

Analysis of Spectrally resolved transient

21 Oct 07

CINA

grating spectroscopy, motivated by an unpublished manuscript: IU Goldschleger, V Senekerimyan, and VA Apkarian, "Recoherence and emergence of wavefunctions in the portrait of a dissipative quantum oscillator: Br₂ doped ice" rec'd 18 Sept 07.

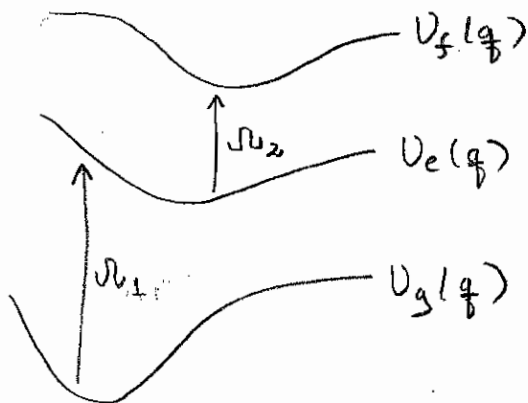
Molecular Hamiltonian

$$H(\mathbf{r}, t) = H + V(\mathbf{r}, t)$$

↑
molecular location,
assumed fixed

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

nuclear Hamiltonians $\mathcal{H}_i = K(\mathbf{p}) + U_i(\mathbf{q})$



↑
kinetic energy
operator

Interaction Hamiltonian

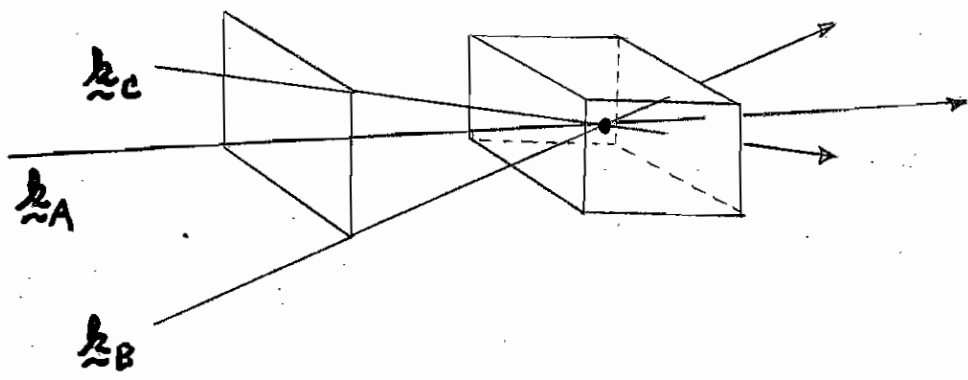
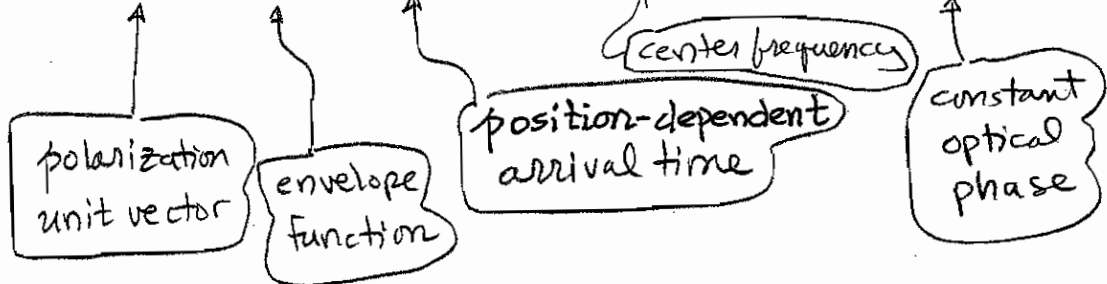
(2)

