+\underline{k}_4-\underline{k}_3)\,\theta_1\theta_2\theta_3\theta_4$$

$$\hookrightarrow \mathrm{Re}\Big\{ e^{i\varphi_{21}+i\varphi_{43}} \langle\psi_0|\, P_4^{(ge)}(\infty;u_4)\,P_3^{(eg)}(u_4;u_3)\,P_2^{(ge)}(u_3;u_2)\,P_1^{(eg)}(u_2;u_1)$$

$$+ P_4^{(ge)}(\infty;u_4)\,P_1^{(eg)}(u_4;u_1)\,P_2^{(ge)}(u_1;u_2)\,P_3^{(eg)}(u_2;u_3)$$

$$+ P_2^{(ge)}(u_1;u_2)\,P_1^{(eg)}(u_4;u_1)\,P_4^{(ge)}(\infty;u_4)\,P_3^{(eg)}(u_4;u_3)$$

$$+ P_2^{(ge)}(u_3;u_2)\,P_3^{(eg)}(u_4;u_3)\,P_4^{(ge)}(\infty;u_4)\,P_1^{(eg)}(u_4;u_1)\,|\psi_0\rangle \Big\}$$

and

$$\Delta U_{-+} = -2\hbar\Omega\rho\,\delta_V(\underline{k}_1-\underline{k}_2+\underline{k}_4-\underline{k}_3)\,\theta_1\theta_2\theta_3\theta_4$$

$$\hookrightarrow \mathrm{Re}\Big\{ e^{-i\varphi_{21}+i\varphi_{43}} \langle\psi_0|\, P_4^{(ge)}(\infty;u_4)\,P_3^{(eg)}(u_4;u_3)\,P_1^{(ge)}(u_3;u_1)\,P_2^{(eg)}(u_1;u_2)$$

$$+ P_4^{(ge)}(\infty;u_4)\,P_2^{(eg)}(u_4;u_2)\,P_1^{(ge)}(u_2;u_1)\,P_3^{(eg)}(u_1;u_3)$$

$$+ P_1^{(ge)}(u_3;u_1)\,P_3^{(eg)}(u_4;u_3)\,P_4^{(ge)}(\infty;u_4)\,P_2^{(eg)}(u_4;u_2)$$

$$+ P_1^{(ge)}(u_2;u_1)\,P_2^{(eg)}(u_4;u_2)\,P_4^{(ge)}(\infty;u_4)\,P_3^{(eg)}(u_4;u_3)\,|\psi_0\rangle \Big\}.$$

Of the four wave-packet overlaps contributing to the FWM signal of each phase signature, two depend on the 1, 2, and 3 pulses acting "out of sequence," and would vanish in the absence of temporal pulse overlap.

The signal field can also be detected by spectral interferometry, in which a local oscillator precedes the other pulses ($t_4 < t_1 \le t_2 \le t_3$) and propagates along the direction ($\underline{n}_4 = \underline{n}_3 + \underline{n}_2 - \underline{n}_1$ or $\underline{n}_3 - \underline{n}_2 + \underline{n}_1$) of one component of the trilinear radiated signal. Both fields are spectrally filtered before detection.

The filtered local oscillator is

$$E_4'(t;\bar{\omega}) = \int_{\bar{\omega}-\frac{\delta\omega}{2}}^{\bar{\omega}+\frac{\delta\omega}{2}} \frac{d\omega}{2\pi}\, e^{-i\omega t} \int_{-\infty}^{\infty} d\tau\, e^{i\omega\tau} E_4(\tau) + c.c.$$

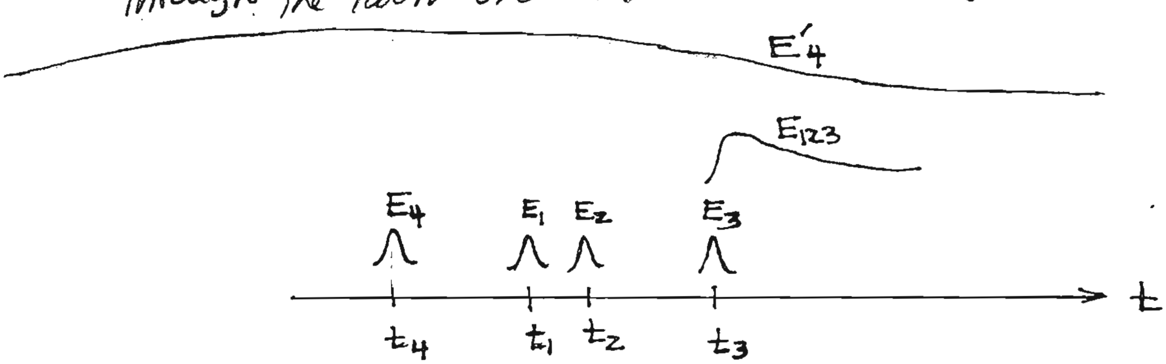
$$= \int_{-\infty}^{\infty} d\tau\, E_4(\tau) \frac{1}{2\pi} \int_{\bar{\omega}-\frac{\delta\omega}{2}}^{\bar{\omega}+\frac{\delta\omega}{2}} d\omega\, e^{i\omega(\tau - t)} + c.c.$$

$$= \int_{-\infty}^{\infty} d\tau\, E_4(\tau)\, e^{i\bar{\omega}(\tau - t)} \frac{\sin\frac{\delta\omega}{2}(\tau - t)}{\pi(\tau - t)} + c.c.$$

$$= 2\int_{-\infty}^{\infty} d\tau\, E_4(\tau) \cos\bar{\omega}(t-\tau) \frac{\sin\frac{\delta\omega}{2}(t-\tau)}{\pi(t-\tau)},$$

and similarly for $E_{123}'(t;\omega)$.

If the slit-width $\delta\omega$ is much less than $2\pi/\sigma_4$, the pulse is spectrally narrowed and temporally elongated. In particular, if $2\pi/\delta\omega$ is much greater than t_{34}, $E_4'(t;\bar{\omega})$ persists through the turn-on and eventual decay of $\mu_{123}(t)$.



