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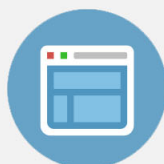
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Coherent-control of linear signals: Frequency-domain analysis

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The dependence of various types of linear signals on the phase profile of broadband optical pulses is examined using fundamental time translation invariance symmetry of multipoint correlation functions. The frequency-domain wave-mixing analysis presented here unifies several arguments made earlier with respect to the conditions whereby coherent control schemes may be used. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4824857>]

Recent experiments of Miller *et al.*¹ had demonstrated the coherent control of the photoisomerization of Rhodophin to linear order in the pump intensity. A 20% change in yield was achieved by varying the amplitude and phase profile of the pump. These findings were challenged by Joffe^{2,3} who argued that linear stationary signals should be independent on phase. The issue has been subsequently addressed by several theoretical and experimental studies.^{4–8} It has also been argued that coupling to a bath is essential for such observations.⁸ In this paper, we show how this problem may be generally addressed by treating signals obtained with broadband pulses as wave mixing in the frequency-domain. The origin of phase dependence, which is essential for any coherent-control scheme, is clarified by using a general argument based on time translation symmetry of observables.

In the frequency-domain description, the various signals obtained by broadband pulses can be viewed as path integrals in the joint matter/field space; we must sum over all possible ways in which the relevant field modes interact with the various molecular transitions. To describe these signals, we introduce a general multipoint correlation function:⁹

$$\begin{aligned} \langle V_{v_n}(\omega_n) \cdots V_{v_1}(\omega_1) \rangle_0 &= \iint \cdots \int d\tau_1 \cdots d\tau_n \\ &\times \exp(i\omega_1 \tau_1 + \cdots + i\omega_n \tau_n) \\ &\times \langle T V_{v_n}(\tau_n) \cdots V_{v_1}(\tau_1) \rangle, \end{aligned} \quad (1)$$

where we use a compact superoperator notation in the frequency domain.⁴ Superoperators are labeled by $v = L, R$ which indicates whether they act from the left or from the right, $A_L X = AX$, $A_R X = XA$ and T is a time-ordering operator which enforces the time-ordered interactions in a given diagram.

The time-domain correlation function must be invariant to shifting of all time arguments by a constant t

$$\langle T V_{v_n}(t + \tau_n) \cdots V_{v_1}(t + \tau_1) \rangle = \langle T V_{v_n}(\tau_n) \cdots V_{v_1}(\tau_1) \rangle.$$

When all time arguments in the right-hand side of Eq. (1) are shifted by t , we find that $\langle V_{v_n}(\omega_n) \cdots V_{v_1}(\omega_1) \rangle_0$ is multiplied by the factor $\exp(i(\omega_1 + \omega_2 \cdots + \omega_n)t)$. Since, on physical grounds, this quantity must be independent on

the translation time t , the sum over all frequencies in $\langle V_{v_n}(\omega_n) \cdots V_{v_1}(\omega_1) \rangle$ should vanish,

$$\omega_1 + \omega_2 \cdots + \omega_n = 0.$$

We can then write

$$\begin{aligned} \langle V_{v_n}(\omega_n) \cdots V_{v_1}(\omega_1) \rangle_0 \\ = \langle V_{v_n}(\omega_n) \cdots V_{v_1}(\omega_1) \rangle \delta(\omega_1 + \omega_2 + \cdots + \omega_n). \end{aligned}$$

The frequency-domain expressions for signals will thus involve one less integral thanks to this conservation, which simplifies the analysis.

This symmetry is well established for nonlinear susceptibilities¹⁰ but can be applied more broadly to other types of observables. Below we use it to discuss three types of linear signals in molecules whose coupling to the radiation field is given by

$$H' = V[\varepsilon(t) + \varepsilon^*(t)].$$

Here $\varepsilon(t)$ is the complex field amplitude and V is the dipole operator.

THE ABSORPTION OF A WEAK PROBE BY A MOLECULE INITIALLY AT EQUILIBRIUM

If the molecule is initially in thermal equilibrium, the absorption rate of a weak probe pulse which can be read off Fig. 1(a) is given by the linear response function

$$S = \text{Im} \iint d\omega_1 d\omega_2 \langle V_L(\omega_2) V_L(\omega_1) \rangle \varepsilon(\omega_2) \varepsilon(\omega_1) \delta(\omega_1 + \omega_2),$$

where

$$\begin{aligned} \langle V_L(\omega_2) V_L(\omega_1) \rangle_0 &= \iint d\tau_1 d\tau_2 \langle T V_L(\tau_1) V_L(\tau_2) \rangle \varepsilon(\tau_1) \varepsilon(\tau_2) \\ &\times \exp(i\omega_1 \tau_1 + i\omega_2 \tau_2). \end{aligned}$$

Time translation invariance gives

$$\langle V_L(\omega_2) V_L(\omega_1) \rangle_0 = \langle V_L(\omega_2) V_L(\omega_1) \rangle \delta(\omega_1 + \omega_2).$$