$$V(\mathbf{r}, t) = -\hat{\underline{\mu}} \cdot \underline{E}(\mathbf{r}, t)$$

$$\begin{aligned} \langle \hat{\underline{\mu}} \rangle &= \underline{\mu}_{eg} |e\rangle\langle g| \\ &+ \underline{\mu}_{fe} |f\rangle\langle e| \\ &+ \underline{\mu}_{fg} |f\rangle\langle g| \\ &+ \text{H.c.} \end{aligned}$$

$$\underline{E}(\mathbf{r}, t) = \underline{E}_A(\mathbf{r}, t) + \underline{E}_B(\mathbf{r}, t) + \underline{E}_C(\mathbf{r}, t)$$

$$\underline{E}_I(\mathbf{r}, t) = \underline{e}_I E_I f_I(t - t_I(\mathbf{r})) \cos[\omega_I \cdot (t - t_I(\mathbf{r})) + \phi_I]$$



center frequencies: $\omega_A = \omega_B \equiv \omega_1$; $\omega_C \equiv \omega_2$

arrival times are

location dependent: $t_I(\mathbf{r}) = t_I + \underline{k}_I \cdot \underline{r} / \omega_I$

t_I is the arrival time at some spatial origin within the sample

$\underline{k}_I = \omega_I \underline{k}_I / \nu$; $\nu = c/n$ is the speed of light in the sample.

unit vector in the direction of propagation

In working through the optical response to the incident fields, we temporarily suppress the Ω -dependence of the pulse arrival times. Time evolution is governed by the Schrödinger equation ($\hbar \equiv 1$),

$$i \frac{\partial}{\partial t} |\Psi(t)\rangle = H(t) |\Psi(t)\rangle ;$$

$$|\Psi(t \ll t_A)\rangle = e^{-iH(t-t_A)} |g\rangle |\psi_0\rangle .$$

an eigenstate of H_g

Switching to the interaction picture,

$$\begin{aligned} i \frac{\partial}{\partial t} e^{iHt} |\Psi(t)\rangle &= e^{iHt} (-H + H(t)) |\Psi(t)\rangle \\ &= e^{iHt} V(t) |\Psi(t)\rangle . \end{aligned}$$

The formal solution is

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

or, reverting to the Schrödinger picture,

$$|\Psi(t)\rangle = [t - t_A] |g\rangle |\psi_0\rangle + \frac{1}{i} \int_{-\infty}^t d\tau [t - \tau] V(\tau) |\Psi(\tau)\rangle .$$

We've introduced notation for the free-evolution operator

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$$[t] \equiv e^{-iHt} = |g\rangle [t]_g \langle g| + |e\rangle [t]_e \langle e| + |f\rangle [t]_f \langle f|,$$

with $[t]_I = e^{-iH_I t}$

In order to obtain the transient grating signal, we need to calculate $|\Psi(t)\rangle$ through third order in the incident field amplitudes. By virtue of the choice of center frequencies $\omega_1 \approx \omega_e - \omega_g$ and $\omega_2 \approx \omega_f - \omega_e$, the sought-after contributions to the expectation value of the electronic dipole moment operator trilinear in E_A , E_B , and E_C (i.e. proportional to $E_A E_B E_C$) involve only the overlap of two-pulse wave packet proportional to $E_A E_C$ (or $E_B E_C$) with a one-pulse wave packet proportional to E_B (or E_A); there is no three-pulse wave packet (proportional to $E_A E_B E_C$).

In iterating the formal solution of the time-dependent Schrödinger equation (p. ③) to obtain a perturbative expression for the state ket, we can therefore stop at second order:

$$|\Psi(t)\rangle = [t - t_c] \left\{ [t_{cA}] + \sum_{I=A,B} [t_{cI}] P_I(\infty; \tau_1) [t_{IA}] \right. \quad (5)$$

$$\left. + P_C(\infty; \tau_2) \sum_{I=A,B} [t_{cI}] P_I(\tau_2; \tau_1) [t_{IA}] \right\} |g\rangle |\psi_0\rangle$$

We have introduced pulse propagators

$$P_I(\tau_2; \tau_1) = i \int_{-\infty}^{\tau_2} d\tau [t_I - \tau] \hat{u} \cdot \underline{E}_I(\tau) [\tau - t_I]$$

Annotations:

- upper limit of integration (points to τ_2)
- variable of integration (points to $d\tau$)

The temporal overlap (in fact, nearcoincidence) of pulses A & B requires no special accounting in the perturbative expression for $|\Psi(t)\rangle$ because the action of their pulse propagators is superposed rather than sequential. If we are willing to neglect the effect of overlap of A and B with C (at short t_{cA}), then P_C and P_I become disentangled in the last term above; all upper limits can be replaced by ∞ and the time arguments of the pulse propagators no longer explicitly indicated.