The change in electromagnetic energy due to interference between the co-propagating, filtered fields is

$$\Delta \mathcal{U}'(\bar\omega) = \frac{1}{2\pi}\int d^3R\; E_4'(t;\bar\omega)\, E_{123}'(t;\bar\omega)$$

$$= \frac{1}{2\pi}\int d^3R \left(\int_{\bar\omega-\frac{\delta\omega}{2}}^{\bar\omega+\frac{\delta\omega}{2}} \frac{d\omega}{2\pi}\, e^{-i\omega t}\, \tilde E_4(\omega;\underset{\sim}{R}) + c.c.\right)\left(\int_{\bar\omega-\frac{\delta\omega}{2}}^{\bar\omega+\frac{\delta\omega}{2}} \frac{d\omega'}{2\pi}\, e^{-i\omega' t}\, \tilde E_{123}(\omega';\underset{\sim}{R}) + c.c.\right).$$

$$\tilde E_4(\omega;\underset{\sim}{R}) = \tilde E_4(\omega;\underset{\sim}{R}_0+\Delta\underset{\sim}{R}) = e^{i\omega \underset{\sim}{n}_4\cdot\Delta\underset{\sim}{R}/c}\, \tilde E_4(\omega;\underset{\sim}{R}_0) = e^{i\omega\Delta Z/c}\, \tilde E_4(\omega;\underset{\sim}{R}_0)$$

and, similarly

$$\tilde E_{123}(\omega';\underset{\sim}{R}) = e^{i\omega'\underset{\sim}{n}\cdot\Delta\underset{\sim}{R}/c}\, \tilde E_{123}(\omega';\underset{\sim}{R}_0) \cong e^{i\omega' \underset{\sim}{n}_4\cdot\Delta\underset{\sim}{R}/c}\, \tilde E_{123}(\omega';\underset{\sim}{R}_0) = e^{i\omega'\Delta Z/c}\, \tilde E_{123}(\omega';\underset{\sim}{R}_0).$$

within the narrow angular range where the fields interfere (see p. 11)

$$\therefore\; \Delta\mathcal{U}'(\bar\omega) = \frac{1}{2\pi} A \int d(\Delta Z)\left(\int_{\bar\omega-\frac{\delta\omega}{2}}^{\bar\omega+\frac{\delta\omega}{2}} \frac{d\omega}{2\pi} \int_{\bar\omega-\frac{\delta\omega}{2}}^{\bar\omega+\frac{\delta\omega}{2}} \frac{d\omega'}{2\pi}\, e^{i(\omega-\omega')t - i(\omega-\omega')\Delta Z/c}\, \tilde E_4^*(\omega;\underset{\sim}{R}_0)\, \tilde E_{123}(\omega';\underset{\sim}{R}_0) + c.c.\right)$$

$A \cong \frac{2cR_0\pi}{\Omega}$, cross-section of interference region (see p. 11)

$$= \frac{Ac}{\pi}\, \mathrm{Re} \int_{\bar\omega-\frac{\delta\omega}{2}}^{\bar\omega+\frac{\delta\omega}{2}} \frac{d\omega}{2\pi}\, \tilde E_4^*(\omega;\underset{\sim}{R}_0)\, \tilde E_{123}(\omega;\underset{\sim}{R}_0)$$

It's enough for the spectral components of <u>either</u> pulse to be confined to the range $\bar\omega - \frac{\delta\omega}{2} < |\omega| < \bar\omega - \frac{\delta\omega}{2}$. We can therefore determine the spectrally resolved FWM signal by evaluating

$$\Delta \mathcal{U}'(\bar\omega) = \frac{1}{2\pi}\int d^3R \; E_4'(t;\bar\omega)\, E_{123}(t) \,,$$

where the time is chosen late enough so that both signal and filtered local-oscillator fields lie in the far-field region. We denote this arbitrarily chosen time as $t = t_4 + R_0/c$; then (see p. 14)

$$\Delta \mathcal{U}'(\bar\omega) = \frac{1}{2\pi}\int d^3R \; 2\int_{-\infty}^{\infty} d\tau\, E_4(\tau) \cos\bar\omega\left(t_4+\frac{R_0}{c}-\tau\right) \frac{\sin\frac{\delta\omega}{2}\left(t_4+\frac{R_0}{c}-\tau\right)}{\pi\left(t_4+\frac{R_0}{c}-\tau\right)} \times E_{123}\left(t_4+\frac{R_0}{c}\right)$$

$$t' = t_4 + \frac{R_0}{c} - \tau$$

$$= 2\int_{-\infty}^{\infty} dt' \cos\bar\omega t' \, \frac{\sin\frac{\delta\omega}{2}t'}{\pi t'} \; \underbrace{\frac{1}{2\pi}\int d^3R \; E_4\left(t_4+\frac{R_0}{c}-t'\right) E_{123}\left(t_4+\frac{R_0}{c}\right)}$$

This quantity is the spectrally <u>unresolved</u> FWM signal with E_4 delayed by t', to be calculated by means of the expression on page 13.

$$\Delta \mathcal{U}'_{t_4}(\bar\omega) = 2\int_{-\infty}^{\infty} dt' \cos\bar\omega t' \, \frac{\sin\frac{\delta\omega}{2}t'}{\pi t'} \; \Delta\mathcal{U}_{t_4 \to t_4+t'} \,.$$

The lower limit of integration could be replaced by a minimal delay of t_{34} less $\sim \sigma_3, \sigma_4$, below which the integrand vanishes; note that t' is therefore always positive.

Inverse Fourier transformation gives (for $t > 0$)

$$\int_{-\infty}^{\infty} \frac{d\bar{\omega}}{2\pi}\, e^{-i\bar{\omega} t}\, \Delta U'(\bar{\omega}) = \int_{-\infty}^{\infty} dt' \,\frac{\sin \frac{\delta\omega}{2} t'}{\pi t'}\, \Delta U_{t_4 \to t_4 + t'} \underbrace{\int_{-\infty}^{\infty} \frac{d\bar{\omega}}{2\pi}\, e^{i\bar{\omega}(t'-t)}}_{\delta(t'-t)} + \underbrace{\int_{-\infty}^{\infty} \frac{d\bar{\omega}}{2\pi}\, e^{i\bar{\omega}(t'+t)}}_{\text{counter-rotating contribution vanishes}}$$

$$= \frac{\sin \frac{\delta\omega}{2} t}{\pi t}\, \Delta U_{t_4 \to t_4 + t}$$

$\Delta U'(\bar{\omega})$ for the full range of frequencies determines ΔU for the full range of local-oscillator arrival times, and vice versa.

