Coherence Observation by Interference Noise with Finite-Width Pulses

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Abstract

General formulae are derived for the Coherence-Observation-by-Interference-Noise (COIN) signal under the application of finite width pulses. These formulae are then applied to the Gaussian and exponential forms of the pulses. Qualitative agreement with experiment is found as for the form of the COIN signal. As compared to previous studies using the δ-function form of the pulses, however, unexpected sensitivity of the signal to the pulse-width, transversal relaxation, and detuning is found.

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I. INTRODUCTION

Probing optical coherent transients via femtosecond pulse preparation has received enormous attention over the last decade in the study of static level beating, vibrational coherence, molecular wavepacket motion as well as related dynamic interactions. Moreover, experiments that trace the damping of coherences have become powerful vehicles to interrogate the nature of quantum-stochastic relaxation physics. Oscillatory modulation patterns of nonlinear observables revealing the loss of coherences from electronic and vibrational states have been observed by four-wave mixing techniques [1] and gated fluorescence [2]. Related methodologies to map out coherences are interferometric correlation-techniques using pairs of pulses with distinct phase and delay times in symmetric, collinear pump-probe configurations [3] In the fluorescence correlation method proposed by Scherer et al. [4] and employed to interrogate the nuclear motion in the diatomic J2 potential, the relative phase between the delayed pulses was controlled by sophisticated phase-locking techniques to assure satisfactory interferometric stability, on moderate-to-longer relaxation scales. An alternative, experimental approach to stabilizing the interferometric set-up and to obtain precise fluorescence interferograms has been pioneered in Prior's group and is based upon the use of phase-randomized pulses and on the analysis of correlated fluorescence noise as a function of the delay (Coherence Observation by Interference Noise, COIN) [5]. Fluorescence intensities generated by the correlation of two sequential, random- phase pulses fluctuate due to the interferences between both the optical processes of enhanced absorption and stimulated fluorescence, respectively.

The tricky principle of the COIN-method has been applied to the measurement and the analysis of dephasing and the interrogation of quantum beats in an atomic three-level system already in the first paper [5]. The system under investigation was atomic potassium (vapour) and the coherent dynamics was between $4S_{1/2}$ and $4P_{3/2}$ states. In [10], general theory was used to predict results for Na_2 molecules. No corresponding experimental data have been, however, reported so far. Also experiments on molecular systems, crystalline Pentacene/p-Terphenyl, have been performed [12,13] where the oscillatory COIN signal evolves from a coherent superposition of optical free induction contributions combining different electronic transition energies of the pentacene absorber sites designated as O1, O2, O3, and O4. Correspondence of the Fourier transformed COIN signal and absorption spectrum of course exists which makes it possible to interpret different coherencies contributing to the oscillating COIN signal.

One should add here an important comment concerning physical relevance of such experiments. COIN is sometimes considered as just a way how to measure Fourier transformed (frequency shifted) absorption spectrum. It is certainly true that COIN as a time domain technique is correlated to the absorption spectrum in the frequency domain. On the other hand, it is certainly *not* reducible to *just* the Fourier transformation of the absorption. The main point is that it involves the form of the excitation pulse, providing the experimentalist with further flexibility.

This importance of the pulse shape is sometimes overlooked and underestimated as most of the theory made so far is finally made explicit for just 'infinitely' short pulses (δ-pulses) which lead to an infinitely broad range of excitation frequencies. Let us for a while turn our attention also to other important works done in this direction. First, one should notice a recent paper by Leichtle, Schleich, Averbukh, and Shapiro [10] where a simplified theory was given fully neglecting coupling of the system investigated to the bath. This may be sometimes well justified as, e.g., transversal relaxation may be a slower (e.g. nanosecond) process than coherence COIN oscillations. If the system bath coupling gets incorporated, the theory gets much complicated as wave functions are not sufficient to describe the system dynamics. Basic theory incorporating the density matrix of the system developing under the influence of both the exciting electromagnetic pulse and the interaction with bath has already been presented in [5] under the two basic approximations (as usually) of lowest order perturbation theory (second order on the level of the density matrix, i.e. the fourth order in the COIN signal) and the rotating wave approximation (RWA) ignoring highly oscillating terms proportional to $\sim \mathrm{e}^{\pm 2i\omega t}$. Here ω is the mean frequency of the pulse. Szöcs and Kauffmann [11] recently succeeded, upon investigating effects of the (spatial) propagation of the excitation on the COIN signal, in performing analytical calculations for a symmetric as well as asymmetric dimer omitting RWA. However for the final results both of them had to invoke the δ pulse approximation which we would like to avoid here. We will apply the RWA which in fact, for finite width pulses, is likely to be even a better approximation than in the case of formally infinitely short (δ-) pulses as in [11]. As for the higher order terms in the acting field, there are no indications so far that they could change the result qualitatively. That is why we shall ignore these higher order effects here.