(6)

$$|\Psi(t)\rangle = [t-t_c] \left\{ [t_{cA}] + [t_{cB}] P_B [t_{BA}] + [t_{cA}] P_A + P_C [t_{cA}] P_A + P_C [t_{cB}] P_B [t_{BA}] \right\} |g\rangle |\psi_0\rangle$$

$$|\Psi(t)\rangle = |g\rangle [t-t_c]_g [t_{cA}]_g |\psi_0\rangle + |e\rangle [t-t_c]_e \left\{ [t_{cB}]_e \langle e|P_B|g\rangle [t_{BA}]_g + [t_{cA}]_e \langle e|P_A|g\rangle \right\} |\psi_0\rangle + |f\rangle [t-t_c]_f \left\{ \langle f|P_C|e\rangle [t_{cA}]_e \langle e|P_A|g\rangle + \langle f|P_C|e\rangle [t_{cB}]_e \langle e|P_B|g\rangle [t_{BA}]_g \right\} |\psi_0\rangle$$

The trilinear portion of $\langle \Psi(t) | \mu | \Psi(t) \rangle$ is therefore given by the sum $\mu_{fe} \langle B|CA \rangle + \mu_{fe} \langle A|CB \rangle + c.c.$, in which

$$\langle B|AC \rangle_t = \langle \psi_0 | [-t_{BA}]_g \langle g | P_B^\dagger | e \rangle [-t_{cB}]_e [-t+t_c]_e \times [t-t_c]_f \langle f | P_C | e \rangle [t_{cA}]_e \langle e | P_A | g \rangle | \psi_0 \rangle$$

and

$$\langle A|CB \rangle_t = \langle \psi_0 | \langle g | P_A^\dagger | e \rangle [-t_{cA}]_e [t-t_c]_e \times [t-t_c]_f \langle f | P_C | e \rangle [t_{cA}]_e \langle e | P_B | g \rangle | \psi_0 \rangle$$

When summed over the contributing chromophores at ⑦ distributed locations within the sample, the trilinear polarization resulting from each of these nuclear wave-packet overlaps generates a signal beam that propagates in a distinct, experimentally isolable direction (as we shall see explicitly below). Since these two signal beams simply have swapped the roles of pulses A & B, which are nominally the same in a transient grating experiment, except for their direction of incidence, we arbitrarily pick the first one as the focus of further analysis (making the same choice as GSA).

The relevant electronic matrix elements of the pulse propagators can be evaluated with the help of the rotating-wave approximation:

$$\begin{aligned} \langle e | P_A | g \rangle &= i \underline{\mu}_{eg} \cdot \underline{e}_A E_A \int_{-\infty}^{\infty} d\tau [t_A - \tau] e^{i\tau} [\tau - t_A]_g f_A(\tau - t_A) \cos[\Omega_A(\tau - t_A) + \phi_A] \\ &= i \underline{\mu}_{eg} \cdot \underline{e}_A E_A \int_{-\infty}^{\infty} d\tau [-\tau] e^{i\tau} [\tau]_g f_A(\tau) \cos(\Omega_A \tau + \phi_A) \end{aligned}$$

$$\langle e | P_A | g \rangle \approx i \frac{\underline{\mu}_{eg} \cdot \underline{e}_A E_A}{2} e^{-i\phi_A} \int_{-\infty}^{\infty} d\tau f_A(\tau) e^{-i\Omega_A \tau} [-\tau] e^{i\tau} [\tau]_g$$