Let's work out the corresponding md-WPI signal. All four pulses pass through the sample, and the measured quantity is the contribution to the e-state fluorescence that is quadrilinear in the WPI-pulse field strengths. On the assumption that all vibronic levels in the e-manifold have identical quantum yields for fluorescence, the md-WPI signal becomes a measure of the quadrilinear population of the electronic e-state.

To determine the quadrilinear e-state population, we need its linear and trilinear amplitudes:

$$\langle e|\Psi(t)\rangle = |\psi_1(t)\rangle + |\psi_2(t)\rangle + |\psi_3(t)\rangle + |\psi_4(t)\rangle$$

$$+ \overset{+\,\text{bra}}{|\psi_{234}(t)\rangle} + \overset{-\,\text{ket}}{|\psi_{243}(t)\rangle} + \overset{-\,\text{ket}}{|\psi_{342}(t)\rangle} + |\psi_{324}(t)\rangle + |\psi_{423}(t)\rangle + \overset{+\,\text{bra}}{|\psi_{432}(t)\rangle}$$

$$+ \overset{-\,\text{bra}}{|\psi_{134}(t)\rangle} + \overset{+\,\text{ket}}{|\psi_{143}(t)\rangle} + \overset{+\,\text{ket}}{|\psi_{341}(t)\rangle} + |\psi_{314}(t)\rangle + |\psi_{413}(t)\rangle + \overset{-\,\text{bra}}{|\psi_{431}(t)\rangle}$$

$$+ \overset{-\,\text{bra}}{|\psi_{124}(t)\rangle} + |\psi_{142}(t)\rangle + |\psi_{241}(t)\rangle + \overset{+\,\text{bra}}{|\psi_{214}(t)\rangle} + \overset{+\,\text{bra}}{|\psi_{412}(t)\rangle} + \overset{-\,\text{bra}}{|\psi_{421}(t)\rangle}$$

$$+ \overset{+\,\text{ket}}{|\psi_{123}(t)\rangle} + |\psi_{132}(t)\rangle + |\psi_{231}(t)\rangle + \overset{-\,\text{ket}}{|\psi_{213}(t)\rangle} + \overset{-\,\text{ket}}{|\psi_{312}(t)\rangle} + \overset{+\,\text{ket}}{|\psi_{321}(t)\rangle}.$$

The md-WPI signal evidently comprises **24 distinct wave-packet overlaps**. Among these, though, **eight** would carry uncontrolled phase factors such as $e^{-i\varphi_1 - i\varphi_2}$ and/or $e^{-i\varphi_3 - i\varphi_4}$ and **can be ignored**. The trilinear amplitudes giving rise to these uncontrolled are labelled with under-squiggles above.

The quadrilinear population of a chosen molecule's e-state comprises terms of two phase signatures and can be evaluated for any time well in excess of the pulse-4 arrival:

$$\langle \Psi(t \gg t_4(\tau)) | eXe | \Psi(t \gg t_4(\tau)) \rangle = S_{-+} + S_{++} ,$$

where

$$S_{-+} = 2\mathrm{Re}\Big\{ \overset{*}{\langle \psi_1 | \psi_{243} \rangle} + \overset{*}{\langle \psi_1 | \psi_{342} \rangle} + \langle \psi_{134} | \psi_2 \rangle + \overset{*}{\langle \psi_{431} | \psi_2 \rangle}$$

$$+ \langle \psi_{124} | \psi_3 \rangle + \overset{*}{\langle \psi_{421} | \psi_3 \rangle} + \langle \psi_4 | \psi_{213} \rangle + \langle \psi_4 | \psi_{312} \rangle \Big\}$$

and

$$S_{++} = 2\mathrm{Re}\Big\{ \overset{*}{\langle \psi_{234} | \psi_1 \rangle} + \overset{*}{\langle \psi_{432} | \psi_1 \rangle} + \langle \psi_2 | \psi_{143} \rangle + \overset{*}{\langle \psi_2 | \psi_{341} \rangle}$$

$$+ \overset{*}{\langle \psi_{214} | \psi_3 \rangle} + \langle \psi_{412} | \psi_3 \rangle + \langle \psi_4 | \psi_{123} \rangle + \langle \psi_4 | \psi_{321} \rangle \Big\} .$$

Notice that elimination of the four terms (*) of each phase signature in which pulse 4 manifestly <u>does not act last</u> would leave four terms of each phase signature, just as was seen in the FWM signal (compare p. 13). Even within the remaining overlaps, however, there are in general (for small enough t_{43}) contributions for which pulse 4 <u>does</u> and <u>does not</u> act last on the system.

It is also worth emphasizing the fact that $S^{(e)}_{-+}$ and $S^{(e)}_{++}$ can in principle be accumulated from repeated measurement on an individual molecule - there is no inherent need for an extended sample containing many of the target chromophores, as is the case with FWM.

If the md-WPI experiment is to be performed on an extended sample containing many of the target molecules, the signal becomes $\mathcal{S} = \mathcal{S}_{-+} + \mathcal{S}_{++}$, with

$$\mathcal{S}_{-+} = \rho \int_V d^3r \; S_{-+} \quad \text{and} \quad \mathcal{S}_{++} = \rho \int_V d^3r \; S_{++} .$$

The analysis is similar to, but markedly simpler than, that of FWM. We must evaluate, for example,

$$\rho \int_V d^3r \, \langle \Psi_{134} | \Psi_2 \rangle = \rho \, \theta_1 \theta_2 \theta_3 \theta_4 \, e^{-i\varphi_{21} + i\varphi_{43}}$$

$$\int_V d^3r \, \langle \Psi_0 | \, p_1^{(ge)}(\bar{\tau}'; \bar{\tau}'') [-t_{31}(\underset{\sim}{r})]_{ee} \, p_3^{(eg)}(\bar{\tau}; \bar{\tau}') [-t_{43}(\underset{\sim}{r})]_{gg}$$

$$p_4^{(ge)}(\infty; \bar{\tau}) [t_{42}(\underset{\sim}{r})]_{ee} \, p_2^{(eg)}(\infty; \tau) [t_{21}(\underset{\sim}{r})]_{gg} | \Psi_0 \rangle .$$

The $\underset{\sim}{r}$-dependence of the reduced pulse propagators again turns out to play no significant role (compare p. 9).