Since the electric field is real, then $\varepsilon(-\omega) = \varepsilon^*(\omega)$ and we finally get

$$S = \text{Im} \int d\omega_1 \langle V_L(-\omega_1) V_L(\omega_1) \rangle \varepsilon(\omega_1) \varepsilon^*(\omega_1).$$

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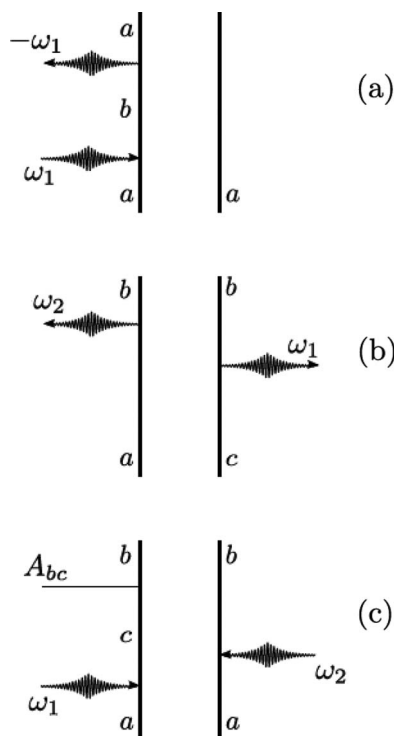


FIG. 1. Double-sided density matrix diagrams for (a) Eq. (2), (b) Eq. (4), and (c) Eq. (6).

The $\delta(\omega_1 + \omega_2)$ factor in this case leaves us no freedom in the frequency domain; the signal depends on a single mode, $\omega_1 = -\omega_2$ and the phase of $\varepsilon(\omega)$ and $\varepsilon^*(\omega)$ is cancelled out. The signal only depends on the power spectrum of the pulse $|\varepsilon(\omega)|^2$ and is independent on the phase of $\varepsilon(\omega)$.

Here and hereafter we invoke the rotating wave approximation. Expanding the correlation function in molecular eigenstates $a, b \dots$ and assuming that the system is initially in state $|a\rangle$ gives (see Fig. 1(a))

$$\langle V_L(-\omega_1)V_L(\omega_1) \rangle = \sum_{a,b} P(a) \frac{|V_{ab}|^2}{\omega_1 - \omega_{ba} + i\varepsilon}. \quad (2)$$

THE ABSORPTION OF A WEAK PROBE BY A SYSTEM PREPARED IN A NON-STATIONARY STATE

We now assume that the system is prepared in an arbitrary non-stationary superposition state described by the density matrix,

$$\rho(\tau_0) = \sum_{a,c} \rho_{ac}(\tau_0) |a\rangle \langle c|.$$

Starting with this state, the linear absorption rate of an external probe field is given by (see Fig. 1(b))

$$S = \text{Im} \sum_{a,c} d\omega_1 d\omega_2 \langle V_L(\omega_1)V_R(\omega_2)\rho_{ac}(\tau_0) \rangle_0 \varepsilon(\omega_1)\varepsilon(\omega_2),$$

where

$$\begin{aligned} & \langle V_L(\omega_1)V_R(\omega_2)\rho_{ac}(\tau_0) \rangle_0 \\ &= \iint d\tau_1 d\tau_2 \langle T V_L(\tau_2)V_R(\tau_1)\rho_{ac}(\tau_0) \rangle \\ & \times \exp(i\omega_1\tau_1 + i\omega_2\tau_2 - i\omega_{ac}\tau_0). \end{aligned}$$

By shifting all time arguments, we now obtain

$$\begin{aligned} & \langle V_L(\omega_1)V_R(\omega_2)\rho_{ac}(\tau_0) \rangle_0 \\ &= \langle V_L(\omega_1)V_R(\omega_2)\rho_{ac}(\tau_0) \rangle \delta(\omega_1 + \omega_2 - \omega_{ac}). \end{aligned}$$

This gives

$$\begin{aligned} S &= \text{Im} \sum_{a,c} \int d\omega_1 \langle V_L(\omega_1)V_R(\omega_{ca} - \omega_1)\rho_{ac}(\tau_0) \rangle \\ & \times \varepsilon(\omega_1)\varepsilon^*(\omega_1 - \omega_{ac}). \end{aligned} \quad (3)$$

Now ω_1 is different from ω_2 thanks to the coherence frequency ω_{ca} of the initial state, and the signal will generally depend on pairs of modes $\omega_1, \omega_2 = -\omega_1 + \omega_{ac}$ and on their relative phase. If the molecule is initially in a population state $\omega_{ac} = 0$ then the signal will be independent on the delay and the signal is independent on phase. By expanding in eigenstates, we obtain for the correlation function (see Fig. 1(b))

$$\begin{aligned} & \langle V_L(\omega_1)V_R(\omega_{ca} - \omega_1)\rho_{ac}(\tau_0) \rangle \\ &= \sum_{a,b,c} \frac{V_{cb}V_{ba}\rho_{ac}}{\omega_1 - \omega_{ab} + i\varepsilon} \exp(-i\omega_{ac}\tau_0). \end{aligned} \quad (4)$$