Similarly,

$$\langle g | P_B^+ | e \rangle \approx -i \frac{\underline{\mu}_{eg} \cdot \underline{e}_B E_B}{2} e^{i\phi_B} \int_{-\infty}^{\infty} d\tau f_B(\tau) e^{i\Omega_B \tau} [-\tau]_g [\tau] e$$

The propagators are independent of the pulse arrival time; as, in addition, $\Omega_B = \Omega_A$, $f_B(t) = f_A(t)$, $\underline{e}_B = \underline{e}_A$, and $\underline{e}_B = \underline{e}_A$, by assumption, we have

(B)

$$\langle g | P_B^\dagger | e \rangle = \langle g | P_A^\dagger | e \rangle .$$

In just the same way,

$$\langle f | P_c | e \rangle = i \frac{\mu_{fe} \cdot \underline{e}_c E_c}{2} e^{-i\phi_c} \int_{-\infty}^{\infty} d\tau f_c(\tau) e^{-i\Omega_c \tau} [-\tau]_f [\tau]_e$$

We note the important feature that none of the pulse propagators depends on the pulse arrival time or, as a result on the molecular location (see p. (2)).

The free evolution appearing in $\langle B | A \rangle_t$ (p. (6)) depend on molecular location through the pulse arrival times. In addition, we must take account of the location dependence of the signal transmission time from the molecular source to the detector. If the detector is at position \underline{R} , the signal arriving there at time t has a contribution originating from a source molecule located at \underline{r} at the time

$$t(\underline{R}-\underline{r}) = t - |\underline{R}-\underline{r}|/v .$$

Since $|\underline{R} - \underline{\Sigma}| = \sqrt{R^2 - 2R \cdot \underline{\Sigma} + \Sigma^2}$ (9)

$$= R \sqrt{1 - 2\underline{\kappa} \cdot \underline{\Sigma} / R + \Sigma^2 / R^2}$$

$$|\underline{R} - \underline{\Sigma}| \cong R - \underline{\kappa} \cdot \underline{\Sigma}$$

$\underline{\kappa} = \underline{R}/R$ is a unit vector in the direction of the detector from the sample origin

we have

$$t(\underline{R} - \underline{\Sigma}) \cong t - R/v + \underline{\kappa} \cdot \underline{\Sigma} / v$$

$$t(\underline{R} - \underline{\Sigma}) \cong t(\underline{R}) + \underline{\kappa} \cdot \underline{\Sigma} / v$$

Restoring explicit location dependence to the free-evolution operators in $\langle B | A \rangle_{t(\underline{R} - \underline{\Sigma})}$ (p. (6)) we have

$$[t_{CA}(\underline{\Sigma})]_e = [e^{i \underline{\kappa}_C \cdot \underline{\Sigma} / v_C}]_e [t_{CA}]_e [-e^{-i \underline{\kappa}_A \cdot \underline{\Sigma} / v_A}]_e$$

$$[t_{CA}(\underline{\Sigma})]_e = e^{-i \hbar E_C \underline{\kappa}_C \cdot \underline{\Sigma} / v} [t_{CA}]_e e^{i \hbar E_A \underline{\kappa}_A \cdot \underline{\Sigma} / v}$$

Recall that $t_{CA} = t_{CA}(\underline{\Sigma} = 0)$ is the interpulse delay at the sample origin

Similarly,

$$[-t_{CB}(\underline{\Sigma})]_e = e^{i \hbar E_C \underline{\kappa}_C \cdot \underline{\Sigma} / v} [-t_{CB}]_e e^{-i \hbar E_B \underline{\kappa}_B \cdot \underline{\Sigma} / v}$$

and

$$[-t_{BA}(\Sigma)]_g = e^{i\hbar g \kappa_B \cdot \Sigma / \nu} [-t_{BA}]_g e^{-i\hbar g \kappa_A \cdot \Sigma / \nu}$$