Set $u_2 = \tau - \underset{\sim}{n}_2 \cdot \underset{\sim}{r}/c$. Then

$$p_2^{(eg)}(\infty; \tau) = p_2^{(eg)}(\infty; u_2 + \underset{\sim}{n}_2 \cdot \underset{\sim}{r}/c) = p_2^{(eg)}(\infty; u_2),$$

with the understanding that the rightmost member of this equality is reckoned at $\underset{\sim}{r} = 0$.

Likewise, setting $u_4 = \bar{\tau} - \underline{n}_4 \cdot \underline{r}/c$, $u_3 = \bar{\tau}' - \underline{n}_3 \cdot \underline{r}/c$,

and $\bar{\tau}'' = u_1 - \underline{n}_1 \cdot \underline{r}/c$, we get

$$p_1^{(ge)}(\bar{\tau}'; \bar{\tau}'') \circ\circ\circ \, p_3^{(eg)}(\bar{\tau}; \bar{\tau}') \circ\circ\circ \, p_4^{(ge)}(\infty; \bar{\tau})$$

$$= p_1^{(ge)}(u_3 + \underline{n}_3 \cdot \underline{r}/c;\, u_1 + \underline{n}_1 \cdot \underline{r}/c) \circ\circ\circ \, p_3^{(eg)}(u_4 + \underline{n}_4 \cdot \underline{r}/c;\, u_3 + \underline{n}_3 \cdot \underline{r}/c)$$

$$\circ\circ\circ \, p_4^{(ge)}(\infty;\, u_4 + \underline{n}_4 \cdot \underline{r}/c)$$

$$\cong \underline{p_1^{(ge)}(u_3; u_1) \cdots p_3^{(eg)}(u_4; u_3) \cdots p_4^{(ge)}(\infty; u_4)}$$

with all reduced pulse propagators evaluated at $\underline{r} = 0$

We've argued as follows (and et cetera):

$$p_1^{(ge)}(u_3 + \underline{n}_3 \cdot \underline{r}/c;\, u_1 + \underline{n}_1 \cdot \underline{r}/c)$$

$$= \frac{1}{\sigma_1} \int_{-\infty}^{u_3 + \underline{n}_3 \cdot \underline{r}/c} d(u_1 + \underline{n}_1 \cdot \underline{r}/c)\, [-u_1 + t_1]_{gg}\, [u_1 - t_1]_{ee}$$

$$f_1(u_1 - t_1)\, e^{i\Omega_1(u_1 - t_1)}$$

$$= \frac{1}{\sigma_1} \int_{-\infty}^{u_3 + \underline{n}_{31} \cdot \underline{r}/c} du_1\, [-u_1 + t_1]_{gg}\, [u_1 - t_1]_{ee}$$

$$f_1(u_1 - t_1)\, e^{i\Omega_1(u_1 - t_1)}$$

$$= p_1^{(ge)}(u_3 + \underline{n}_{31} \cdot \underline{r}/c;\, u_1)$$

with the reduced pulse-propagator, but not its upper limit, reckoned at $\underline{r} = 0$.

$$\cong p_1^{(ge)}(u_3; u_1)$$

because $\delta\theta_{31}\, d/c$ is assumed to be much less than σ_1 (see p. 7)

The only remaining $\underline{r}$-dependence in $\langle \Psi_{134} | \Psi_2 \rangle$ (p. 20) is in the free-evolution operators; as on p. 9, we get

$$\rho \int_V d^3r \, \langle \Psi_{134} | \Psi_2 \rangle = \rho \, \Theta_1 \Theta_2 \Theta_3 \Theta_4 \, e^{-i\varphi_{21} + i\varphi_{43}} \, \delta_V(\underline{k}_4 - \underline{k}_3 - \underline{k}_2 + \underline{k}_1)$$

$$\hookrightarrow \langle \Psi_0 | P_1^{(ge)}(u_3; u_1) [-t_{31}]_{ee} P_3^{(eg)}(u_4; u_3) [-t_{43}]_{gg} P_4^{(ge)}(\infty; u_4)$$

$$\hookrightarrow [t_{42}]_{ee} P_2^{(eg)}(\infty; u_2) [t_{21}]_{gg} | \Psi_0 \rangle \; .$$

Applying similar arguments to the other contributing wave-packet overlaps, and again leaving out the free-molecular evolution operators for interpulse delays reckoned at the sample origin, we obtain (p. 19)

$$S_{-+} = 2\rho \, \Theta_1 \Theta_2 \Theta_3 \Theta_4 \, \delta_V(\underline{k}_4 - \underline{k}_3 - \underline{k}_2 + \underline{k}_1) \, \mathrm{Re}\Big\{ e^{-i\varphi_{21} + i\varphi_{43}}$$

$$\hookrightarrow \langle \Psi_0 | P_1^{(ge)}(\infty; u_1) P_2^{(eg)}(\infty; u_2) P_4^{(ge)}(u_2; u_4) P_3^{(eg)}(u_4; u_3) \quad *$$

$$+ P_1^{(ge)}(\infty; u_1) P_3^{(eg)}(\infty; u_3) P_4^{(ge)}(u_3; u_4) P_2^{(eg)}(u_4; u_2) \quad *$$

$$+ P_1^{(ge)}(u_3; u_1) P_3^{(eg)}(u_4; u_3) P_4^{(ge)}(\infty; u_4) P_2^{(eg)}(\infty; u_2)$$

$$+ P_4^{(ge)}(u_3; u_4) P_3^{(eg)}(u_1; u_3) P_1^{(ge)}(\infty; u_1) P_2^{(eg)}(\infty; u_2) \quad *$$

$$+ P_1^{(ge)}(u_2; u_1) P_2^{(ge)}(u_4; u_2) P_4^{(ge)}(\infty; u_4) P_3^{(eg)}(\infty; u_3)$$

$$+ P_4^{(ge)}(u_2; u_4) P_2^{(eg)}(u_1; u_2) P_1^{(ge)}(\infty; u_1) P_3^{(eg)}(\infty; u_3) \quad *$$

$$+ P_4^{(ge)}(\infty; u_4) P_2^{(eg)}(\infty; u_2) P_1^{(ge)}(u_2; u_1) P_3^{(eg)}(u_1; u_3)$$

$$+ P_4^{(ge)}(\infty; u_4) P_3^{(eg)}(\infty; u_3) P_1^{(ge)}(u_3; u_1) P_2^{(eg)}(u_1; u_2) | \Psi_0 \rangle \Big\}$$

