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Communication

Diagram Technique for Nonlinear Optical Spectroscopy in the Fast Electronic Dephasing Limit

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We show that applying the double-sided Feynman diagrams to systems with fast electronic dephasing opens up new possibilities for using this technique in resonance nonlinear optical spectroscopy. The novel potentials are including non-perturbative system-bath interactions (non-Markovian relaxation) and the summation of diagrams. The last procedure enables us to obtain new equations for a nonperturbative description of the light-matter interaction.

INTRODUCTION

The diagrammatic technique for the evaluation of density matrix elements (the double-sided Feynman diagrams)[1-3] is of considerable current use for the analysis of nonlinear optical processes.[4,5] However, the efficiency of this approach is confined to a simple picture of damping when the impact approximation or the approximation of a weak relaxation interaction are correct. This approach does not take into account the memory (non-Markovian) effects in relaxation. This is not the case, for example, for electron-vibrational systems (complex molecules, impurity centers in a crystal, etc.) where relaxation interactions are not weak, and the perturbation theory with respect to system-bath interactions is incorrect. Using the double-sided Feynman diagrams for such systems results in formal operator expressions, the calculations of which in the resonance case are very cumbersome if the processes under consideration are of the order higher than 4.

Furthermore, each rational diagrammatic technique must enable us to make the graphical summation of diagrams. However, to our knowledge, there is not any information about such potentials of the double-sided Feynman diagrams in the literature. Therefore, the technique was not used for a nonperturbative description of the light-matter interaction. This is unfortunate since the problem of a nonperturbative description of the interaction of strong pulse radiation with large molecules in solutions is the topic of active recent research.[6-10] Especially, such a problem is of great interest for interaction of phase modulated (chirped) pulses with molecular systems because it is one of the powerful and promising methods developed recently for study and control of processes in condensed matter.[9-15]

In this study we show that applying the double-sided Feynman diagrams[1-3] to systems with fast optical dephasing opens up new possibilities for using this technique in ultrafast resonance spectroscopy. The novel potentials are including nonperturbative system-bath interactions (non-Markovian relaxation) and the summation of diagrams. In the communication we outline some of the preliminary results. A full account of this study will be given elsewhere.

DIAGRAMMATIC TECHNIQUE FOR FAST OPTICAL DEPHASING

Let us consider a molecule with three electronic states $n = 1,2,3$ in a solvent described by the Hamiltonian

$$H_0 = \sum_{n=1}^{3} |n>[E_n + W_n(\mathbf{Q})]<n| \tag{1}$$

where $E_3 > E_2 > E_1$, E_n is the energy of state n, $W_n(\mathbf{Q})$ is the adiabatic Hamiltonian of reservoir R (the vibrational subsystems of a molecule and a solvent interacting with the three-level electron system under consideration in state n).

The molecule is affected by electromagnetic radiation of a number of beams

$$\begin{aligned}\mathbf{E}(\mathbf{r},t) &= \mathbf{E}^{+}(\mathbf{r},t) + \mathbf{E}^{-}(\mathbf{r},t)\\ &= \frac{1}{2}\sum_{m} \vec{E}_m(t)\exp[i(\mathbf{k}_m\mathbf{r} - \omega_m t)] + c.c.\end{aligned} \tag{2}$$

Electromagnetic field (2) induces an optical polarization in the medium $\mathbf{P}(\mathbf{r},t)$ which can be expanded in powers of $\mathbf{E}(\mathbf{r},t)^4$:

$$\mathbf{P}^{(n)}(\mathbf{r},t) = N < Tr_R(\mathbf{D}\rho^{(n)}(t)) >_{or} \tag{3}$$

where N is the density of particles in the system; $\mathbf{D}$ is the dipole moment operator of a solute molecule; $\langle \ldots \rangle_{or}$ denotes averaging over the different orientations of solute molecules;

$\rho^{(n)}$ is the density matrix of the system calculated in n-th approximation with respect to $\mathbf{E}(\mathbf{r}, t)$. The density matrix satisfies the Liouville equation:

$$i\hbar\frac{\partial\rho}{\partial t} = [H_0 + H'(t), \rho] \tag{4}$$

where $H'(t) = -\mathbf{DE}(\mathbf{r}, t)$.

