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**EXCITON PROPAGATION
IN THE FIELD OF A DRIVEN VIBRATION**

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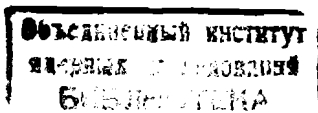
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I. Introduction

In the last years exciton propagation in condensed molecular systems and the influence of the exciton-phonon interaction on the propagation process have been considered in a number of papers (see, e.g. ^{1-5/}). In particular, the generalized master equation (GME) method ^{1/} and the stochastic Liouville equation approach ^{2/} were developed to treat the coherent and incoherent exciton motion from a unified point of view. In the explicit calculations the exciton is assumed to interact with a phonon bath in thermal equilibrium ^{4,6/} which in a high temperature approximation can be replaced by the interaction with a classical stochastic field. The stochastic approximation can be particularly useful in treating the optical lineshape problem ^{2,7/} and the disorder influence ^{8/}.

On the other hand exciton propagation can also be of interest in a non-equilibrium situation when some selected vibrations of the phonon system are strongly excited. This situation might be of importance for solids in which the phonon system is brought into a non-equilibrium state ^{9/}, but also in molecular aggregates relevant in biological systems for which the presence of vibrational states having a non-thermal distribution has been discussed since a long time ^{10/}. Furthermore in the light exposed chlorophyll system of green leaves energy transfer to the reaction centres is realized by excitons and there are indications for the simultaneous presence of non-equilibrium phonon states in this system ^{11/}.

This paper is an attempt to address the problem of exciton motion in a non-equilibrium situation by investigating exciton propagation in the presence of a strongly excited coherent vibration within the GME concept. The amplitude of the driven vibration is considered as an order parameter in the phenomenological theory of second order phase transitions. We use this general formulation in order to omit the microscopic details of the driving mechanism. This mechanism is described by some phenomenological pumpparameter which fixes the position of the amplitude. The pumpparameter is assumed to fluctuate around some mean value. These fluctuations model variations of the energy supply into the driven mode and result in



a radial relaxation mechanism of the amplitude. The degeneracy of the equilibrium positions of the complex amplitude with respect to the phase angle is taken into account by introducing the corresponding phase average. Both the radial relaxation and the phase average are important for obtaining the GME kernel in the final form.

Our model is formulated in section 2. Section 3. is devoted to the explicit calculation of the kernel. The properties of exciton propagation in the field of a driven vibration are discussed in section 4.

2. Formulation of the model and GME derivation

We consider a one-dimensional system described by the following Hamiltonian in site representation

$$\hat{H} = \hat{H}_{exc} + \hat{H}_{int}, \quad (1)$$

where

$$\hat{H}_{exc} = \sum_{n,j,m} (\varepsilon_n \delta_{nm}^j + V_{nm}) \hat{a}_n^+ \hat{a}_m \quad (2)$$

and

$$\hat{H}_{int} = \sum_n \Delta_n(t) \hat{a}_n^+ \hat{a}_n. \quad (3)$$

Here \hat{a}_n^+ (\hat{a}_n) are exciton creation (annihilation) operators at molecule n (m), ε_n and V_{nm} are the exciton site energy and transfer matrix element, respectively, and $\Delta_n(t)$ is the shift of the site energy of the exciton due to the interaction with a standing wave excited in the phonon system. The shift $\Delta_n(t)$ is expressed in terms of the complex amplitudes $u^{(\pm)}(t)$ of two waves running in opposite directions as

$$\Delta_n(t) = \Delta_n^{(+)}(t) + \Delta_n^{(-)}(t) \quad (4)$$

where

$$\Delta_n^{(\pm)}(t) = \frac{1}{2} u^{(\pm)}(t) e^{i(qx_n \pm \omega_q t)} + (c.c.). \quad (5)$$