When t_4 is late enough that pulse 4 does not overlap with the preceding pulses (and thereby always acts last on the system) we find, by comparison with p. 13, that $-\hbar\Omega\delta_{-+} = \Delta U_{-+}$, as we should expect. An analogous expression for δ_{++} can easily be written out; in the limiting case of a temporally well separated pulse 4, we find the expected relation $-\hbar\Omega\delta_{++} = \Delta U_{++}$.

Further considerations on the physical content and perturbative calculation of two-dimensional electronic spectroscopy signals from a molecule with two relevant electronic states.

$\boxed{29Jul11}$
CINA

These notes delve into two related issues concerning the treatment in my $\boxed{26Jun11}$ notes of md-WPI or FWM approaches to 2D optical-phase-sensitive spectroscopic signals from a molecule with two electronic states resonantly coupled by an optical pulse sequence. Because that treatment is based on a pure-state description, it might be supposed to apply only to an isolated molecule, say one in the gas phase. The first task taken on here is to show that this is not the case: by investigating the formal application of the pure-state description to a composite system comprising the target chromophore, the medium in which it may be immersed, and the environment surrounding both (the lab, or "universe"), we show – by means of a standard reduction – that the pure-state treatment includes an arbitrary mixed-state situation as a special case. The pure-state description therefore includes (in particular) the generic situation of a chromophore immersed in a continuous medium at a chosen initial temperature T.

The second issue addressed is the more involved and practical one of framing – within the pure- or mixed-state description – a systematic treatment of the common circumstance in which some nuclear degrees of freedom (referred to as vibrational modes, though they may also include torsions, rotations, librations or center-of-mass motions of the target chromophore or within the surrounding medium) that experience sizable Franck-Condon displacement upon electronic excitation of the chromophore, which may give rise to discernible quantum beats in the signal, while many others experience only small displacements or none at all.

In the notation of $\boxed{26\text{Jun}11}$

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

Here, we take $\mathcal{H}_g = h_g + h_{env} + v$ and $\mathcal{H}_e = h_e + h_{env} + v$. $h_g (h_e)$ is the nuclear Hamiltonian of the sample (including the target chromophore and the medium containing it) in the ground (excited) electronic state. h_{env} is the nuclear Hamiltonian of the environment (say the sample holder and the laboratory in which the experiment is performed); v governs the coupling between the sample and the environment. With the assumption that the sample walls are sufficiently distant from the target chromophore (further than the speed of sound times t_{41}), it becomes possible safely to ignore any dynamical effects of sample-environment interaction for the duration of the experiment (i.e. to set $|\nu t_{41}/\hbar| \approx 0$ in the overall time-evolution operator).

The initial state of the sample-plus-environment may in general be written as a sum of tensor products,

$$|\Psi_0\rangle = \sum_{\xi} |\xi\rangle |env_{\xi}\rangle ,$$

where $|env_{\xi}\rangle$ is the state of the environment accompanying a member $|\xi\rangle$ of some complete set of sample states.

The free-evolution operators appearing the basic signal expressions of $\boxed{26Jun11}$ can be approximated as $[t_{IJ}] \cong [t_{IJ}]_{samp} \otimes [t_{IJ}]_{env}$, since sample-environment coupling is negligible for any relevant interpulse delay. As the pulse durations σ_I are shorter than the longest interpulse delays, the reduced pulse propagators can also be approximated,

$$p_I^{(eg)}(t;\tau) = \int_{-\infty}^{t} \frac{d\tau}{\sigma_I} e^{i\mathcal{H}_e(\tau - t_I)/\hbar} e^{-i(\mathcal{H}_g + \Omega_I)(\tau - t_I)/\hbar} f_I(\tau - t_I)$$

$$\cong \int_{-\infty}^{t} \frac{d\tau}{\sigma_I} e^{ih_e(\tau - t_I)/\hbar} e^{-i(h_g + \Omega_I)(\tau - t_I)/\hbar} f_I(\tau - t_I) \otimes \mathbb{1}_{env} = p_{I,samp}^{(eg)}(t;\tau) \otimes \mathbb{1}_{env} .$$

These "approximations" can be made arbitrarily minor by means of a sufficient enlargement of the "sample" at the expense of the effectively limitless "environment." With their use, any of the contributions to the 2D electronic spectroscopy signal can be evaluated. For example, the third term of $\mathcal{S}_{-+}$ ($\boxed{26 Jun 11}$ p. 22) involves the quantity

$$\langle \Psi_0 | p_1^{(ge)} [-t_{31}]_{ee} \, p_3^{(eg)} [-t_{43}]_{gg} \, p_4^{(ge)} \, [t_{42}]_{ee} \, p_2^{(eg)} [t_{21}]_{gg} | \Psi_0 \rangle$$

$$\boxed{\text{insert} \quad \mathbb{1}_{samp} \otimes \mathbb{1}_{env} = \sum_{\bar{s}} |\bar{s}\rangle\langle\bar{s}| \otimes \sum_{\phi_{env}} |\phi_{env}\rangle\langle\phi_{env}|}$$

$$\cong \sum_{\bar{s}} \langle \bar{s} | [t_{42}]_{ee,samp} \, p_{2,samp}^{(eg)} [t_{21}]_{gg,samp} \sum_{\phi_{env}} \langle \phi_{env} | [t_{42}]_{ee,env} [t_{21}]_{gg,env} | \Psi_0 \rangle$$

$$\to \langle \Psi_0 | [-t_{31}]_{ee,env} [-t_{43}]_{gg,env} | \phi_{env} \rangle \, p_{1,samp}^{(ge)} [-t_{31}]_{ee,samp} \, p_{3,samp}^{(eg)} [-t_{43}]_{gg,samp} \, p_{4,samp}^{(ge)} | \bar{s} \rangle$$