This observable can represent, e.g., the coherent control of peptide ionization to discriminate between various tryptophans.¹¹

EXPECTATION VALUE OF A NON-STATIONARY OBSERVABLE

Suppose we measure the expectation value of an operator A that does not commute with the Hamiltonian: $A = \sum_{b,c} A_{cb}|c\rangle\langle b|$. As an example consider the probability of the system to be in some group of states. This may be represented by a projection operator $A = \sum_n |n\rangle\langle n|$ where $\{|n\rangle\}$ is not a complete basis and $|n\rangle$ are not eigenstates of the Hamiltonian but, represent the observed space (such as the cis isomer in Rhodopsin): $A_{cb} = \sum_n \langle c|n\rangle\langle n|b\rangle$.

To linear order in the incoming pulse intensity, this time-dependent probability (Fig. 1(c)) is given by

$$\begin{aligned} \langle A(\tau_0) \rangle &= \iint d\omega_1 d\omega_2 \langle V_L(\omega_1)A_L^{bc}(\tau_0)V_R(\omega_2) \rangle \\ & \times \varepsilon(\omega_1)\varepsilon(\omega_2)\delta(\omega_1 + \omega_2 + \omega_{bc}), \end{aligned}$$

where

$$\begin{aligned} \langle V_L(\omega_1)A_L^{bc}(\tau_0)V_R(\omega_2) \rangle &= \iint d\tau_1 d\tau_2 \langle T V_R(\tau_2)V_L(\tau_1)A_L^{bc} \rangle \\ & \times \exp(i\omega_1\tau_1 + i\omega_2\tau_2 + i\omega_{bc}\tau_0). \end{aligned}$$

Time translational invariance then yields

$$\begin{aligned} \langle V_L(\omega_1)A_L^{bc}(\tau_0)V_R(\omega_2) \rangle &= \langle V_L(\omega_1)A_L^{bc}(\tau_0)V_R(\omega_2) \rangle_0 \\ & \times \delta(\omega_1 + \omega_2 + \omega_{bc}). \end{aligned} \quad (5)$$

We finally obtain

$$\langle A(\tau_0) \rangle = \text{Im} \sum_{b,c} \int d\omega_1 \langle V_L(\omega_1) A_{bc}(\tau_0) V_R(-\omega_{bc} - \omega_1) \rangle \\ \times \varepsilon(\omega_1) \varepsilon^*(\omega_{bc} + \omega_1).$$

This observable again involves pairs of modes ω_1 , ω_2 which differ by the observation frequency ω , $\omega_1 = -\omega_2 - \omega_{bc}$, and thus depends on their relative phase. By expanding it in eigenstates, we obtain

$$\langle V_L(\omega_1) A_{bc}(\tau_0) V_R(\omega_2) \rangle = \sum_{a,b,c} P(a) \\ \times \frac{V_{ab} A_{bc} V_{ca}}{(\omega_1 - \omega_{ca} + i\varepsilon)(\omega_1 + \omega_2 - \omega_{cb} + i\varepsilon)} \exp(i\omega_{bc}\tau_0). \quad (6)$$

If the observable A commutes with the molecular Hamiltonian (say we measure the population of a group of eigenstates $|n\rangle$) it is diagonal in the eigenstates basis $A_{cb} = A_{cc}\delta_{cb}$. Then $\omega_{bc} = 0$ and the above signal becomes independent on the phase of the field.

In summary, the key factor in determining the phase dependence of the signal is not its linearity in the field but the multimode nature of the process. This becomes most transparent in the frequency domain representation adopted here. Observables in broadband measurements may generally be recast as path integrals over field modes, with one constraint stemming from time translational invariance: the sum of all frequencies in each contribution must be zero. These path integrals represent a wave mixing of the relevant modes. Linear absorption depends on paths involving two modes. Because of the constraint this number reduces to one, thus eliminating the phase dependence in Eq. (1) altogether. When starting in a non-stationary state, the linear response depends on three frequencies. The extra frequency is related to the initial coherence which must be present in a non-stationary state. We thus have phase dependence in Eq. (3). Similarly, observing a non-stationary operator after linear excitation again requires three frequencies. With a single constraint this reduces to two, and phase dependence is maintained in Eq. (5). By either starting in a non-stationary state (Eq. (3)) or looking at a non-stationary variable (Eq. (5)), a new frequency enters compared to Eq. (1) which causes the phase dependence, despite the constraint. This frequency stems from an extra coherence

that enters the picture either through the initial state (Eq. (3)) or at the final detection stage (Eq. (5)).

Equation (3) can represent a pump-probe signal with an impulsive pump that creates the superposition state. Equation (5) can represent, e.g., a photoisomerization signal with a gated fluorescence measurement that probes the population of one isomer (which is not an eigenstate of the total Hamiltonian). In either case, the extra frequency is responsible for the phase dependence and enables the application of coherent-control schemes.

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