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DYNAMICS AND OPTICAL ABSORPTION OF ELECTRONIC EXCITATIONS UNDER THE INFLUENCE OF COLOURED NOISE

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Abstract For a model dimer the influence of vibrational degrees of freedom on electronic excitations is described by a dichotomic Markov process with coloured noise. Within this model the energy transport between the two units of the dimer, especially the transition between coherent and incoherent motion is discussed. Furthermore the optical absorption line shape is evaluated for various values of the model parameters.

INTRODUCTION

The interaction between electronic and vibrational degrees of freedom is a problem of widespread interest, because on the one hand it is of importance in various fields of molecular and condensed matter physics when e.g. transport or spectroscopic properties of these materials are described, on the other hand the Hamiltonian operator is to some extent generic for the description of the nontrivial interaction between two kinds of degrees of freedom and therefore of general interest in theoretical physics. A general solution for this problem has not yet been achieved, and therefore various approximation schemes have been used.

One approximation, which has been used when describing the influence of phonons on exciton dynamics in the Haken-Strobl-Reineker[1–3] approach, consists in replacing the vibrational degrees of freedom by a stochastic process, giving rise to modulation of the parameters (energy, transfer matrix element) of the excitonic system. In Ref. 1-3 the fluctuations were assumed to be described by a δ-correlated, Gaussian Markov process with vanishing mean value, which implies the occurrence of phonon induced fluctuations with arbitrary high frequencies.

With decreasing temperature however, the high frequency phonons vanish and thus the decay of the correlation function is slowed down. To get insight into this situation we have described the influence of the phonons by a stochastic process with exponentially decaying correlation function and applied this description to two

model situations : transport of electronic excitation energy in a dimer and optical absorption in a dimer.

The calculations should be of relevance for guest dimers in molecular crystals, such as naphthalene and anthracene, to the energy transport between chromophores in polymers, and to the energy transfer in photosynthetic systems.

MODEL HAMILTONIAN

The Hamiltonian of our model is given by :

$$H(t) = H_0 + H_1(t) \tag{1}$$

$$= \sum_n J\,(a_n^\dagger a_{n+1} + a_{n+1}^\dagger a_n) + \sum_n h_n(t)\; a_n^\dagger a_n \; . \tag{2}$$

Here $a_n^\dagger$ (a_n) are creation (annihilation) operators for an electronic excitation at site $n \epsilon \{1,2\}$, J is the transfer matrix element between the molecules and $h_n(t)$ describes energy fluctuations at site n (dichotomic Markov process [4] with vanishing mean value $\langle h_n(t)\rangle = 0$). The two-time correlation function is given by :

$$\langle h_m(t)\, h_n(t')\rangle = \delta_{mn}\Delta^2 e^{-\lambda|t-t'|} \tag{3}$$

and higher order correlation function are given by :

$$\langle h_n(t_1)\, h_n(t_2) \ldots h_n(t_n)\rangle = \langle h_n(t_1)\, h_n(t_2)\rangle\, \langle h_n(t_3) \ldots h_n(t_n)\rangle \tag{4}$$

$$t_1 > t_2 > \ldots > t_n \quad .$$

EXCITON TRANSPORT

The transport of electronic excitation energy may conveniently be described in terms of the density operator. Its equation of motion is given by :

$$\langle \dot{\rho}\rangle = -\,i\,\langle\,[H(t), \rho]\,\rangle \tag{5}$$

where the angular brackets denote averaging over the stochastic process. For the stochastic processes of our model this average may be evaluated using a theorem of Shapiro and Loginov [5] :

$$\frac{d}{dt}\langle h(t)\,\phi_t[h]\rangle = \langle h(t)\,\frac{d}{dt}\phi_t[h]\rangle - \lambda\,\langle h(t)\,\phi_t[h]\rangle \; . \tag{6}$$

In Eq. (6) $\phi_t[h]$ is an arbitrary functional of the stochastic process $h(t)$. In the case of our model (dimer, dichotomic fluctuations of the local excitation energies)

we end up at a set of 16 coupled linear differential equations for various correlation functions of the density operator, which may be written in the following way :

$$\dot{\rho} = L\rho \ . \tag{7}$$

ρ is a 16-dimensional column vector summarizing correlation functions of the density operator mentioned above and L is a 16×16 non-hermitian matrix (for details see Ref. 6).