We consider only resonance light-matter interactions. We assume that a strong pump $\frac{1}{2}\vec{E}(\mathbf{r}, t)\exp(-i\omega t) + c.c.$ acts at the electronic transition 1→2, and a weak probe resonance field $\frac{1}{2}\vec{E}_{pr}(t-\tau)\exp[i(\mathbf{k}'\mathbf{r} - i\omega'(t-\tau))] + c.c.$ delayed by a variable τ acts at the same or another transition (2→3) and does not overlap in time with the pump, i. e.

$$\sum_m \vec{E}_m(t)\exp[i(\mathbf{k}_m\mathbf{r} - \omega_m t)] = \vec{E}(\mathbf{r}, t)\exp(-i\omega t) + \vec{E}_{pr}(t-\tau)\exp[i(\mathbf{k}'\mathbf{r} - i\omega'(t-\tau))]$$

where $\vec{E}(\mathbf{r}, t) = \vec{E}(t)\,\Sigma_l \exp(i\mathbf{k}_l\mathbf{r})$. To include the phase modulated (chirped) pump in our technique, we present the pump field amplitude $E(t)$ in the form[9]

$$E(t) = \varepsilon(t)\exp(i\varphi(t)), \tag{5}$$

where $\varepsilon(t)$ and $\varphi(t)$ are real functions of time, and $\varphi(t)$ describes the change of the pulse phase in a time t. The instantaneous frequency of the pump pulse is determined by $\omega(t) = \omega - \frac{d\varphi(t)}{dt}$.

We consider the case of appreciable Stokes losses when the perturbation of the electronic system by a nuclear one under electronic excitation 1→2 (a quantity $V(\mathbf{Q}) = W_2(\mathbf{Q}) - W_1(\mathbf{Q})$) is large. It corresponds to the fast electronic dephasing limit. In the last case one can consider the density matrix diagonal with respect to electronic indices $\rho_{nn}(t)$. The last one can be represented as the sum of the even approximations with respect to the amplitude of an external field:

$$\rho_{nn}(t) = \sum_{m=0}^{\infty} \rho_{nn}^{(2m)}(t) \tag{6}$$

Where $\rho_{nn}^{(0)}(t) = \rho_{nn}(-\infty)$.

We introduce the rectangular vertices (Fig. 1) presenting the interactions between the system and the relevant pair of fields. These rectangular vertices are the sums of two subdiagrams corresponding to the nondiagonal density matrix elements in technique,[1] since the main processes occurring in a system with fast optical dephasing are related to nonequilibrium luminescence and absorption. Introducing such vertices strongly diminishes a number of the diagrams under consideration.

Damping is included as a random perturbation by a Markovian process (diffusional or discontinuous) in the configuration coordinate space in the relevant electronic state. Introducing the configuration coordinate q corresponds to a reduced description, when q represents only a partial set of coordinates related to optically active modes which give a contribution to $V(\mathbf{Q})$. As this takes place, the relaxation itself is not Markovian since a system-bath interaction can be strong. A Markovian nature of a random perturbation enables us to write easily an expression for the corresponding diagram in any order with respect to the light-matter interaction. It can be done using the corresponding Liouville space Green functions $G_{nc}(q,t;q')$ which give the density of the conditional probability in electronic states $n=1,2$ for a Markovian process. They satisfy the following equation:

$$\left(\frac{\partial}{\partial t} - L_n\right)G_{nc}(q,t;q') = 0, \qquad G_{nc}(q,t;q') = \delta(q-q')$$

where L_n is the Liouville operator in the configuration coordinate space.

Double-sided Feynman diagrams for fast optical dephasing

Let us consider the density matrix diagonal with respect to electronic indices $\rho_{nn}(t)$. It is represented by two vertical lines. The left line represents the ket- $|n\rangle$ and the right line represents the bra-vector $\langle n|$. We can state the following rules for the double-sided Feynman diagrams for fast optical dephasing and a Markovian random evolution in the configuration coordinate space:

1. The system evolution depends only on "even" times. Time increases from bottom to top (see Fig. 2).

2. The interactions between system and the pump fields of frequency ω are presented by three types of the rectangular

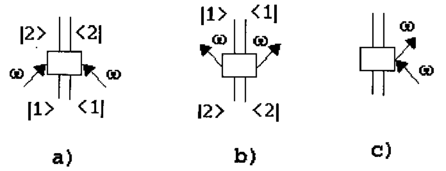

Fig. 1. Three types of rectangular vertices with double horizontal lines.

vertices (see Fig. 1). The vertex of the *a*) type corresponds to electronic transition 1→2, the vertex of the *b*) type - to electronic transition 2→1, and the vertex of the *c*) type does not change an electronic state.