What makes, however, the experimental results additionally interesting is the short-time form of the $\overline{(\Delta I)^2}(\tau)$ signal for pulse delays where the two COIN pulses in fact overlap. In particular, remarkable increase in the COIN intensity $\overline{(\Delta I)^2}(\tau)$ for $\tau \lesssim$ 200fs (roughly width of the pulses used) found in [12,13] is interpreted as being due to the pulse overlap. No explicit theory able to verify this interpretation exists in general as practically always, for technical reasons, theoretical dependencies can be made analytical just for ultrashort- (δ-) pulses mentioned above where this short-time region is naturally absent. The only exception is the COIN form derived for rectangular pulses [14]. These results are, however, of little help owing to an abrupt form of the model pulse used.

That is why we have turned our attention here to, in particular, finite-width pulses and ensuing short- as well as intermediate- and long-time COIN signals as predicted by a general theory based on just two approximations mentioned above: RWA and just the lowest order in the acting pulse. Both these approximations, in particular RWA, have already been tested as mentioned above. This inclusion of finite pulse width should reveal new aspects about the dependence of the COIN signal on the delicate balance of pulse length, dephasing rates, level splittings. The problem gets technically complicated because of the four-dimensional time integral via which the COIN signal is in general expressed. Details of the calculation and numerical modelling may be found below.

II. MODEL

The problem to be solved here is connected with the model of arbitrary number N of the excited states (numbered as $i = 1,\ 2,\ \ldots\ N$) above the ground state ($i = 0$). These states $|i\rangle$ are eigenstates of the Hamiltonian of the system alone, say H_0, i.e.

$$H_0|i\rangle = \epsilon_i|i\rangle, \quad i = 0,\ 1,\ 2, \ldots\ N. \tag{1}$$

The total Hamiltonian

$$H(t) = H_0 + H_1(t) \tag{2}$$

includes that of the interaction with a classical electric field, i.e.

$$H_1(t) = -\hat{\vec{d}}\vec{\mathcal{E}}(t). \tag{3}$$

The (vector) operator $\hat{\vec{d}}$ of the dipole momentum is assumed to connect just the ground state with any of the excited ones, i.e.

$$\hat{\vec{d}} = \sum_{i=1}^{N} [|0\rangle\langle 0|\hat{\vec{d}}|i\rangle\langle i| + |i\rangle\langle i|\hat{\vec{d}}|0\rangle\langle 0|]. \tag{4}$$

This means that

- we omit diagonal elements of the dipole momentum operator $\hat{\vec{d}}$ (i.e. all our states are assumed nonpolar), and that
- we omit transitions induced by the electric field among excited states.

Both these steps would be just approximate in general situations. In our treatment here, however, when we want to

- start with the initial condition that the system is fully unexcited before the light pulses appear, and to
- work just to the second order for the diagonal elements of the density matrix between arbitrary two excited states,

Omission of the field-induced transitions among excited states provides no approximation but just a technical simplification. Keeping the above matrix elements of $\hat{\vec{d}}$ would add nothing provided we stick to the above accuracy and the initial conditions just mentioned.