1, because $t_B = t_A$;
The two pulses arrive
simultaneously at the
sample origin

$$[-t_{BA}(\Sigma)]_g = e^{i\hbar g \kappa_B \cdot \Sigma / \nu - i\hbar g \kappa_A \cdot \Sigma / \nu}$$

Turning to the evolution operators that depend on $t(R-\Sigma)$,

we have

$$[t(R-\Sigma) - t_c(\Sigma)]_f = e^{-i\hbar f \kappa \cdot \Sigma / \nu} [t(R) - t_c]_f e^{i\hbar f \kappa_c \cdot \Sigma / \nu}$$

and

$$[-t(R-\Sigma) + t_c(\Sigma)]_e = e^{i\hbar e \kappa \cdot \Sigma / \nu} [-t(R) + t_c]_e e^{-i\hbar e \kappa_c \cdot \Sigma / \nu}$$

Substitution on p. (6) gives

(11)

$$\begin{aligned}
 \langle B|CA \rangle_{\pm(R-\tau)} &= \langle \psi_0 | e^{-iH_g(\tau \cdot \underline{k}_B - \tau \cdot \underline{k}_A)/\nu} \langle g|P_B^+|e \rangle \\
 &\times e^{iH_e \underline{k}_c \cdot \tau/\nu} [-t_{CB}]_e e^{-iH_e \underline{k}_B \cdot \tau/\nu} e^{iH_e \underline{k}_c \cdot \tau/\nu} [-t(B)+t_c]_e e^{-iH_e \underline{k}_c \cdot \tau/\nu} \\
 &\times e^{-iH_f \underline{k}_c \cdot \tau/\nu} [\pm(R)-t_c]_f e^{iH_f \underline{k}_c \cdot \tau/\nu} \langle f|P_c|e \rangle \\
 &\times e^{-iH_e \underline{k}_c \cdot \tau/\nu} [t_{CA}]_e e^{iH_e \underline{k}_A \cdot \tau/\nu} \langle e|P_A|g \rangle |\psi_0 \rangle
 \end{aligned}$$

$$\langle B|AC \rangle_{\pm(R-\tau)} \approx e^{i(\underline{k}_A - \underline{k}_B + \underline{k}_c - \underline{k}_c) \cdot \tau} \langle B|CA \rangle_{\pm(R)}$$

where $\underline{k} = \nu_2 \underline{k}/\nu$. The approximate equality, under which all dependence on molecular location resides in the phase pre-factor, results from the assumption of electronic resonance, $\nu_1 \approx U_{eg}$ and $\nu_2 \approx U_{fe}$ (see pp. (1) & (2)) or, more specifically, the quantitative requirement — necessary to prevent a loss of vibrational time resolution due to geometrical broadening of the pulse arrival

times — that

$$|U_{eg}(q) - \nu_1| \frac{a}{\nu}, |U_{fe}(q) - \nu_2| \frac{a}{\nu} \ll 2\pi$$

for all populated nuclear configurations q , where the parameter a is the spatial width of the illuminated sample.

A spectrally resolved transient grating measurement monitors the spectral density of the signal beam from a macroscopic sample as a function of the delay time $t_d \equiv t_{CA} = t_{CB}$ (recall again that pulses A & B are temporally coincident at the sample origin):

$$S_{SRTG}(t_d, \omega) \cong \text{const} \left| \int_{t_c}^{\infty} dt(R) e^{i\omega t(R)} \int_{V_{\text{sample}}} d^3r \left\{ \langle B|CA \rangle_{t(R-t)} + \text{c.c.} \right\} \right|^2$$

The integral over the sample volume vanishes unless the detector is placed in the wave-vector-matched direction,