Here q and ω_q are the wave vector and dispersion relation of one running wave, respectively, x_n denotes the site of the n th molecule and the second term in (5) is complex conjugated with respect to the first one. For shortness the exciton-phonon interaction constants

are included into the amplitudes $u^{(\pm)}(t)$ which have the dimension of an energy; in what follows the upper indices (\pm) are dropped when $u^{(+)}$ and $u^{(-)}$ are treated in an equal way. The microscopic mechanism responsible for driving the amplitude u out of its thermal equilibrium position is not specified explicitly, but u is treated as an order parameter in a second order phase transition. In particular, the equilibrium positions of u are given by the minima of the Landau potential $F(u)$

$$F(u) = \frac{1}{2} A |u|^2 + \frac{1}{4} B |u|^4, \quad (6)$$

where A and B are phenomenological constants. The situations $A > 0$ and $A < 0$ (driven state) correspond to the equilibrium positions at $u_0 = 0$ and $u_0^2 = |A|/B$, respectively, as usual $B > 0$. In order to describe the evolution of the amplitude we use a time dependent generalisation of the Landau theory (see, e.g. ^{/12/}). Then $u(t)$ is determined by the equation

$$\frac{du}{dt} = -(A + B|u|^2)u \quad (7)$$

which describes the relaxation of u in the potential (6). In the driven state, which is of interest in what follows, we assume the pumpparameter A to be subjected to stochastic variations modelling the fluctuations of the energy supply into the driven mode. Correspondingly, we set

$$A = A_0 + \xi(t), \quad (8)$$

where A_0 is the mean value of A ($A_0 < 0$) and $\xi(t)$ is a Gaussian white noise process with the correlation function

$$\langle \xi(t) \xi(t') \rangle = 2 \delta(t-t'), \quad (9)$$

Here the brackets $\langle \dots \rangle$ denote the average over the noise. Inserting (8) into (7) one obtains the following stochastic differential equation (SDE)

$$\frac{du}{dt} = -(A_0 + B|u|^2)u + u \cdot \xi(t) \quad (10)$$

with the noise $\xi(t)$ multiplicatively coupled to the amplitude. By introducing white noises in (10) we consider the variations of the amplitude as slow compared to the stochastic fluctuations due to the noise. Eq.(10) is analogous to the equation of motion for the amplitude of a laser field in the case of pumpparameter fluctuations from which the statistical properties of the laser light result (see, e.g. ^{/13/}).

In our case of exciton propagation in the field of a driven wave the average over the amplitude fluctuations is essential to obtain the kernel of the GME, because this average replaces the usual quantum mechanical trace over the bath variables performed with the density matrix.

In order to derive the GME we start from the equation of motion for the one-particle density matrix corresponding to (I)-(3)

$$i \frac{\partial \rho_{ke}}{\partial t} = [\epsilon_k(t) - \epsilon_e(t)] \rho_{ke} + \sum_m (V_{km} \rho_{me} - \rho_{km} V_{me}) \quad (II)$$

where for shortness

$$\epsilon_k(t) = \epsilon_k + \Delta_k(t) \quad (12)$$

was introduced. Representing (II) as

$$\rho_{ke}(t) = i \int_0^t d\tau e^{i \int_0^\tau [\epsilon_e(\tau') - \epsilon_k(\tau')] d\tau'} \sum_m [\rho_{km}(\tau) V_{me} - V_{km} \rho_{me}(\tau)] + \rho_{ke}(t=0) \quad (13)$$

and inserting (13) into the r.h.s. of (11) one obtains for the exciton occupation functions $n_k(t) = \rho_{kk}(t)$ the equation

$$\frac{\partial n_k}{\partial t} = \int_0^t d\tau \sum_{n,m} \left\{ e^{i \int_0^\tau [\epsilon_k(\tau') - \epsilon_m(\tau')] d\tau'} (V_{km} \rho_{mn}(\tau) V_{nk} - V_{mn} \rho_{nk}(\tau) V_{km}) + c.c. \right\} + i \sum_m [V_{mk} \rho_{km}(t=0) - V_{km} \rho_{mk}(t=0)] \quad (14)$$

