Annals of Physics 325 (2010) 711–747

Contents lists available at ScienceDirect

Annals of Physics

journal homepage: www.elsevier.com/locate/aop

A time convolution less density matrix approach to the nonlinear optical response of a coupled system–bath complex

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ARTICLE INFO

Article history:
Received 28 November 2008
Accepted 24 December 2009
Available online 4 January 2010

Keywords:
Time-convolution less (TCL) theory
Electron–phonon interaction
Nonlinear optical response
Open quantum systems

ABSTRACT

Time convolution less density matrix theory (TCL) is a powerful and well established tool to investigate strong system–bath coupling for linear optical spectra. We show that TCL equations can be generalised to the nonlinear optical response up to a chosen order in the optical field. This goal is achieved via an time convolution less perturbation scheme for the reduced density matrices of the electronic system. In our approach, the most important results are the inclusion of a electron–phonon coupling non-diagonal in the electronic states and memory effects of the bath: First, the considered model system is introduced. Second, the time evolution of the statistical operator is expanded with respect to the external optical field. This expansion is the starting point to explain how a TCL theory can treat the response up to in a certain order in the external field. Third, new TCL equations, including bath memory effects, are derived and the problem of information loss in the reduced density matrix is analysed. For this purpose, new dimensions are added to the reduced statistical operator to compensate lack of information in comparison with the full statistical operator. The theory is benchmarked with a two level system and applied to a three level system including non-diagonal phonon coupling. In our analysis of pump–probe experiments, the bath memory is influenced by the system state occupied between pump and probe pulse. In particular, the memory of the bath influences the dephasing process of electronic coherences developing during the time interval between pump and probe pulses.

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doi:10.1016/j.aop.2009.12.008

1. Introduction

Examples for strong electron–phonon coupling range from molecular structures such as light-harvesting complexes [1,2] to solid state materials such as nitride compounds [3]. For these electronic systems exhibiting strong system–bath coupling (electron–phonon interaction), often used schemes like perturbation theory [4], Nakajima–Zwanzig [5,6,2] or correlation expansion [7–10] for the evaluation of the optical response fail. So far, only for a strict diagonal coupling in the system–bath coupling the linear and nonlinear optical response can be calculated exactly for two level systems using the independent boson model [11,12], cumulant expansion [13,14] and the TCL scheme [15]. An extension of the TCL approach to non-diagonal coupling is not fully worked out.

To be specific, the TCL method is a projection operator technique to solve equations like the von Neumann equation including system–bath interaction for the system density matrix (relevant density matrix) without using time retarded formulations. The relevant part of the density matrix $\mathcal{P}\rho(t)$ is necessary to calculate the expectation value of the system operators. A equation of motion in a convolution less form or secular form, i.e. $\partial_t \mathcal{P}\rho(t) = \mathcal{K}(t)\mathcal{P}\rho(t)$, is a convenient description of the dynamics cf. Section 5.1 for a detailed discussion.

In this paper, we extend the actual existing TCL schemes to an arbitrary order in the electric field's response (nonlinear optics). However, the complexity of the equations will practically limit the evaluation to third order in the external field. Using this scheme, our approach takes dynamical changes of the bath into account, important for delay times within polarisation dephasing times between optical excitation pulses in pump–test and four wave mixing experiments.

2. Description of the system

We study a system consisting of a many level system (Hamiltonian $H_{0,el}$), coupled via the interaction Hamiltonian (H_{el-ph}) to a bath (here a vibron/phonon system with $H_{0,ph}$) and to an external field (Hamiltonian H_E), cf. Fig. 1. In the simplest case, a single two level system is known as a theoretical benchmark since it is an exactly solvable system [13,16]. The total Hamiltonian H reads:

$$H = H_0 + H_1, \tag{1}$$

$$H_0 = H_{0,el} + H_{0,ph}, \tag{2}$$

$$H_1 = H_E + H_{el-ph}. \tag{3}$$

In order to illustrate the following derivation of the generalised TCL approach, we will refer to the following model system Hamilton operator for electronic states:

$$H_{0,el} = \hbar \sum_i \varepsilon_{c_i} a^\dagger_{c_i} a_{c_i} + \varepsilon_v a^\dagger_v a_v. \tag{4}$$

Here $a^\dagger, a$ are the fermion creation and annihilation operators for the two or three electronic states. The index v and c_i denotes the lower level v and the upper levels c_i, respectively, cf. Fig. 1. ε_{c_i} and ε_v

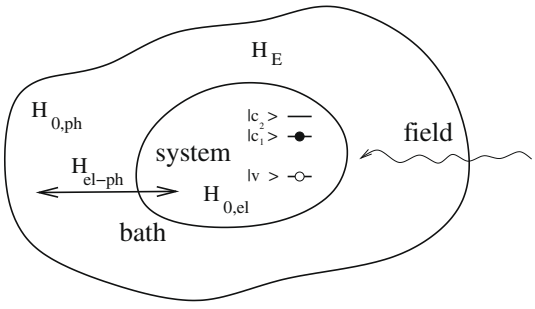

Fig. 1. Illustration of a three level system coupled to a phononic bath.