Interaction with surroundings (thermodynamic bath or reservoir) may cause bath-induced transitions among the ground and excited states (so called longitudinal relaxation) as well as dephasing leading to a bath-induced decay of the off-diagonal elements of the density matrix $\rho(t)$ of our system (transversal relaxation). Standard relation exists between typical longitudinal and transversal relaxation times T_1 and T_2 of the form

$$T_1 \gtrsim 0.5T_2 \tag{5}$$

[15] which may exceptionally be slightly violated [16] but usually reads as a sharp inequality

$$T_1 \gg 0.5T_2. \tag{6}$$

Because of it and also because in standard COIN experimental conditions, T_1 can be (as compared to, e.g., duration of pulses and their time shift) regarded as infinitely large, we do not take the longitudinal relaxation (i.e. direct bath-induced transitions among eigenstates $|i\rangle$ of H_0) into account here setting formally $T_1 \to +\infty$.

The set of Bloch equations for diagonal as well as off diagonal elements of the density matrix $\rho(t)$ of the system then reads

$$i\frac{d}{dt}\rho_{00}(t) = \frac{1}{\hbar}\sum_{j=1}^{N}[(\hat{\vec{d}})_{j0}\rho_{0j}(t) - (\hat{\vec{d}})_{0j}\rho_{j0}(t)]\vec{\mathcal{E}}(t),$$

$$i\frac{d}{dt}\rho_{jj}(t) = \frac{1}{\hbar}[-(\hat{\vec{d}})_{j0}\rho_{0j}(t) + (\hat{\vec{d}})_{0j}\rho_{j0}(t)]\vec{\mathcal{E}}(t), \quad j = 1, \ldots N$$

$$i\frac{d}{dt}\rho_{0j}(t) = \frac{1}{\hbar}(\hat{\vec{d}})_{0j}[\rho_{00}(t) - \rho_{jj}(t)]\vec{\mathcal{E}}(t) - (\frac{\epsilon_j}{\hbar} + \frac{i}{T_2^{(j)}})\rho_{0j}(t),$$

$$i\frac{d}{dt}\rho_{j0}(t) = \frac{1}{\hbar}(\hat{\vec{d}})_{j0}[\rho_{jj}(t) - \rho_{00}(t)]\vec{\mathcal{E}}(t) - (-\frac{\epsilon_j}{\hbar} + \frac{i}{T_2^{(j)}})\rho_{0j}(t). \tag{7}$$

We omit equations for the off-diagonal elements $\rho_{jj'}(t), \quad j \neq j' = 1, \ 2 \ldots N$ as unimportant here. Moreover, we have set $\epsilon_0 = 0$ by setting properly zero on the energy axis. Hence, ϵ_j designates henceforth the excitation energy of the j-th level. Worth mentioning is that we so far distinguish among transversal relaxation times $T_2^{(j)}$, each of them describing dephasing between the corresponding j-th excited state ($j = 1, \ 2 \ldots N$) and the ground state.

Now, we shall integrate the third and fourth equations of (7) to the first order in $\vec{\mathcal{E}}(t)$ by applying the initial condition

$$\rho_{00}(t_0) = 1 - \rho_{jj}(t_0) = 1, \quad j = 1, \ 2 \ldots N, \tag{8}$$

implying that (in order to preserve the positive semidefiniteness of $\rho(t_0)$)

$$\rho_{jj'}(t_0) = 0, \quad j \neq j'. \tag{9}$$

We formally set here $t_0 \to -\infty$ and assume that the pulses appear (i.e. $\vec{\mathcal{E}}(t)$ gets nonzero) at finite times only. Choosing the electric field as

$$\vec{\mathcal{E}} = F(t)\mathrm{e}^{-i\omega t} + F(t)^*\mathrm{e}^{i\omega t} \tag{10}$$

we get from (7) and (8-9)

$$\rho_{0j}(t) = -\frac{i}{\hbar}\int_{-\infty}^{t} \vec{d}_{0j}[\vec{F}(t')\mathrm{e}^{-i\omega t'} + \vec{F}(t')^*\mathrm{e}^{i\omega t'}][\rho_{00}(\tau) - \rho_{jj}(t')]\mathrm{e}^{i\epsilon_j(t-t')/\hbar-(t-t')/T_2^{(j)}}\, dt'$$