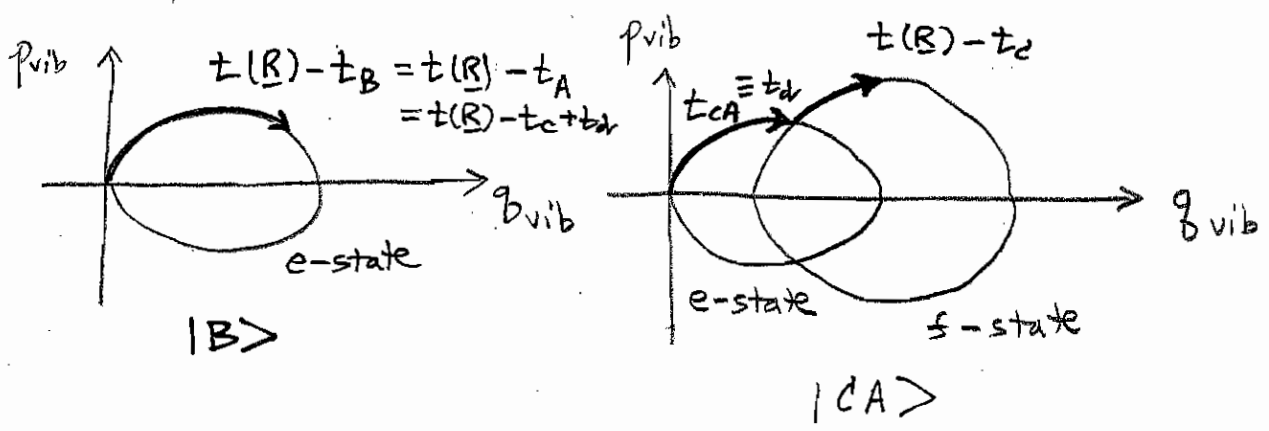
$$\vec{k} = \frac{v}{v_{G2}} (\vec{k}_C - \vec{k}_B + \vec{k}_A), \text{ and in that case}$$

$$S_{SRTG}(t_d, \omega) \cong \text{const}' \left| \int_{t_c}^{\infty} dt(R) e^{i\omega t(R)} \left\{ \langle B|CA \rangle_{t(R)} + \text{c.c.} \right\} \right|^2$$

SPECTRALLY RESOLVED TRANSIENT GRATINGS SIGNAL in the wave-vector matched direction.

We've made the approximation - a reasonable one for reasons that should already be clear - that the macroscopic polarization arises abruptly at $t(R) = t_c$, i.e. when the C-pulse arrives at the sample origin.

In condensed molecular systems - including those of the type studied by GSA - The wave packet overlap $\langle B|CA \rangle_{t(R)}$ will typically be maximal in magnitude at $t(R) = t_c$ and decay (perhaps with some short-lived beat structure) with increasing $t(R)$. We can diagram schematically the wave-packet dynamics of a strongly Franck-Condon active vibrational mode:



ω_{vib} being the effective vibrational frequency in the f -state

The overlap of the intramolecular vibrational components of $|CA\rangle$ and $|B\rangle$ should be quasiperiodic, exhibiting maxima at $t(R) - t_c = \frac{2\pi}{\omega_{vib}} \times \text{nonnegative integer}$.

The more-or-less monotonic decay of the overlap due to all other intra- and intermolecular modes contributes to an overall decay with increasing $t(R)$. This behavior, including "undecoherece" corresponding to a single beat with n^{th} nonnegative integer equal to one, is clearly exhibited by panel B of GSA's Figure 5.

The fact that the overlap,

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$$\langle B|CA \rangle_{t(R)} = \langle \psi_0 | \langle g | P_B^\dagger | e \rangle [-t_{cB}]_e [-t(R) + t_c]_e \\ \times [t(R) - t_c]_g \langle f | P_c | e \rangle [t_{cA}]_e \langle e | P_A | g \rangle | \psi_0 \rangle,$$

decays rapidly with increasing $t(R) > t_c$ motivates an approximate short-time treatment.*

Let

$$|\psi_A(t_d)\rangle = [t_{cA}]_e \langle e | P_A | g \rangle | \psi_0 \rangle \\ = [t_{cB}]_e \langle e | P_B | g \rangle | \psi_0 \rangle$$

and $\tau = t(R) - t_c$. Then

$$\langle B|CA \rangle_{t(R)} = \langle \psi_A(t_d) | [-\tau]_e [\tau]_g \langle f | P_c | e \rangle | \psi_A(t_d) \rangle$$

is a function of τ that decays on the timescale of the Franck-Condon active molecular vibrations.