Now we assume that only nearest neighbour transfer elements $V_{k \pm 1}$ are different from zero and employ diagonal initial conditions $\rho_{km}(T=0) = \delta_{km} n_k(T=0)$ in (14). Then neglecting non-diagonal elements of the form $\rho_{k \pm 2}$ and performing the stochastic average

by decoupling the product of the exponentials and ρ_{kk} in the r.h.s. of (14) (the brackets $\langle \dots \rangle$ are included into the definition of $n_k(t)$) one obtains the following GME

$$\frac{\partial n_k}{\partial t} = \sum_{e=k\pm 1} \int_0^t d\tau K_{ke}(t-\tau) [n_e(\tau) - n_k(\tau)] \quad (15)$$

with the second order kernel in $|V|$

$$K_{ke}(t-\tau) = |V_{ke}|^2 e^{i(\epsilon_k - \epsilon_e)(t-\tau)} \langle e^{i \int_0^\tau [\Delta_k(\tau') - \Delta_e(\tau')] d\tau'} \rangle + c.c. \quad (16)$$

Here the time argument of the kernel is written in the stationary form, i.e. as a function of $t-\tau$. This form results after the complete noise average indicated by the brackets has been performed. We note that the kernel (16) is the classical version of that one arising from the polaron transformation (see section 2.6.3 of ref. ^{1/}). Finally considering a periodic system with equal site energies as well as transfer matrix elements and taking the fluctuations of the amplitudes $u^{(-)}(t)$ and $u^{(+)}(t)$ of the forward and backward tunnelling waves as independent we obtain

$$K(t-\tau) = |V|^2 M^{(+)}(t-\tau) M^{(-)}(t-\tau), \quad (17)$$

where

$$M^{(\pm)}(t-\tau) = \langle \exp \left\{ i \int_\tau^t \left[\frac{1}{2} e^{\pm i \omega_q \tau' + i q x_k} \cdot (1 - e^{i q(x_e - x_k)}) u(\tau') + c.c. \right] d\tau' \right\} \rangle \quad (18)$$

Here $|V|^2$ is the nearest neighbour transfer matrix element $|V_{k1}|^2$ for $l=k\pm 1$ and $x_l - x_k = \pm a$, a being the lattice constant.

3. Calculation of the GME kernel

The explicit calculation of the kernel is a central point of any transport theory based on the GME. In our case the GME kernel is found by performing the average over the fluctuations of the amplitude resulting from the noise in (10). As a consequence of the real parameter fluctuations (8) the phase cancels out of the SDE(10), i.e. the average corresponding to (10) reduces to that over the fluctuations of the

radial part of the amplitude $r = |u|$ around the equilibrium value $|u_0|$. According to the symmetry of the potential (6), however, the equilibrium values u_0 are distributed along the valley of the radius r_0 of the minimum of (6). This continuous symmetry makes it necessary to consider the average over the phases β_0 of the equilibrium positions $u_0 = r_0 e^{i\beta_0}$. As will be seen below, both averages: the radial average as well as that over β_0 are necessary to obtain the kernel of the GME in the stationary form.

In a first step we consider the radial average. Inserting

$$u(t) = r(t) e^{i\beta} \quad (19)$$

into (10) we obtain the SDE for the radial fluctuations. Setting in this equation

$$r(t) = r_0 + x(t), \quad (20)$$

where $x(t)$ is the deviation from the equilibrium value $r_0 = (|A_0|/B)^{1/2}$, and assuming $x(t)$ as well as $\xi(t)$ to be small, we approximate eq.(10) by its linearized version

$$\dot{x} = -2|A_0| x - r_0 \xi(t). \quad (21)$$

Eq.(21) is the SDE for the standard Ornstein - Uhlenbeck process. This process is Gaussian and the correlation function is given by

$$\langle x(t)x(t') \rangle = \Delta_0^2 \cdot e^{-\chi|t-t'|}, \quad (22)$$

where $\Delta_0^2 = 2/4B$ and $\chi = 2|A_0|$. Now inserting eqs. (19), (20) into (18) and performing the average over the Gaussian fluctuations using (22) we find