Using the ansatz $\rho(t) = e^{Rt}\rho$ the set of differential equations is transformed to a 16-dimensional non-hermitean eigenvalue problem $R_i\rho_i = L\rho_i$, where ρ_i are are the eigenvectors and $R_i = -\gamma_i + i\omega_i$ the generally complex eigenvalues. The general solution is then given by a superposition of the eigensolutions $\rho(t) = \sum_{i=1}^{16} c_i\rho_i exp(R_i t)$; the coefficients c_i are determined from the initial conditions. A detailed discussion of numerical solutions with the excitation being initially localized at one site and for various values of the parameters λ, Δ, and J is given in Ref. 6.

Recently we have succeeded in getting analytical expressions for the eigensolutions using the symbolic computation program MAPLE[7]. The consideration of the eigenvectors shows that only 4 of the 16 eigensolutions determine the exciton transport. Depending on whether these eigenvalues are complex or purely real the exciton occupation probabilities at the two sites show damped oscillations or a purely exponential behaviour. In the first case the exciton motion is denoted as coherent, in the second as incoherent.

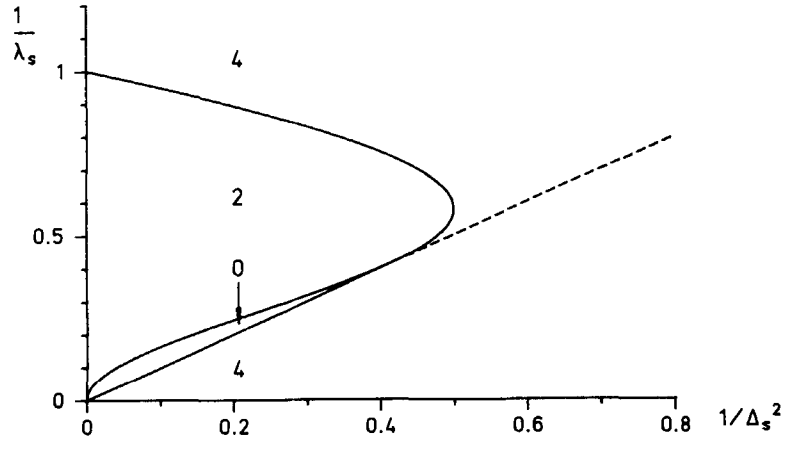

FIGURE 1 Number of complex eigenvalues in the $\Delta_s^{-2} - \lambda_s^{-1}$ plane. (The dashed line corresponds to the transition between coherent and incoherent motion in the limit of white noise).

In Fig. 1 we show in a $1/\lambda_s$ versus $1/\Delta_s^2$ diagram ($\lambda_s = \lambda/2J$, $\Delta_s = \Delta/2J$) the areas where 4 eigenvalues are complex, where two of them are complex and two purely real, and where all of them are real (none complex). The dashed line describes in the limit $\Delta_s \to \infty$, $\lambda_s \to \infty$, Δ_s^2/λ_s *finite* the transition between coherent and incoherent motion in the Haken-Strobl model (white noise). In contrast to the latter model our extension to the case of coloured noise shows an additional range of coherent motion for $\lambda_s \to 0$ which describes the case of frozen fluctuations.

OPTICAL ABSORPTION

In our dimer model optical absorption[8] may easily be considered by explicitly including the ground state of the system. From linear response theory the line shape is given by

$$I(\omega) = Re \int_0^\infty dt\ e^{i\omega t} \langle \mu(t)\, \mu(0) \rangle \tag{8}$$

where in terms of creation and annihilation operators the dipole moment operator is $\mu = \sum_n \mu_n (a_n^\dagger + a_n)$. Assuming that the dipole moment μ_n is the same for all molecules we have

$$I(\omega) = \mu^2 Re \int_0^\infty dt\ e^{i\omega t} \sum_{mn} \langle U_{mn}(t) \rangle\ . \tag{9}$$