$$= \mathrm{Tr}_{samp} \Big\{ [t_{42}]_{ee,samp} \, p_{2,samp}^{(eg)} [t_{21}]_{gg,samp} \, \rho_0$$

$$\to p_{1,samp}^{(ge)} [-t_{31}]_{ee,samp} \, p_{3,samp}^{(eg)} [-t_{43}]_{gg,samp} \, p_{4,samp}^{(ge)} \Big\} ,$$

where

$$\boxed{\rho_0 = \mathrm{Tr}_{env} |\Psi_0\rangle\langle\Psi_0|}$$

is the initial density operator of the sample, which can be seen from its construction to be an arbitrary stationary or nonstationary distribution (under h_g), including, within the first category, $\rho_0 \propto e^{-\beta h_g}$, corresponding to canonical equilibrium at some chosen temperature $T = (k_B \beta)^{-1}$.

The argument just given applies to all the terms in $\mathcal{S}_{-+}$ and $\mathcal{S}_{++}$ (or $\Delta\mathcal{U}_{-+}$ and $\Delta\mathcal{U}_{++}$) and thereby demonstrates, as asserted, that the pure-state description of md-WPI (or FWM) signal yields the corresponding mixed-state description as a particular example. In the remainder of these notes, we drop the subscript "samp," but regard ρ_0 as the initial density operator of the entire electronically-two-level sample, which is governed by unperturbed nuclear Hamiltonians h_g and h_e in its ground and excited electronic states, respectively.

To set the stage for an analysis of 2D electronic spectroscopy signals in samples with some combination of strongly, weakly, and non Franck-Condon active intra- or intermolecular vibrational degrees of freedom, we break up the nuclear Hamiltonians as follows:

$$h_g = h_s + h_b + v_g$$

$$h_e = h_s + u_s + h_b + u_b + v_e \quad .$$

In the "system" (s) we include all strongly Franck-Condon active modes. The system will typically include some intramolecular vibrations of the target chromophore but may also include some medium degrees of freedom; the change in its potential-energy operator upon electronic excitation is denoted by u_s. The bath (b) comprises all remaining modes, perhaps including some that are weakly Franck-Condon active, as accounted for by the change u_b

in bath potential upon electronic excitation. v_g and v_e are the (possibly different) system-bath-interaction operators in the two electronic states.

Whereas the potential shift u_s of the strongly Franck-Condon active modes cannot be ignored for even the short pulse durations σ_I, it is assumed that the shift u_b of the weakly (or non) Franck-Condon active modes — along with v_g and v_e — can safely be neglected for these brief times. Thus, we partition the sample between system and bath in such a way that

$$|u_s \sigma_I / \hbar| \gtrsim 1$$

and

$$|u_b \sigma_I/\hbar|, \; |v_g \sigma_I/\hbar|, \; |v_e \sigma_I/\hbar| << 1 .$$

In this situation, the reduced pulse propagators simplify as, for example,

$$P_I^{(eg)}(t;\tau) = \int_{-\infty}^{t} \frac{d\tau}{\sigma_I} \, e^{i h_e(\tau - t_I)/\hbar} \, e^{-i(h_g + \Omega_I)(\tau - t_I)/\hbar} \, f_I(\tau - t_I)$$

$$\cong \int_{-\infty}^{t} \frac{d\tau}{\sigma_I} \, e^{i(h_s + u_s + h_b)(\tau - t_I)/\hbar} \, e^{-i(h_s + h_b + \Omega_I)(\tau - t_I)/\hbar} \, f_I(\tau - t_I)$$

$$= p_{I,s}^{(eg)}(t;\tau) \otimes \mathbb{1}_b ,$$

These cancel because $[h_b, h_s] = [h_b, u_s] = 0$

and we see that the electronic transition distorts the nuclear amplitude solely of the system degrees of freedom.*

The contribution to $\mathcal{S}_{-+}$ that we have been considering (p. 4) as an example now becomes

$$\mathrm{Tr}_s \mathrm{Tr}_b \left\{ [t_{42}]_{ee} P_{2,s}^{(eg)} [t_{21}]_{gg} \rho_0 P_{1,s}^{(ge)} [-t_{31}]_{ee} P_{3,s}^{(eg)} [-t_{43}]_{gg} P_{4,s}^{(ge)} \right\}.$$

We completely ignored u_b, v_g, and v_e in the pulse propagators. We treat them perturbatively in the free-evolution operators $[t]_{gg}$ and $[t]_{ee}$. If $h = h_0 + h_1$, then $[t] \equiv e^{-iht/\hbar}$ obeys $i\hbar \frac{d}{dt}[t] = (h_0 + h_1)[t]$. Forming an "interaction picture," we consider

$$\begin{aligned}
i\hbar \frac{d}{dt}\left(e^{ih_0 t/\hbar} e^{-iht/\hbar}\right) &= e^{ih_0 t/\hbar}\left(-h_0 + h_0 + h_1\right) e^{-iht/\hbar} \\
&= \left(e^{ih_0 t/\hbar} h_1 e^{-ih_0 t/\hbar}\right) e^{ih_0 t/\hbar} e^{-iht/\hbar} \\
&\equiv h_1(t)\, e^{ih_0 t/\hbar} e^{-iht/\hbar}.
\end{aligned}$$

The presence of a time-argument identifies the otherwise constant perturbation h_1 in the interaction picture.

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* It should be apparent that the system-bath decomposition may depend on the pulse durations. For longer pulses, some vibrations of lower frequency may have to be included in the system.