3. Interactions with applied pump fields are labelled by the pairs of arrows. The contributions from the *j* -th vertices of the *a*) , *b*) and *c*) types in Fig. 1 are equal to

$$a)=b)=-c)=\frac{\pi}{2\hbar^2}|DE(t-\tau_{2m}-\tau_{2m-2}-\ldots-\tau_{2j})|^2\exp[i(\boldsymbol{k}_{l'}-\boldsymbol{k}_{l''})\boldsymbol{r}]$$
$$\times\hbar\sum_i|V'[q_i(t-\tau_{2m}-\tau_{2m-2}-\ldots-\tau_{2j})]|^{-1}$$

where the wave vector $\boldsymbol{k}_{l'}$ corresponds to the arrow in the corresponding pair pointing to the right, and the wave vector $\boldsymbol{k}_{l''}$ corresponds to the arrow in the pair pointing to the left; $V'(q_i) \equiv \frac{dV}{dq}|_{q=q_i}$, $q_i(t-\tau')$ are the solutions of the following equation:

$$\omega(t-\tau')-\omega_{21}^{el}-V(q)/\hbar=0 \tag{9}$$

4. The overall wave vector of each diagram is the sum of all $\boldsymbol{k}_{l'}$ minus the sum of all $\boldsymbol{k}_{l''}$: $\Sigma_{l'}\boldsymbol{k}_{l'}-\Sigma_{l''}\boldsymbol{k}_{l''}$.

5. The system evolution between adjacent rectangular vertices *j* and *j*+1 along the double vertical line in electronic state *n* is described by the corresponding Liouville space Green function $G_{nc}(q_{i'}(t-\tau_{2m}-\ldots-\tau_{2j+2}),\ \tau_{2j};\ q_i(t-\tau_{2m}-\ldots-\tau_{2j}))$. The evolution of the system in a last "even" time τ_{2m} is described by the term $G_{nc}(q,\tau_{2m};\ q_i(t-\tau_{2m}))$.

6. The contribution from each diagram to $\rho_{nn}^{(2m)}(t)$ is obtained by integration with respect to all times $\tau_2, \tau_4, \ldots, \tau_{2m}$.

For example, contributions from the diagrams shown in Fig. 2 are equal to

$$\rho_{22}^{(2\leftarrow n\leftarrow 1)}(q,t)=-\int_0^\infty d\tau_4\int_0^\infty d\tau_2\frac{\pi}{2\hbar^2}|D\mathcal{E}(t-\tau_4)|^2\frac{\pi}{2\hbar^2}$$
$$\times|D\mathcal{E}(t-\tau_4-\tau_2)|^2\rho_{22}^{ev(2\leftarrow n\leftarrow 1)}(q,\tau_4,\tau_2) \tag{10}$$

Where

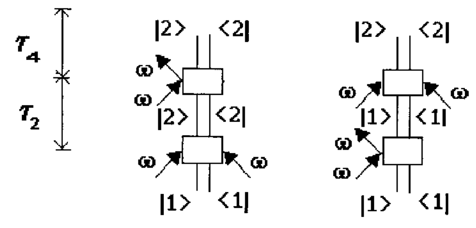

Fig. 2. The fourth order contribution to $\rho_{22}(t)$.

$$\rho_{22}^{ev(2\leftarrow n\leftarrow 1)}(q,\tau_4,\tau_2)=\hbar\sum_j|V'[q_j(t-\tau_4)]|^{-1}\,G_{2c}(q,\tau_4;q_j(t-\tau_4))$$
$$\times\hbar\sum_i|V'[q_i(t-\tau_4-\tau_2)]|^{-1}$$
$$\times G_{nc}(q_j(t-\tau_4),\tau_2;q_i(t-\tau_4-\tau_2))$$
$$\times\rho_{11}(q_i(t-\tau_4-\tau_2),-\infty), \tag{11}$$

$$\rho_{11}(q'',-\infty)=\left(\frac{\beta}{2\pi}\right)^{1/2}\exp[-\beta U_1(q'')]\left(\int_{-\infty}^{\infty}\exp[-\beta U_1(q)]dq\right)^{-1} \tag{12}$$

is the equilibrium density matrix of the ground state 1, $\beta = 1/(kT)$, U_1 is the potential energy in the electronic state 1.