$$\approx -\frac{i}{\hbar}\vec{d}_{0j}\mathrm{e}^{i\omega t}\int_{-\infty}^{t} \vec{F}(t')^*\mathrm{e}^{-i\Delta_j\cdot(t-t')-(t-t')/T_2^{(j)}}\, dt' \tag{11}$$

and similarly for $\rho_{j0}(t) = \rho_{0j}(t)^*$. Here, we have designated $\Delta_j = \omega - \epsilon_j/\hbar$, simplified our notation setting $\vec{d}_{jl}$ for $(\hat{\vec{d}})_{jl}$, j, $l = 1,\ 2, \ldots N$, and used the rotating wave approximation (RWA). Now, we should put the result into the first and second equations in (7). We now set

$$\vec{F}(t) = \vec{f}(t) + \vec{f}(t-\tau)\mathrm{e}^{i\varphi}. \tag{12}$$

Further, we assume the linear light polarization, i.e.

$$\vec{f}(t) = \vec{e}\cdot f(t). \tag{13}$$

Let us assume that $f(t)$ is real and designate $a_j = 2|\vec{e}\cdot\vec{d}_{j0}|^2/\hbar^2$. Then the result for diagonal elements $\rho_{jj}(t)$, which is exact to the second order in $\vec{\mathcal{E}}$, reads

$$\rho_{jj}(t) = a_j\{\int_{-\infty}^{t} dt' f(t')\int_{-\infty}^{t'} dt'' f(t'')\mathrm{e}^{-(t'-t'')/T_2^{(j)}}\cos(\Delta_j(t'-t''))$$

$$+\int_{-\infty}^{t} dt' f(t'-\tau)\int_{-\infty}^{t'} dt'' f(t''-\tau)\mathrm{e}^{-(t'-t'')/T_2^{(j)}}\cos(\Delta_j(t'-t''))$$

$$+\int_{-\infty}^{t} dt' f(t')\int_{-\infty}^{t'} dt'' f(t''-\tau)\mathrm{e}^{-(t'-t'')/T_2^{(j)}}\cos(\Delta_j(t'-t'')-\varphi)$$

$$+\int_{-\infty}^{t} dt' f(t'-\tau)\int_{-\infty}^{t'} dt'' f(t'')\mathrm{e}^{-(t'-t'')/T_2^{(j)}}\cos(\Delta_j(t'-t'')+\varphi)\}. \tag{14}$$

We now take time t greater than times at which already the second pulse is over. Then $\rho_{jj}(t)$ turns to constant. As far as we designate number of centres with the j-th level in the active region as N_j, we get the integrated luminescence intensity

$$I(\tau,\varphi) = \sum_{j=1}^{N} N_j \rho_{jj}(t)$$

$$= \sum_{j=1}^{N} A_j \{ \int_{-\infty}^{t} dt' f(t') \int_{-\infty}^{t'} dt'' f(t'') \mathrm{e}^{-(t'-t'')/T_2^{(j)}} \cos(\Delta_j (t'-t''))$$

$$+ \int_{-\infty}^{t} dt' f(t'-\tau) \int_{-\infty}^{t'} dt'' f(t''-\tau) \mathrm{e}^{-(t'-t'')/T_2^{(j)}} \cos(\Delta_j (t'-t''))$$

$$+ \int_{-\infty}^{t} dt' f(t') \int_{-\infty}^{t'} dt'' f(t''-\tau) \mathrm{e}^{-(t'-t'')/T_2^{(j)}} \cos(\Delta_j (t'-t'')-\varphi)$$

$$+ \int_{-\infty}^{t} dt' f(t'-\tau) \int_{-\infty}^{t'} dt'' f(t'') \mathrm{e}^{-(t'-t'')/T_2^{(j)}} \cos(\Delta_j (t'-t'')+\varphi) \}. \tag{15}$$

Here $A_j = a_j N_j$.