Formal integration gives

$$e^{ih_0 t/\hbar}\, e^{-iht/\hbar} = 1 + \frac{1}{i\hbar}\int_0^t d\tau\, h_1(\tau)\left(e^{ih_0\tau/\hbar}\, e^{-ih\tau/\hbar}\right);$$

iterating twice and ignoring third- and higher-order terms gives

$$e^{ih_0 t/\hbar}\, e^{-iht/\hbar} \cong 1 + \frac{1}{i\hbar}\int_0^t d\tau\, h_1(\tau) + \left(\frac{1}{i\hbar}\right)^2 \int_0^t d\tau \int_0^\tau d\tau'\, h_1(\tau)\, h_1(\tau') \,.$$

Returning to the Schrödinger picture provides the sought-after approximate expression for the time-evolution operator:

$$e^{-iht/\hbar} = e^{-ih_0 t/\hbar}\left\{1 + \frac{1}{i\hbar}\int_0^t d\tau\, h_1(\tau) + \left(\frac{1}{i\hbar}\right)^2 \int_0^t d\tau \int_0^\tau d\tau'\, h_1(\tau)\, h_1(\tau')\right\} .$$

We could use this expression directly to evaluate $[t]_{gg}$ with $h_0 = h_s + h_b$ and $h_1 = v_g$, and to evaluate $[t]_{ee}$ with $h_0 = h_s + u_s + h_b$ and $h_1 = u_b + v_e$. On the other hand, we could make the perturbations "smaller" in each case by using $h_1 = v_g - \langle v_g \rangle$ and $h_0 = h_s + h_b + \langle v_g \rangle$, in the first instance, and $h_1 = u_b - \langle u_b \rangle + v_e - \langle v_e \rangle$ and $h_0 = h_s + u_s + \langle u_b \rangle + \langle v_e \rangle$, in the second, where $\langle \cdots \rangle \equiv Tr_b\{\cdots Tr_s\, \rho_0\}$ is an average over the initial reduced density operator of the bath.*

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* $\langle v_g \rangle$ and $\langle v_e \rangle$ are system operators, while $\langle u_b \rangle$ is a real number.

The latter approach ought to be superior, but it can be realized within the simpler framework of the former (thereby also obviating a need to reconsider our earlier treatment of the pulse propagators) by a the following device:

$$h_g = h_s + h_b + v_g \;=\; h_s + \langle v_g \rangle + h_b + (v_g - \langle v_g \rangle)$$

$$= h_s' + h_b + v_g' \;; \qquad h_s' \equiv h_s + \langle v_g \rangle$$

$$v_g' \equiv v_g - \langle v_g \rangle \;.$$

$$h_e = h_s + u_s + h_b + \langle u_b \rangle + (u_b - \langle u_b \rangle) + \langle v_e \rangle + (v_e - \langle v_e \rangle)$$

$$= \underbrace{h_s + \langle v_g \rangle}_{h_s'} + \underbrace{u_s + \langle v_e - v_g \rangle + \langle u_b \rangle}_{u_s'} + h_b + \underbrace{(u_b - \langle u_b \rangle)}_{u_b'} + \underbrace{(v_e - \langle v_e \rangle)}_{v_e'}$$

$$= h_s' + u_s' + h_b + u_b' + v_e' \;.$$

Because the ground- and excited-state nuclear Hamiltonians can evidently be written in their native forms, but with u_b, v_g, and v_e centered about their bath-averaged values, by means of suitable

redefinitions of h_s and u_s (the primed versions above), we shall henceforward assume that these (p_0-dependent) definitions have been adopted from the start and, accordingly, make use of the facts that $\langle u_b \rangle = \langle v_g \rangle = \langle v_e \rangle = 0$.

In the contribution to $\mathcal{S}_{-+}$ being used as an example, we need

$$[t_{21}]_{gg} \cong [t_{21}]_{gg,s}[t_{21}]_b \left\{1 - \frac{i}{\hbar}\int_0^{t_{21}} d\tau\, v_g(\tau) - \frac{1}{\hbar^2}\int_0^{t_{21}} d\tau \int_0^{\tau} d\tau'\, v_g(\tau) v_g(\tau')\right\}$$

and

$$[-t_{43}]_{gg} = \left([t_{43}]_{gg}\right)^{+} = \left\{1 + \frac{i}{\hbar}\int_0^{t_{43}} d\tau\, v_g(\tau) - \frac{1}{\hbar^2}\int_0^{t_{43}} d\tau \int_0^{\tau} d\tau'\, v_g(\tau') v_g(\tau)\right\}[-t_{43}]_b [-t_{43}]_{ee,s}$$

where $[t]_b = e^{-ih_b t/\hbar}$ and $[t]_{gg,s} = e^{-ih_s t/\hbar}$; and also

$$[t_{42}]_{ee} \cong [t_{42}]_{ee,s}[t_{42}]_b \left\{1 - \frac{i}{\hbar}\int_0^{t_{42}} d\tau\, (v_e(\tau) + u_b(\tau)) - \frac{1}{\hbar^2}\int_0^{t_{42}} d\tau \int_0^{\tau} d\tau'\, (v_e(\tau) + u_b(\tau))(v_e(\tau') + u_b(\tau'))\right\}$$

and

$$[-t_{31}]_{ee} \cong \left\{1 + \frac{i}{\hbar}\int_0^{t_{31}} d\tau (v_e(\tau) + u_b(\tau)) - \frac{1}{\hbar^2}\int_0^{t_{31}} d\tau \int_0^{\tau} d\tau' (v_e(\tau') + u_b(\tau'))(v_e(\tau) + u_b(\tau))\right\}[-t_{31}]_b [-t_{31}]_{ee,s}$$

where $[t]_{ee,s} = e^{-i(h_s + u_s)t/\hbar}$. It is perhaps apposite to the task at hand to recall that these approximate time-evolution operators make use of two **different interaction pictures** (see p. ⑦), which ought not to be conflated:

$$v_g(\tau) = [-\tau]_b [-\tau]_{gg,s}\, v_g\, [\tau]_{gg,s} [\tau]_b \quad ,$$

$$v_e(\tau) = [-\tau]_b [-\tau]_{ee,s}\, v_e\, [\tau]_{ee,s} [\tau]_b \quad ,$$

and

$$u_b(\tau) = [-\tau]_b [-\tau]_{ee,s}\, u_b\, [\tau]_{ee,s} [\tau]_b = [-\tau]_b\, u_b\, [\tau]_b \quad ,$$

the last of which is, in effect, "the same" as either of the preceding two, as it involves a pure bath operator.