Summation of diagrams

Only three types of the rectangular vertices exist (Fig. 1). The last enables us to make the graphical summation of diagrams (see Fig. 3). Two thick vertical lines correspond to the complete density matrix.

The diagram equations displayed graphically in Fig. 3 for $n = 1$ and 2 can be written analytically as

$$\rho_{nn}(q,t)=\rho_{nn}(q,-\infty)+(-1)^n\frac{\pi}{2\hbar^2}\int_0^\infty d\tau'|D\mathcal{E}(t-\tau'|^2$$
$$\times\hbar\sum_i|V'[q_i(t-\tau')]|^{-1}\,G_{nc}(q,\tau';q_i(t-\tau'))$$
$$\times[\rho_{11}(q_i(t-\tau'),t-\tau')-\rho_{22}(q_i(t-\tau'),t-\tau')] \tag{13}$$

In doing so we obtain new equations for a nonperturbative description of the light-matter interaction[16] and rediscover

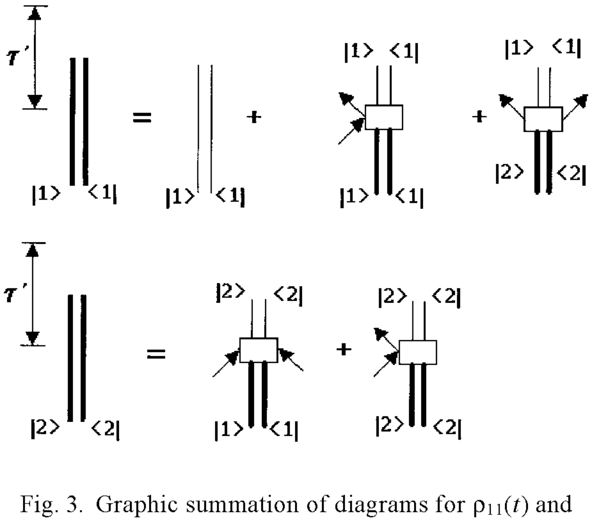

Fig. 3. Graphic summation of diagrams for $\rho_{11}(t)$ and $\rho_{22}(t)$.

also known results.[9]

CONCLUSION

In this communication we have outlined some of the preliminary results concerning the application of the double-sided Feynman diagrams to systems with fast electronic dephasing. We have formulated the diagrammatic technique for fast optical dephasing by introducing the rectangular vertices, which are the sums of two subdiagrams corresponding to the nondiagonal density matrix elements in technique.[1] Damping is included as a random perturbation by a Markovian process (diffusional or discontinuous) in the relevant electronic state. As this takes place, the relaxation itself is not Markovian since a system-bath interaction can be strong. A Markovian nature of a random perturbation enables us to write easily an expression for the corresponding diagram in any order with respect to the light-matter interaction.

Furthermore, only three types of the rectangular vertices exist. This point enables us to make the graphical summation of diagrams and obtain new equations for a nonperturbative description of the light-matter interaction. These equations will be used for the generalization and further developments of a new approach to the description of the interaction of intense ultrashort chirped pulses with molecules in solution: the picture of "moving potentials".[9]

By applying the technique outlined in this work to non-diffusional Markovian processes, we have shown that the methods of pump-probe spectroscopy enable us to study the vibrational coherence induced by relaxation.[17]

Finally, the relaxation in Debye solvent provides an example of a relaxation corresponding to a random perturbation of a Markovian nature with the exponential correlation function. However, as recent studies show, the solvent relaxation is "biphasic": its correlation function typically consists of a fast (femtosecond) and a slower component.[18-23] "Biphasic" relaxation provides an example of relaxation corresponding to a *non-Markovian* random perturbation. The technique outlined in this communication can be extended to relaxation induced by stochastic processes of a non-Markovian nature if they are represented as *multidimensional* Markovian processes. It will be done elsewhere.

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Key Words

Diagram technique; Summation of diagrams; Nonperturbative description of light-matter interaction.

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