* At the corresponding stage of their data work-up, SSA truncate $\langle B|CA \rangle_{t(R)}$ at $t(R) = t_c + 100\text{fs}$ (i.e. before the development of "undecoherece" at $\sim t_c + 100\text{fs}$).

In the integrand on p. (12), we need

$$e^{i\omega t(R)} [-\tau]_e [\tau]_f = e^{i\omega t_c} e^{i\omega \tau} [-\tau]_e [\tau]_f$$

$$= e^{i\omega t_c} e^{i\mathcal{H}_e \tau} e^{-i(\mathcal{H}_e + (U_f - \omega))\tau}$$

We seek a short- τ expansion of

$$e^{i\mathcal{H}_e \tau} e^{-i(\mathcal{H}_e + U)\tau}$$

↑

$$U \equiv U_{fe} - \omega$$

$$" \Big|_{\tau=0} = 1$$

$$\frac{d}{d\tau} " = e^{i\mathcal{H}_e \tau} (-iU) e^{-i(\mathcal{H}_e + U)\tau}$$

$$\frac{d}{d\tau} " \Big|_0 = -iU$$

$$\frac{d^2}{d\tau^2} " = e^{i\mathcal{H}_e \tau} \{ \mathcal{H}_e U - U \mathcal{H}_e - U^2 \} e^{-i(\mathcal{H}_e + U)\tau}$$

$$\frac{d^2}{d\tau^2} " \Big|_0 = [\mathcal{H}_e, U] - U^2.$$

Through second order in τ ,

$$e^{i\omega t(R)} [-\tau]_e [\tau]_f = e^{i\omega t_c} \left\{ 1 - iU\tau - \frac{\tau^2}{2} U^2 + \frac{\tau^2}{2} [\mathcal{H}_e, U] \right\}$$

The c.c. term in the integrand on p. (12) involves

(16)

$$\begin{aligned}
 e^{i\omega t} \int_{-T}^T e^{i(\omega + \gamma_f)\tau} e^{-i\gamma_e \tau} d\tau &= e^{i\omega t} e^{i(\gamma_e + \omega_f + \omega)\tau} e^{-i\gamma_e \tau} \\
 &= e^{i\omega t} e^{i(\gamma_e + \omega_f + \omega)\tau} e^{-i\gamma_e \tau}
 \end{aligned}$$

If we regard ω as a positive frequency, in the general range of $f \leftarrow e$ resonance, then the c.c. term is highly oscillatory as a function of τ ; its integral is therefore small and it makes a negligible contribution to the SRTS signal, which we neglect henceforward.

$$\begin{aligned}
 S_{\text{SRTS}} \approx \text{const}' \left| \int_0^\infty d\tau \langle \psi_A(t_d) | \left\{ 1 - iU\tau - \frac{\tau^2}{2} U^2 \right. \right. \\
 \left. \left. + \frac{\tau^2}{2} [\gamma_e, U] \right\} \langle f | P_c | e \rangle | \psi_A(t_d) \rangle \right|^2
 \end{aligned}$$

This expression is symbolic at best, as all four integrals inside the absolute value sign appear to diverge!

We reorganize the integrand to give one convergent term, rather than several divergent terms.

kinetic energy operator; see p. ① (12)

$$\langle \Psi_A(t_d) | \left\{ 1 - iU\tau - \frac{\tau^2}{2} U^2 - \tau^2 \frac{\langle \Psi_A(t_d) | [U, K] \langle f | P_c | e \rangle | \Psi_A(t_d) \rangle}{2 \langle \Psi_A(t_d) | \langle f | P_c | e \rangle | \Psi_A(t_d) \rangle} \right\} | \Psi_A(t_d) \rangle \equiv \alpha$$

$$\rightarrow \times \langle f | P_c | e \rangle | \Psi_A(t_d) \rangle \approx \langle \Psi_A(t_d) | e^{-iU\tau - \alpha\tau^2} \langle f | P_c | e \rangle | \Psi_A(t_d) \rangle$$

The new, reexponentiated integrand is equal to the old one through 2nd order in τ , but should lead to a convergent integral in S_{SRTG} (provided $\text{Re}[\alpha] \geq 0$, which we assume for the time-being that it is)*.