III. COIN SIGNAL

The question now is what is the intensity variance upon averaging over φ. Direct calculation yields

$$\overline{(\Delta I)^2}(\tau) \equiv \overline{(I)^2}(\tau) - (\overline{I})^2(\tau)$$

$$= \frac{1}{2} \sum_{j,j'} \int_{-\infty}^{+\infty} dt_1 f(t_1) \int_{-\infty}^{t_1} dt'_1 f(t'_1-\tau) \mathrm{e}^{-(t_1-t'_1)/T_2^{(j)}} \int_{-\infty}^{+\infty} dt_2 f(t_2) \int_{-\infty}^{t_2} dt'_2 f(t'_2-\tau) \mathrm{e}^{-(t_2-t'_2)/T_2^{(j')}}$$

$$\cdot A_j A_{j'} \cos[\Delta_j (t_1-t'_1) - \Delta_{j'} (t_2-t'_2)]$$

$$+ \frac{1}{2} \sum_{j,j'} \int_{-\infty}^{+\infty} dt_1 f(t_1-\tau) \int_{-\infty}^{t_1} dt'_1 f(t'_1) \mathrm{e}^{-(t_1-t'_1)/T_2^{(j)}} \int_{-\infty}^{+\infty} dt_2 f(t_2-\tau) \int_{-\infty}^{t_2} dt'_2 f(t'_2) \mathrm{e}^{-(t_2-t'_2)/T_2^{j'}}$$

$$\cdot A_j A_{j'} \cos[\Delta_j (t_1-t'_1) - \Delta_{j'} (t_2-t'_2)]$$

$$+\sum_{j,j'}\int_{-\infty}^{+\infty}dt_1 f(t_1)\int_{-\infty}^{t_1}dt'_1 f(t'_1-\tau)\mathrm{e}^{-(t_1-t'_1)/T_2^{(j)}}\int_{-\infty}^{+\infty}dt_2 f(t_2-\tau)\int_{-\infty}^{t_2}dt'_2 f(t'_2)\mathrm{e}^{-(t_2-t'_2)/T_2^{(j')}}$$

$$\cdot A_j A_{j'}\cos[\Delta_j(t_1-t'_1)+\Delta_{j'}(t_2-t'_2)]. \tag{16}$$

Here, the bar $\overline{\cdots}$ designates averaging over the relative phase of the pulses φ. Formula

$$\overline{\cos(\chi_1-\varphi)\cos(\chi_2\mp\varphi)}=\frac{1}{2}\cos(\chi_1\mp\chi_2) \tag{17}$$

has also been applied. After a bit of algebra, the result can be put into a technically more advantageous form

$$\overline{(\Delta I)^2}(\tau)=\frac{1}{2}|\int_{-\infty}^{+\infty}dt\int_{-\infty}^{t}dt'[f(t)f(t'-\tau)+f(t-\tau)f(t')]\sum_{j=1}^{N}\mathrm{e}^{-(t-t')/T_2^{(j)}}A_j\cos[\Delta_j(t-t')]|^2$$

$$+\frac{1}{2}|\int_{-\infty}^{+\infty}dt\int_{-\infty}^{t}dt'[f(t)f(t'-\tau)-f(t-\tau)f(t')]\sum_{j=1}^{N}\mathrm{e}^{-(t-t')/T_2^{(j)}}A_j\sin[\Delta_j(t-t')]|^2. \tag{18}$$

involving only two-dimensional integrals. Already this makes the problem numerically treatable even for general finite-width pulses. We report here also another form of formula for the COIN signal which can be used even when the pulse shape function $f(t)$ is complex. Let

$$\phi_j(\tau)=\int_{-\infty}^{+\infty}dt\int_{-\infty}^{t}dt' f(t)f^*(t'-\tau)\mathrm{e}^{(t-t')(-1/T_2^{(j)}+i\Delta_j)},$$

$$\psi_j(\tau)=\int_{-\infty}^{+\infty}dt\int_{-\infty}^{t}dt' f^*(t-\tau))f(t')\mathrm{e}^{(t-t')(-1/T_2^{(j)}-i\Delta_j)}. \tag{19}$$

Then the COIN signal (16) (properly generalized to allow also complex $f(t)$) equals to

$$\overline{(\Delta I)^2}(\tau)=\frac{1}{2}|\sum_{j=1}^{N}A_j(\phi_j(\tau)+\psi_j(\tau))|^2. \tag{20}$$

For real pulse shape functions $f(t)$, (20) and (18) coincide. We shall argue below that in most important cases, however, at least one next integration can still be performed in (18) or (20) analytically. This makes the problem numerically treatable, containing at most one-dimensional integrals.

