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EXCITATION PROPAGATION IN THE PRESENCE OF A DRIVEN AND KICKED VIBRATION

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Распространение возбуждений в присутствии сильно возбужденной и периодически возмущенной волны

Рассматривается распространение экситонов, взаимодействующих с сильно возбужденной и периодически возмущенной волной, с использованием обобщенного кинетического уравнения. Амплитуда колебаний описывается с помощью нелинейного уравнения, содержащего член, который моделирует периодическое возмущение. Устанавливается связь между ядром кинетического уравнения и дискретным отображением, описывающим динамику колебаний. Эта связь используется для обсуждения поведения ядра и результирующего экситонного движения, следующего из периодических и хаотических решений дискретного отображения.

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Excitation Propagation in the Presence of a Driven and Kicked Vibration

The propagation of excitons interacting with a driven and kicked vibration is considered using the generalized master equation (GME) approach. The amplitude of the vibration is described by a nonlinear evolution equation with a kicking term modelling a periodic perturbation. The connection between the GME kernel (memory function) and a map describing the dynamics of the vibration is established. This connection is used to discuss the behaviour of the GME kernel and resulting exciton motion following from the periodic and chaotic solutions of the map.

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

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I. Introduotion

The theory of exciton propagation in the presenoe of an equilibrium bath of phonons has been intensively developed in the past years [1-3]. Among the approaches the generalized master equation (GME) must be mentioned for treating such important points as the coherent an incoherent exciton motion from a unified point in view[1]. The properties of exciton motion oan however be of oonsiderable interest also in a nonequilibrium situation, where by a driving mechanism some vibrational states are selectively exoited. Thus, recently new methods for the generation and detection of phonons have been developed[4,5] and hence it might be of oonsiderable interest to investigate the properties of exciton propagation in a non-equilibrium phonon field with controlled parameters. Besides that transport in the presenoe of non-thermal vibrations seems to be of importance for moleoular aggregates relevant in biological systems [6]. This paper addresses the problem of exciton propagation in the field of a driven vibration described in classical terms within the GME oonoept. Omitting the details of the driving meohanism the amplitude of the vibration is described by a nonlinear equation as in a time dependent Landau theory. In a previous paper this approaoh was used to consider the influence of noise [7]. Here the amplitude is assumed to be periodically kicked. As is well known a periodio perturbation of a nonlinear system can generate solutions of different types which beoomes particularly transparent by oonsidering disorete mappings suoh as the standard map [8]. In the model of this paper the vibration is related to the dissipative standard map[9]. The vibration can display periodio or chaotio solutions and oorrespondingly different behaviours of the memory funotion result. The oonneotion between the different solutions of mapping for the vibrational phase (sine - map) and the memory funotion of the GME is oonsidered in detail. Another point addressed here is the averaging over vibrational states in the GME kernel. In the oase of ohaotio solutions the vibration aots effeotively like a noise produoed by a bath on the exoiton motion. Then, by introduoing an ensemble of vibrational trajeotories and the oorresponding average, an explicit expression for the deoay of the memory funotion oan be derived.

The model is presented in section 2. In section 3 the connection between different vibrational solutions and the memory function is discussed. The section 4 is devoted to the calculation of the decay parameter of the memory function for chaotic solutions.

2. Formulation of the Model

The excitons are described by the following Hamiltonian in site representation

$$\hat{H}_{exc} = \sum_{n,m}\left[\epsilon_n(t)\delta_{nm} + V_{nm}\right]\hat{a}_n^{+}\hat{a}_m \quad , \tag{1}$$

where

$$\epsilon_n(t) = \varepsilon_n + \Delta_n(t) \quad . \tag{2}$$

Here $\hat{a}_n^{+}(\hat{a}_m)$ are creation (annihilation) operators at molecule n(m), ε_n and V_{nm} are the exciton site energy and transfer matrix element, respectively. The shift $\Delta_n(t)$ of the site energy represents a diagonal exciton - phonon coupling due to the interaction of the exciton with a non-equilibtium vibration excited in the phonon system

$$\Delta_n(t) = C e^{iqx_n} u(t) + (c.c.) \quad , \tag{3}$$

Here u(t) is the phonon amplitude and C an interaction constant.

