сообщения
объединенного
института
ядерных
исследований
дубна

E17-88-248

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ON THE THEORY OF EXCITON TRANSPORT DESCRIBED BY GME

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1988

In recent years several methods have been developed for describing the regime of coherent and incoherent excitation propagation in condensed molecular systems from a unified point of view [1,2]. Among these methods the generalized master equation (GME) concept must be mentioned for formulating the problem in a closed and transparent way [1]. In this concept excitation propagation is determined by the behaviour of the kernel (memory function) and for excitons interacting with a phonon bath kernels were analyzed for different model situations (see, e.g. [1,3]). However, it is evident that by starting from the full quantum mechanical formulation based on the density matrix the explicit calculation of the kernel succeeds in a restricted number of model situations only. Hence the formulation of approximate procedures for evaluating the GME kernel is important. Here such a possible approximation is indicated by subjecting the amplitudes of the phonon modes to a stochastic differential equation (SDE).

We consider exciton propagation in a molecular system and start from the following Hamiltonian in site representation

$$\hat{H} = \sum_{n,m} \left[\left(\varepsilon_n + \Delta_n(t) \right) \delta_{nm} + V_{nm} \right] \hat{a}_n^+ \hat{a}_m , \qquad (1)$$

where $\hat{a}_n^+$ ($\hat{a}_m$) are the 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 the phonon system. Different from the familiar stochastic approaches where $\Delta_n(t)$ is approximated by some stochastic process [4-7] we introduce an eigenmode expansion of the shifts

$$\Delta_n(t) = \sum_q u_q(t) e^{i(q x_n - \omega_q t)} + (c.c.) \qquad (2)$$

and, by assuming slow (compared to the oscillations with the frequency ω_q) variations of the complex amplitudes, subject $u_q(t)$ to a SDE. Proceeding in this way we can qualitatively include into the dynamics of $u_q(t)$.

a) interactions between the phonon modes neglected in the harmonic approximation,

b) interactions of the modes explicitly considered in (2) with yet another bath.

Here for the illustration of this concept we employ a simple linear SDE describing the evolution of the amplitudes $u_q(t)$ and relate the resulting kernel to the quantum-mechanically calculated expression. We set

$$\frac{\partial u}{\partial t} = -\gamma u + \xi(t), \tag{3}$$

where $\xi(t)$ is a complex Gaussian white noise process with a zero mean and the correlation function

$$\langle \xi_i(t)\,\xi_j(t')\rangle = \delta_{ij}\,K\,\delta(t-t')\ , \quad (i,j=1,2)\ . \tag{4}$$

Here ξ_1 (ξ_2) are the real (imaginary) parts of $\xi(t)$ and the brackets denote the average over the noise. Eq.(3) defines a Gaussian process for the amplitude fluctuations and in particular the correlation function is given by

$$\langle u(t)\,u^*(t')\rangle = \frac{K}{\gamma}\, e^{-\gamma|t-t'|}\ . \tag{5}$$

In eqs.(3)-(5) the mode index was dropped for simplicity. In order to investigate the influence of the amplitude dynamics as expressed by (3)-(5) on the exciton propagation we consider the following GME

$$\frac{\partial n_k}{\partial t} = \sum_\ell \int_0^t d\tau\, \mathcal{K}_{k\ell}(t-\tau)\left[n_\ell(\tau) - n_k(\tau)\right] \tag{6}$$

with the kernel

$$\mathcal{K}_{k\ell}(t-\tau) = |V_{k\ell}|^2 e^{i(\varepsilon_k-\varepsilon_\ell)(t-\tau)} \left\langle e^{i\int_\tau^t d\tau'\left[\Delta_k(\tau')-\Delta_\ell(\tau')\right]}\right\rangle + (c.c.). \tag{7}$$

In (6) the l-sum extends over nearest neighbours of k and $\hbar = 1$. Eqs.(6),(7) are easily obtained by using a classical version of the GME derivation based on the polaron transformation (see section 2.6.3 of ref./1/). In eq. (7) the noise average replaces the trace over the bath variables in the full quantum mechanical treatment of the problem. Inserting (2) into (7) and assuming independent modes the average over the stochastic fluctuations of the amplitudes

factorizes. According to the Gaussian character of the fluctuations one obtains

$$\mathcal{K}_{k\ell}(\tau) = |V_{k\ell}|^2 \exp\left\{-\sum_{\bar q} \frac{4K_{\bar q}}{\gamma_{\bar q}(\omega_{\bar q}^2+\gamma_{\bar q}^2)} \sin^2\left[\frac{\bar q(\bar x_k-\bar x_\ell)}{2}\right]\cdot\left[\gamma_{\bar q}\tau - g(\gamma_{\bar q},\tau)\right]\right\}, \tag{8}$$