In evaluating the example contribution to d_{-+} from p. 7, we treat u_b differently from the system-bath interaction perturbations v_g and v_e (in order to set up an eventual **cumulant-style re-exponentiation** of the bath-shift under appropriate conditions). Accordingly, we separately identify portions of the example contribution which are zeroth, first, and second order in v_g and/or v_e, retaining in each all contributions through second order in u_b. The **zeroth-order portion** of the example contribution is

$$\begin{aligned}
\mathbf{ZOP} = \mathrm{Tr}_s \mathrm{Tr}_b \Big\{ & [t_{42}]_{ee,s} [t_{42}]_b \left(1 - \frac{i}{\hbar}\int_0^{t_{42}} d\tau\, u_b(\tau) - \frac{1}{\hbar^2}\int_0^{t_{42}} d\tau \int_0^{\tau} d\tau'\, u_b(\tau) u_b(\tau') \right) \\
& p_{2,s}^{(eg)} [t_{21}]_{gg,s} [t_{21}]_b \, \rho_0 \, p_{1,s}^{(ge)} \left(1 + \frac{i}{\hbar}\int_0^{t_{31}} d\tau\, u_b(\tau) - \frac{1}{\hbar^2}\int_0^{t_{31}} d\tau \int_0^{\tau} d\tau'\, u_b(\tau') u_b(\tau) \right) \\
& [-t_{31}]_b [-t_{31}]_{ee,s} \, p_{3,s}^{(eg)} [-t_{43}]_b [-t_{43}]_{gg,s} \, p_{4,s}^{(ge)} \Big\} .
\end{aligned}$$

This expression is **serviceable as it stands**, as we can push the bath trace all the way inside to obtain

$$\begin{aligned}
\mathrm{ZOP} = \mathrm{Tr}_s \Big\{ & [t_{42}]_{ee,s} \, p_{2,s}^{(eg)} [t_{21}]_{gg,s} \, \mathrm{Tr}_b \Big\{ [t_{42}]_b \left(1 - \frac{i}{\hbar}\int_0^{t_{42}} d\tau\, u_b(\tau) - \frac{1}{\hbar^2}\int_0^{t_{42}} d\tau \int_0^{\tau} d\tau'\, u_b(\tau) u_b(\tau') \right) \\
& [t_{21}]_b \, \rho_0 \left(1 + \frac{i}{\hbar}\int_0^{t_{31}} d\tau\, u_b(\tau) - \frac{1}{\hbar^2}\int_0^{t_{31}} d\tau \int_0^{\tau} d\tau'\, u_b(\tau') u_b(\tau) \right) [-t_{31}]_b [-t_{43}]_b \Big\} \, p_{1,s}^{(ge)} [-t_{31}]_{ee,s} \\
& p_{3,s}^{(eg)} [-t_{43}]_{gg,s} \, p_{4,s}^{(ge)} \Big\} .
\end{aligned}$$

We can write $\rho_0 = \sigma_0 \, \mathrm{Tr}_s \rho_0 + \Delta\rho_0$, where $\sigma_0 = \mathrm{Tr}_b \rho_0$ and $\Delta\rho_0 = \rho_0 - (\mathrm{Tr}_b \rho_0)(\mathrm{Tr}_s \rho_0)$ is the non-product portion of the initial system-bath density operator. Then $ZOP = ZOP_p + ZOP_\Delta$, and, with the reasonable assumption that $\mathrm{Tr}_s \rho_0$ is stationary under (i.e. commutes with) h_b, the product portion simplifies markedly:

$$ZOP_p = \mathrm{Tr}_s \left\{ [t_{42}]_{ee,s} \, P^{(eg)}_{2,s} \, [t_{21}]_{gg,s} \, \sigma_0 \, P^{(ge)}_{1,s} \, [-t_{31}]_{ee,s} \, P^{(eg)}_{3,s} \, [-t_{43}]_{gg,s} \, P^{(ge)}_{4,s} \right\}$$

$$\left(1 + \frac{1}{\hbar^2} \int_0^{t_{31}} d\tau \int_0^{t_{42}} d\tau' \langle u_b(\tau) u_b(\tau') \rangle - \frac{1}{\hbar^2} \int_0^{t_{42}} d\tau \int_0^{\tau} d\tau' \langle u_b(\tau) u_b(\tau') \rangle - \frac{1}{\hbar^2} \int_0^{t_{31}} d\tau \int_0^{\tau} d\tau' \langle u_b(\tau') u_b(\tau) \rangle \right),$$

while ZOP_Δ takes the more general form of ZOP itself with ρ_0 replaced by $\Delta\rho_0$. Under many circumstances, it may be the case that the nonproduct part of ρ_0, and hence ZOP_Δ, is either rigorously zero or else negligibly small.

The expression for ZOP_p can be readily improved by reexponentiating the integrals over the bath-shift autocorrelation function.

Defining

$$g(t) = \frac{1}{\hbar^2}\int_0^t d\tau \int_0^\tau d\tau' \langle u_b(\tau) u_b(\tau')\rangle$$

and *

$$h(t_\alpha, t_\beta) = \frac{1}{\hbar^2}\int_0^{t_\alpha} d\tau \int_0^{t_\beta} d\tau' \langle u_b(\tau) u_b(\tau')\rangle \;,$$

and using

$$\frac{1}{\hbar^2}\int_0^t d\tau \int_0^\tau d\tau' \langle u_b(\tau') u_b(\tau)\rangle = g(-t), \quad \text{we can write}$$

The bath-factor in ZOP_p as

$$\boxed{(\sim) = e^{h(t_{31}, t_{42}) - g(t_{42}) - g(-t_{31})}} \;.$$

Your mission Joachim, should you decide to accept it, is to

- check the above analysis and correct any errors it may contain
- derive expressions for FOP and SOP
- carry out the analogous derivations for all (other) contrib'ns to $\mathcal{S}_{-+}$ and $\mathcal{S}_{++}$
- perform **ab initio electronic structure calculations** in the ground and first excited states of **PERY** to obtain an adequate representation of corresponding potential energy surfaces in both states
- identify system and bath degrees of freedom
- use the theory you have developed to perform **first-principles simulations** of PERY's **2D electronic spectroscopy signals** and compare with the experimental findings of **Olgilvie** and of **Kaufmann**.

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* There might be some tricks for expressing $h(t_\alpha, t_\beta)$ in terms of various g's (see Mukamel's book).