A. COIN for a symmetrical and symmetrically-excited pair of levels:

In this case, owing to the assumed symmetry, we have $N = 2$ and $A_1 = A_2 \equiv A$. If we, in addition to that, have also a symmetric excitation (centre of the exciting line is in the middle between our levels $\epsilon_1 < \epsilon_2$), we have $\omega = (\epsilon_1 + \epsilon_2)/(2\hbar)$ Hence

$$\Delta_1 = (\epsilon_2 - \epsilon_1)/(2\hbar) = -\Delta_2 = \frac{\delta}{2\hbar} \equiv \Delta > 0. \quad (21)$$

Here $\delta\epsilon = \epsilon_2 - \epsilon_1$ is the energy gap between the first and the second excited levels. Then for the case of equal transversal relaxation rates of both levels $T_2^{(1)} = T_2^{(2)} \equiv T_2$, the second term in (18) disappears. Hence, (18) yields for real pulse-shape function $f(t)$

$$\overline{(\Delta I)^2}(\tau) \propto |\int_{-\infty}^{+\infty} dt \int_{-\infty}^{t} dt'[f(t)f(t'-\tau) + f(t-\tau)f(t')] \sum_{j=1}^{N} \mathrm{e}^{-(t-t')/T_2} \cos[\Delta(t-t')]|^2 \quad (22)$$

B. Delta-pulse:

In this case, $f(t) = \delta(t)$. Then (18) yields

$$\overline{(\Delta I)^2}(\tau) = \frac{1}{2}|\sum_{j=1}^{N} \mathrm{e}^{-\tau/T_2^{(j)}} A_j \cos(\Delta_j \tau)|^2$$

$$+\frac{1}{2}|\sum_{j=1}^{N} \mathrm{e}^{-\tau/T_2^{(j)}} A_j \sin(\Delta_j \tau)|^2. \quad (23)$$

In specific cases,

- for a single level, this implies

$$\overline{(\Delta I)^2}(\tau) \propto \mathrm{e}^{-2\tau/T_2^{(1)}}, \quad (24)$$

  while

- for a pair of levels with equal transversal relaxation times, this means that

$$\overline{(\Delta I)^2}(\tau) = \frac{1}{2}\mathrm{e}^{-2\tau/T_2}\{A_1^2 + A_2^2 + 2A_1A_2\cos[\frac{(\epsilon_2-\epsilon_1)\tau}{\hbar}]\}$$

$$= \mathrm{e}^{2\tau/T_2}\{\frac{1}{2}(A_1 - A_2)^2 + 2A_1A_2\cos^2[\frac{(\epsilon_2-\epsilon_1)\tau}{2\hbar}]\}, \quad (25)$$

in both cases irrespective of the frequency detuning. These special cases known already previously well illustrate how our general formula (18) works.

IV. COIN FOR FINITE WIDTH PULSES

A. Gaussian form of the pulse

Assume that the pulse shape is Gaussian, i.e.

$$f(t) = \frac{f_0}{\sigma\sqrt{\pi}} \mathrm{e}^{-t^2/\sigma^2}. \tag{26}$$

Then by substitution $t = \frac{1}{\sqrt{2}}y + \frac{1}{2}(x+\tau),\ t' = \frac{1}{\sqrt{2}}y - \frac{1}{2}(x-\tau)$, one can turn integrals in (18) into

$$\int_{-\infty}^{+\infty} dt \int_{-\infty}^{t} dt' f(t) f(t'-\tau) \mathrm{e}^{(t-t')(-1/T_2^{(j)}+i\Delta_j)} = \frac{f_0}{\sigma\sqrt{2\pi}} \int_0^{+\infty} \mathrm{e}^{-(x+\tau)^2/(2\sigma^2)} \mathrm{e}^{x(-1/T_2^{(j)}+i\Delta_j)} dx \tag{27}$$

and

$$\int_{-\infty}^{+\infty} dt \int_{-\infty}^{t} dt' f(t-\tau) f(t') \mathrm{e}^{(t-t')(-1/T_2^{(j)}+i\Delta_j)} = \frac{f_0}{\sigma\sqrt{2\pi}} \int_0^{+\infty} \mathrm{e}^{-(x-\tau)^2/(2\sigma^2)} \mathrm{e}^{x(-1/T_2^{(j)}+i\Delta_j)} dx. \tag{28}$$

These single integrals can be easily expressed via Gauss error-function with a complex argument which are however not easily numerically calculable. That is why direct numerical integration is more appropriate.