Notice that because it involves a commutator of U , the parameter α becomes INDEPENDENT OF ω ; it is dependent on t_d alone.

* In the case of a vibrationally abrupt c-pulse, the parameter reduces to $\alpha = \langle [U, K] \rangle$, where $\langle \dots \rangle \equiv \frac{\langle \Psi_A(t_d) | \dots | \Psi_A(t_d) \rangle}{\langle \Psi_A(t_d) | \Psi_A(t_d) \rangle}$.

If a single vibrational mode should happen to dominate the difference potential, $U \approx U' q_{\text{vib}} + \text{const}$, then $\alpha = \langle [U' q_{\text{vib}}, \frac{p_{\text{vib}}^2}{2m_{\text{vib}}}] \rangle = \frac{iU'}{m} \langle p_{\text{vib}} \rangle$.

We need the integral

$$\int_0^{\infty} d\tau e^{-iU\tau - \alpha\tau^2} = \frac{1}{\sqrt{\alpha}} \int_0^{\infty} d\tau' e^{-\tau'^2 - i\frac{U}{\alpha}\tau'}$$

$$-\tau'^2 - i\frac{U}{\alpha}\tau' = -\left(\tau' + \frac{iU}{2\alpha}\right)^2 - \frac{U^2}{4\alpha}$$

$$\tau' = \sqrt{\alpha}\tau$$

$$\tau = \frac{1}{\sqrt{\alpha}}\tau'$$

$$d\tau = \frac{1}{\sqrt{\alpha}}d\tau'$$

$$= \frac{1}{\sqrt{\alpha}} e^{-U^2/4\alpha} \int_0^{\infty} d\tau' e^{-\left(\tau' + \frac{iU}{2\alpha}\right)^2}$$

$$\tau'' = \tau' + \frac{iU}{2\alpha}$$

$$d\tau' = d\tau''$$

$$= \frac{1}{\sqrt{\alpha}} e^{-U^2/4\alpha} \int_{iU/2\alpha}^{\infty} d\tau'' e^{-\tau''^2}$$

$$= \frac{1}{\sqrt{\alpha}} e^{-U^2/4\alpha} \left\{ \underbrace{\int_0^{\infty} dx e^{-x^2}}_{\frac{\sqrt{\pi}}{2}} - \int_0^{iU/2\alpha} dx e^{-x^2} \right\}$$

$$= \frac{1}{2} \sqrt{\frac{\pi}{\alpha}} e^{-U^2/4\alpha} \left\{ 1 - \frac{2}{\sqrt{\pi}} \int_0^{iU/2\alpha} dx e^{-x^2} \right\}$$

$$\underbrace{\left\{ 1 - \frac{2}{\sqrt{\pi}} \int_0^{iU/2\alpha} dx e^{-x^2} \right\}}_{\text{erfc}[iU/2\alpha]}$$

$$\underbrace{\left\{ 1 - \frac{2}{\sqrt{\pi}} \int_0^{iU/2\alpha} dx e^{-x^2} \right\}}_{\text{erfc}[iU/2\alpha]}$$

Thus we arrive at a working expression for the signal

(19)

$$S_{SRTS}(t_d, \omega) = \text{const}' \frac{\pi}{4\alpha} \left| \langle \Psi_A(t_d) | e^{-U^2/4\alpha} \{1 - \text{erf}[iU/2\sqrt{\alpha}]\} \right. \\ \left. \times \langle s | P_c | e \rangle | \Psi_A(t_d) \rangle \right|^2$$

which appears as though it will give an approximate measure of the probability density $|\langle s | \Psi_A(t_d) \rangle|^2$ at the configuration(s) of local $s \leftarrow e$ resonance at frequency ω .