where

$$g(\gamma_{\bar q},\tau) = \frac{1}{\omega_{\bar q}^2+\gamma_{\bar q}^2}\left[(\gamma_{\bar q}^2+\omega_{\bar q}^2)(1-e^{-\gamma_{\bar q}\tau}\cos\omega_{\bar q}\tau) + 2\gamma_{\bar q}\omega_{\bar q}e^{-\gamma_{\bar q}\tau}\sin\omega_{\bar q}\tau\right]. \tag{9}$$

In calculating (8) we assumed a periodic system with equal site energies $\varepsilon_k = \varepsilon_\ell$. Considering a definite nearest neighbour pair in a cubic lattice for which $x_k - x_l = a$, a being the corresponding primitive lattice vector, and using $\gamma_{\bar q} \ll \omega_{\bar q}$ eqs.(8) and (9) are reduced to

$$\mathcal{K}_{k\ell}(\tau) = |V_{k\ell}|^2 \exp\left\{-\sum_{\bar q} \frac{4K_{\bar q}}{\gamma_{\bar q}\omega_{\bar q}^2} \sin^2\left(\frac{\bar q\bar a}{2}\right)\left[\gamma_{\bar q}\tau + (1-e^{-\gamma_{\bar q}\tau}\cos\omega_{\bar q}\tau)\right]\right\}. \tag{10}$$

Analysing the time dependence of the kernel (10) we note the following points:

a) In the region $\gamma_{\bar q}\tau \ll 1$ the kernel is oscillating. This indicates coherent exciton propagation. In this time region eq. (10) is seen to be of the same functional form as the GME kernel resulting from the polaron transformation (section 2.6.3 of ref./1/), if in the latter expression the high temperature approximation is performed by setting for the phonon occupation function $N_{\bar q} \approx (k_B T/\omega_{\bar q}) \gg 1$. One can use this correspondence to relate the strength of the stochastic sources to the temperature of a bath. One obtains $K_{\bar q} = \gamma_{\bar q}\omega_{\bar q}|X_{\bar q}|^2 k_B T$. $X_{\bar q}$ being an exciton phonon coupling function.

b) In the region $\Gamma\tau \gg 1$, where

$$\Gamma = \sum_{\bar q} \frac{4K_{\bar q}}{\omega_{\bar q}^2}\sin^2\left(\frac{\bar q\bar a}{2}\right)\ , \tag{11}$$

the kernel is exponentially decaying indicating the transition from coherent to diffusion like exciton propagation (we assumed $\Gamma \ll \gamma$). In particular, the diffusion constant D is given by

$$D = \frac{z a^2 |V|^2}{\Gamma}, \tag{12}$$

where z is the number of nearest neighbours. We note that in the full quantum mechanical treatment the calculation of the decay constant of the kernel is a rather subtle problem. Here the decay constant is simple related to the strength of the stochastic sources $K_{\bar{q}}$. Using the correspondence with a bath of temperature T established in a) we can find the temperature dependence of Γ as $\Gamma \sim T$.

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Received by Publishing Department
on April 15, 1988.

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К теории экситонного транспорта описываемого обобщенным кинетическим уравнением

На основе обобщенного кинетического уравнения рассматривается экситонный транспорт в присутствии фононов. Предлагается метод для вычисления ядра кинетического уравнения путем введения стохастических флуктуаций в амплитудах фононных мод. Стохастические флуктуации связываются с температурой термостата. Анализируется временная зависимость ядра и указываются режимы когерентного и диффузионного распространения экситонов.

Работа выполнена в Лаборатории теоретической физики ОИЯИ.

Сообщение Объединенного института ядерных исследований. Дубна 1988

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On the Theory of Exciton Transport Described by GME

Using the generalized master equation (GME) the propagation of excitons in the presence of phonons is considered. An approach for evaluating the kernel of the GME is proposed by subjecting the amplitudes of the phonon modes to stochastic variations. The stochastic variations are related to the temperature of a heat bath. The time dependence of the kernel is analyzed and the regions of coherent and diffusive exciton propagation are indicated.

The investigation has been performed at the Laboratory of Theoretical Physics, JINR.

Communication of the Joint Institute for Nuclear Research. Dubna 1988