The averaged time-development operator $\langle U_{mn}(t) \rangle$ is defined by

$$\langle U_{mn}(t) \rangle = \langle 0 \mid a_m(t)\, a_n^\dagger \mid 0 \rangle = \langle\langle m \mid \overleftarrow{T}\ \ exp\left(i \int_0^t d\tau\ H(\tau) \right) \mid n \rangle\rangle \tag{10}$$

where the double brackets denote quantum and stochastic average. The optical line shape is calculated via the equations of motion for correlation functions and their Laplace transforms :

$$I(\omega) = \mu^2 Re S(\omega) \tag{11}$$

where $S(\omega)$ is obtained numerically from the following continued fraction :

$$S(\omega) = \ 2\Big[i(\omega - J) + \Delta^2 \Big[i\omega + \lambda + J^2 \big[i\omega + \lambda + \Delta^2 [i(\omega - J) + 2\lambda]^{-1} \big]^{-1} \Big]^{-1} \Big]^{-1}\ . \tag{12}$$

The line shape for $J = \Delta^2 = 1$ and various values of λ is given in Figure 2. For small values of λ the line positions are essentially determined by the time independent part of the Hamiltonian and describe an inhomogeneous broadening because of the various realizations of the stochastic process. The width of a single peak is given

by the inverse lifetime of the realization which is determined by the switching rate of the stochastic process. With increasing values of λ the lines broaden, merge and are finaly motionally narrowed.

The model thus shows a transition between static and dynamic disorder which results in a transition from inhomogeneously to homogeneously broadened line shapes. The question of whether there is a connection between the transition from coherent to incoherent motion and the optical linewidth is at present under investigation[9].

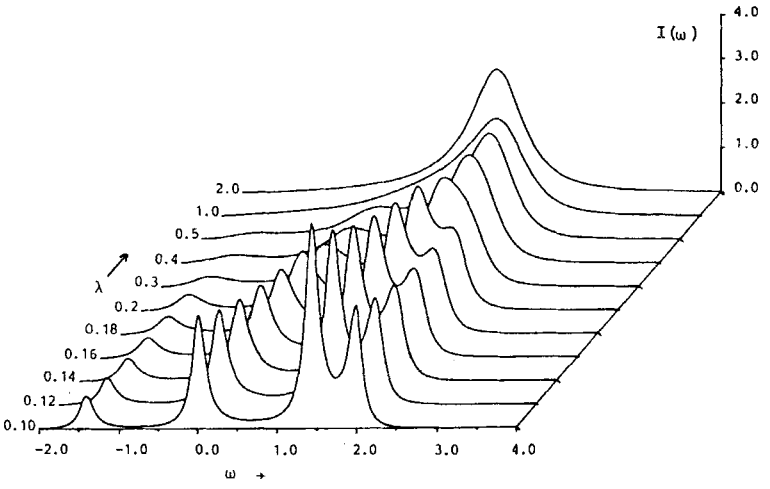

FIGURE 2 Optical line shapes of dimers under the influence of site energy fluctuations for $0.1 \leq \lambda \leq 2.0$ $(J = \Delta^2 = 1)$

REFERENCES

1. H. Haken, G. Strobl, in The Triplet State, edited by A. Zahlan (Cambridge University Press, London, 1967).
2. H. Haken, P. Reineker, Z. Phys., 249, 253 (1972).
3. P. Reineker, in Exciton Dynamics in Molecular Crystals and Aggregates, Springer Tracts in Modern Physics, Vol. 94, edited by G. Höhler (Springer, Berlin, 1982).
4. R. C. Bourret, U. Frisch, A. Pouquet, Physica, 65, 303 (1973).
5. V. E. Shapiro, V. M. Loginov, Physica, 91A, 563 (1979).
6. V. Kraus, P. Reineker, Phys. Rev. A, 43, 4182 (1991).
7. B. W. Char, K. O. Geddes, G. H. Gonnet, M. B. Monangan, S. M. Watt, MAPLE Reference Manual, (Waterloo Maple Software, Waterloo, 1988).
8. B. Kaiser, A. M. Jayannavar, P. Reineker, J. Lumin., 43, 73 (1989).
9. Ch. Warns, P. Reineker, to be published.