$$M(t, \tau; \beta) = \exp \left\{ f_1(t-\tau) \cos \left[\frac{\omega_q}{2}(t+\tau) + \beta \right] - f_2(t-\tau) \cos \left[\omega_q(t+\tau) + 2\beta \right] - \frac{2\Delta_0^2}{\omega_q^2 + \chi^2} \sin^2 \left(\frac{qa}{2} \right) \cdot \left[\chi(t-\tau) - \rho(\chi, t-\tau) \right] \right\}. \quad (23)$$

where

$$\rho(\chi, \tau) = \frac{1}{\omega_q^2 + \chi^2} \left[(\chi^2 - \omega_q^2) (1 - e^{-\chi\tau} \cos \omega_q \tau) + 2\chi\omega_q e^{-\chi\tau} \sin \omega_q \tau \right] \quad (24)$$

$$f_1(\tau) = \frac{4it_0}{\omega_q} \sin \frac{qa}{2} \sin \frac{\omega_q \tau}{2} \quad (25)$$

and

$$f_2(\tau) = \frac{4\Delta_0^2}{\omega_q^2 + \chi^2} \sin^2 \frac{qa}{2} \left[\frac{\chi}{\omega_q} \sin \omega_q \tau - \cos \omega_q \tau + e^{-\chi\tau} \right]. \quad (26)$$

In the function $M(t, \tau; \beta)$ we dropped the indices \pm , the expressions for the forward and backward running waves being equal. Besides the stationary form of the time dependence $t-\tau$, the expression (23) is still a function of the separate times t and τ because of the β dependence in the first and second terms. In order to indicate this point we introduced the β argument explicitly into the function $M(t, \tau; \beta)$.

In a second step we now perform the β average by assuming a homogeneous distribution of β over the circle, i.e. we set

$$M(t-\tau) = \frac{1}{2\pi} \int_0^{2\pi} M(t, \tau; \beta) d\beta. \quad (27)$$

This means that we consider an ensemble of excitons in which each exciton starts to propagate in the field of the driven mode with a different initial phase and that these phases are homogeneously distributed. Using the periodicity of the trigonometric functions in the exponential of (23) it is easily seen that the integral in the r.h.s. of (27) is indeed a function of $t-\tau$.

Inserting eqs. (23) to (26) into (27) a representation for $M^{(\pm)}(t-\tau)$ and consequently the kernel (17) results. This representation can be simplified by using that

$$\chi \ll \omega_q \quad (28)$$

which is justified because the variations of the amplitude in (5) are assumed as sufficiently slow compared to the oscillations occurring with the basic frequency ω_q . Furthermore by introducing

$$\Gamma = \frac{4\Delta_0^2 \chi}{\omega_q^2} \sin^2 \frac{qa}{2} \quad (29)$$

and considering the case

$$\Gamma \ll \chi \quad (30)$$

the term connected with the function (26) is seen to be negligible in the integral in (27). Then using the integral representation of the zeroth order Bessel function $J_0(s)$ we obtain

$$K(\tau) = 2|V|^2 \int_0^{\tau} (g \sin(\frac{\omega_0 t}{2})) \exp\left\{-2\Gamma\left[\tau + \frac{1}{\gamma}\left(1 - e^{-\frac{\gamma t}{2}} \cos\frac{\omega_0 t}{2}\right)\right]\right\} dt$$

where in simplifying $\rho(\gamma, \tau)$ the inequality (28) was used and (31)

$$g = \frac{4\tau_0}{\omega_0} \sin \frac{q a}{2}. \quad (32)$$

4. Discussion of Exciton Propagation

The properties of exciton propagation resulting from the explicit form of the kernel (31) depend on the time scales set by the parameters γ and Γ , as well as on the oscillations due to the Bessel function which are governed by the parameter g proportional to the mean amplitude r_0 of the driven vibration according to (32).