B. Exponential pulse

By exponential pulse we understand pulse with the shape

$$f(t) = \frac{f_0}{2t_0} \mathrm{e}^{-|t|/t_0}. \tag{29}$$

With this form of the pulse, one can easily use our formula (18) or (20). From, e.g., the latter formula, one easily gets that with (29),

$$\overline{(\Delta I)^2}(\tau) = \frac{f_0^4}{32} | \sum_{j=1}^{N} A_j \{ \mathrm{e}^{-\tau/t_0} [\frac{1}{(1 - it_0\Delta_j + t_0/T_2^{(j)})^2}$$

$$-\frac{1}{(1-it_0\Delta_j-t_0/T_2^{(j)})^2}-\frac{2(t_0+\tau)/T_2^{(j)}}{(1-it_0\Delta_j-t_0/T_2^{(j)})(1-it_0\Delta_j+t_0/T_2^{(j)})}]$$

$$+\mathrm{e}^{-\tau(i\Delta_j+1/T_2^{(j)})}(\frac{2}{[1-t_0(i\Delta_j+1/T_2^{(j)})][1+t_0(i\Delta_j+1/T_2^{(j)})]})^2\}|^2. \qquad (30)$$

These analytical formulae are ready for a numerical treatment.

V. NUMERICAL RESULTS

A. Gaussian pulses

We set the reciprocal energy difference between the two excited levels in units of $\hbar$ equal $\hbar/\delta\epsilon = 20fs$ and put the pulse halfwidth $\sigma = 100fs$. Fig. 1 shows dependence of the COIN signal on the transversal relaxation time T_2. We have set here always equal amplitudes (oscillator strength) of the two excited levels involved ($A_1 = A_2$). Main observations are:

- The signal features the expected damped oscillations together with an appreciable increase of the COIN signal for time delays of the pulses $\tau \lesssim \sigma$, which is in qualitative accordance to experimental observations [13] In connection with the fact that the theoretical COIN signal as calculated for the δ-function like forms of $f(t)$ (24-25) fails in describing this increase, it well corresponds to the interpretation that this increase is owing to pulse-pulse correlation functions which are nonzero at such short pulse shifts.

- At time shifts $\tau \gtrsim \sigma$, however, these pulse-pulse correlation functions fast disappear. On the other hand, the COIN signal, in particular the phase shifts (positions of minima of the signal), still preserves a memory of these correlation functions by keeping dependence of, e.g., local COIN-signal minima on the transversal relaxation time T_2. The opposite is true for the δ-function like form of the pulse shapes (25).

Fig. 2 shows dependence of the COIN signal on pulse-shifts τ for different values of detuning. In is clearly seen that already a very small detuning can appreciably distort the signal, suppressing or fully cancelling the oscillatory form observed for full tuning. This feature does not corresponds to the (already previously derived) formula (25) above.

B. Exponential pulses

We again take the energy difference between our excited levels $\delta\epsilon$ as determined by $[\delta\epsilon/\hbar]^{-1} \equiv [(\epsilon_2 - \epsilon_1)/\hbar]^{-1} = 20fs$, and take both transversal relaxation times $T_2^{(1)} = T_2^{(2)} \equiv T_2 = 700fs$. Fig. 3 shows dependence of the COIN signal as a function of τ on the pulse length with the mean pulse frequency tuned just between two excited levels. We have found that

- There is a high increase of the COIN signal at low pulse-shifts τ comparable to or less than pulse duration time.
- Real signal may, however, show appreciable dependence on the pulse duration even in areas where the two (pump and probe) COIN pulses do not overlap ($\tau \gg t_0$). Worth noticing is, e.g., that minima of the COIN signal oscillations depend on the pulse duration, too.
- Decay of amplitudes of the COIN signal oscillation with increasing τ may be, for a few first oscillations at least, nonmonotonous, in the wings of the pulse overlap region. Hence, deducing T_2 from this decay may be sometimes a bit ambiguous.