First of all we note that for $t \gg \Gamma^{-1}$ the time decaying exponential in (31) dominates. In this time region the exciton propagation becomes diffusion like, i.e. the mean square displacement

$$\langle R^2(t) \rangle = 2a^2 \int_0^t dt_1 \int_0^{t_1} dt_2 K(\tau_2) \quad (33)$$

is proportional to t . Using the inequalities (28) and (30) we obtain the following expression for the diffusion coefficient D

$$D = \frac{a^2 |V|^2}{\Gamma} C(g), \quad (34)$$

where $C(g)$ is given by

$$C(g) = \frac{1}{\pi} \int_0^{\pi} \int_0^{\pi} I_0^2(g \sin x) dx. \quad (35)$$

In particular, for $g < 1$ this reduces to

$$D = \frac{a^2 |V|^2}{\Gamma} \left(1 - \frac{g^2}{4}\right). \quad (36)$$

In the time interval $\gamma^{-1} \ll t \ll \Gamma^{-1}$ the exponential $e^{-\Gamma t}$ in (31) ensuring the long time decay of the kernel is not effective, on the other hand the radial relaxation of the amplitude has completely occurred, i.e. $e^{-\gamma t} \ll 1$. In this interval the kernel (31) is non-decaying and oscillating indicating a coherent component in the exciton propagation. As is seen from the argument of the Bessel function

pronounced oscillations occur for $g \gtrsim 1$. These oscillations modify the exciton transport remarkable. As a consequence the time dependent diffusion coefficient $D(t) = \frac{1}{2} \frac{d}{dt} \langle R^2(t) \rangle$ becomes step like increasing instead of a simple linearly increasing behaviour usually found for coherent transfer.

In the shortest time interval $t \lesssim \gamma^{-1}$ radial relaxation has not occurred yet and the kernel contains additional oscillations due to $\cos \omega_0 t$ in the exponential influencing the coherent transfer.

A full discussion of the properties of exciton propagation must be based on a numerical evaluation of the kernel (31) and the resulting displacement (33) ¹⁴. Here we note the following point: The parameter Γ dividing the region of diffusive motion from that of coherent propagation crucially depends on the relaxational properties of the amplitude as expressed by the parameters in the correlation function (22). In particular, Γ increases if the relaxation time of the radial fluctuations $\gamma^{-1} \sim |A_0|^{-1}$ gets shorter, on the other hand, this effect can be compensated by a decrease of the amplitude of pump parameter fluctuations because of $\Delta_0^2 \sim Z/B$. Hence by changing the characteristics of the driven vibration one can influence the transition from the coherent to diffusive like exciton propagation.

References

1. V.M. Kenkre, in: "Exciton Dynamics in Molecular Crystals and Aggregates". Berlin, Heidelberg, New York: Springer Verlag 1982.
2. P. Reineker, *ibenda*.
3. K. Kassner, P. Reineker, *Z. Phys. B*, 1985, B60, p.87.
4. V. Capak, V. Szees, *phys.stat.sol.(b)*, 1985, 131, p.667.
5. Y. Inaba, *J. Phys. Soc. Jap.*, 1983, 52, p.3144.
6. V.M. Kenkre, T.S. Rahman, *Phys. Lett.*, 1974, 50A, p.170.
7. H. Sumi, *J. Chem. Phys.*, 1977, 67, p.2943.
8. B. Esser, F. Marlow, *phys.stat.sol.(b)*, 1986, 137, p.169.
9. W.E. Bron (Ed.) "Nonequilibrium Phenomena Dynamics", New York, London, Plenum press, 1985.
10. H. Fröhlich, F. Kremer (Eds.) "Coherent Excitations in Biological Systems", Berlin, Heidelberg, New York, Tokyo Springer Verlag, 1983.
11. A. Stöckli, A. Furrer, *Rev. Phys. Appl.* 1984, 19, p.751.

12. M.Luban, in: "Phase Transitions and Critical Phenomena".
v. 5A, London, New York, San Francisco Academic Press, 1976.
13. H.Risken, P. Jung, Phys.Lett., 1984, 103A, p.38.
14. F.Marlow, B.Esser, to be published in phys.stat.sol.(b).

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