Fig. 4 shows dependence of the COIN signal as a function of the pulse-shift τ for different values of the detuning. Strong dependence of the overall form of the signal on the detuning is found. Slight detuning may show appreciable distortion of the signal with small oscillations surviving while tuning the main pulse frequency outside the interval between our two levels used may fully suppress all the COIN oscillations. This qualitative behaviour is very different from the δ-function pulse situation (25).

VI. SUMMARY

The aim of this paper was to investigate effects of finite pulse width on the COIN signal in the long as well as in the short time regions for a system of discrete excited states. Effective methods of reducing the problem of originally four-dimensional time integration in general COIN formulae, to at most two-dimensional integrations and, for particular forms of the pulses considered, to just one-dimensional (and numerically well treatable) integrals or even closed analytical formulae for finite-width COIN pulses have been found. Numerical modelling for different pulse forms can therefore be easily performed which was done for the case of Gaussian and exponential shapes. For zero pulse width all results converge to the δ pulse solutions well known previously [5]. For finite pulse widths the calculations indicate a stronger dependence of the final signal on the transversal relaxation time, pulse duration (in both cases even for such time-shifts where the pulses do not overlap any more), and detuning than previously deduced on grounds of zero-pulse-width studies. Increased signal and non exponential behaviour in the pulse overlap region was found. But also on longer timescales influence of finite pulse width can be seen, causing a shift of the beating oscillation. Changes in the detuning can completely change the oscillation patterns. The general forms of the curves are, however, in good agreement with comparable experimental observations upon including more general forms of the theory implementing both the transversal relaxation and finite width of the pulses. Further systematic studies of the delicate interplay of pulse shape, detuning, and dephasing are in progress.

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Figure captions

Fig. 1: COIN signal for the Gaussian form of the pulses for different values of the transversal relaxation times. Values of reciprocal energy splitting in $\hbar$ units $\hbar/\delta\epsilon = 20fs$ and pulse duration $\sigma = 100fs$ were used. The excitation frequency is tuned exactly in the middle between our two levels $\omega = (\epsilon_1 + \epsilon_2)/(2\hbar)$. Transversal relaxation times $T_2^{(1)} = T_2^{(2)} \equiv T_2 = 500fs$ (full curve 1), $700fs$ (dotted curve 2), and $1000fs$ (dashed curve 3).

Fig. 2: The same as in Fig. 1 but for fixed value of the transversal relaxation time $T_2^{(1)} = T_2^{(2)} \equiv T_2 = 600fs$ but different frequency detuning. $\Delta_2/\Delta_1 = -1$ (tuning just in the middle of our two excited levels - full curve 1), $-2/3$ (dotted curve 2), $-7/13$ (dashed curve 3), $-3/7$ (dashed - double dotted line 4) and $-1/3$ (long dashed curve 5).

Fig. 3: COIN signals for exponential form of the pulses and different pulse lengths. $\overline{(\Delta I)^2}(\tau) \cdot t_0^4$ is plotted. $T_2^{(1)} = T_2^{(2)} = 700fs$ and $\hbar/\delta\epsilon = 20fs$. The pulse length parameters (approximately half of the pulse widths) are $t_0 = 90fs$ (the upper curve), $100fs$ (the middle curve) and $120fs$ (the lower fat-dotted curve). The excitation frequency is tuned just between two excited levels assumed.

Fig. 4: For the same situation as in Fig.3, dependence of the COIN signal on the detuning is shown. The pulse duration parameter $t_0 = 90fs$. Three curves correspond to the full tuning of the excitation in the middle between the two excited levels considered ($\Delta_2/\Delta_1 = -1$, lower thin curve), tuning outside the interval between two levels considered ($\Delta_2/\Delta_1 = 2/7$, fat curve) and tuning asymmetrically but inside the interval between the two levels ($\Delta_2/\Delta_1 = -3/7$, upper thin curve).

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