The mechanism for driving the non-equilibrium vibration is not specified explicitly but u is subjected to the following phenomenological nonlinear equation

$$\frac{\partial u}{\partial t} = -(A + B|u|^2)u + F(t), \tag{4}$$

where $A = A_1 + iA_2$ and $B = B_1 + iB_2$ are constants and the function F(t) describes the influence of a periodic kicking on the amplitude. In the absence of kicking eq. (4) corresponds to a time dependent Landau theory, i.e. the complex amplitude u is treated as an order parameter in a second order phase transition. In particular the sign of A_1 fixes the stationary value of $|u_0|$. In what follows the driven state is of interest for which $A_1 < 0$, $I_0 \equiv |u_0|^2 = |A_1|/B_1$ and for F(t) = 0 eq. (4) displays the stationary solution $u(t) = u_0\exp(-i\omega_0 t)$ with the frequency $\omega_0 = A_2 + B_2 I_0$. The influence of kicking in (4) is to push the amplitude out of $u_0(t)$. Then different forms of time dependences of u(t) result as will be

employed below. For F(t) it is sufficient to consider the simplest form consisting of periodically (after T) repeated δ-pulses

$$F(t) = \frac{\varepsilon}{2}\sqrt{I_0}\, e^{i\delta}\sum_{\nu=1}^{\infty}\delta(t-\nu T) \quad . \tag{5}$$

Here the prefactor was chosen in a convenient form, ε is a dimensionless parameter and δ a phase angle. The kicking represented by the δ-pulses can be due to a periodic external source but is also an approximate form for the influence on u of anharmonic interactions in the phonon system/9/.

Passing to action - angle variables

$$u(t) = \sqrt{I(t)}\, e^{i\theta(t)} \tag{6}$$

and inserting (6) into (4) one obtains by separating real and imaginary parts

$$\dot{I} = -2B_1 I(I - I_0) + 2\sqrt{I}\,\mathrm{Re}\, e^{i\theta(t)} F(t) \tag{7}$$

and

$$\dot{\theta} = A_2 + B_2 I - \frac{1}{\sqrt{I}}\,\mathrm{Im}\, e^{i\theta(t)} F(t). \tag{8}$$

In (7),(8) a simplification is made by linearizing the first term of (7) $B_1 I \cong B_1 I_0 = |A_1|$, setting $I \cong I_0$ in the second term of (7) and omitting the last term connected with the kicking in (8) (a justification for the latter procedure is that the influence of F(t) in (7) is proportional to $I_0^{1/2}$ whereas in (8) it is to $I_0^{-1/2}$, i.e. in the strongly driven state where I_0 is sufficiently large the influence of the kicking in (8) becomes smaller than in (7)). This simplification allows one to make contact with the discrete maps in the next section. One obtains

$$\dot{I} = -2|A_1|(I - I_0) + \varepsilon I_0 \cos(\theta + \delta)\sum_{\nu=1}^{\infty}\delta(t - \nu T) \tag{9}$$

and

$$\dot{\theta} = \omega(I), \tag{10}$$

where

$$\omega(I) = A_2 + B_2 I. \tag{11}$$

Starting from the standard equation of motion for the one particle exciton density matrix $\rho_{km}(t)$, assuming nearest neighbour transfer elements $V_{kk\pm1}$ and diagonal initial conditions $\rho_{km}(t=0) = \delta_{km}\, n_k$ one obtains for the site occupation $n_k(t)$ the GME

$$\frac{\partial n_k}{\partial t} = \sum_m \int_0^t d\tau\, \mathcal{K}_{km}(t,\tau)\left[n_m(\tau) - n_k(\tau)\right], \tag{12}$$

in which we use the second order kernel

$$\mathcal{K}_{km}(t,\tau) = |V_{km}|^2 \exp\left\{ i\int_\tau^t dt' \left[\epsilon_k(t') - \epsilon_m(t')\right]\right\} + (c.c.) \tag{13}$$

corresponding to the neglection of the non-diagonal elements of the form $\rho_{kk\pm2}$. In particular, the kernel (13) becomes exact for a two site problem (k=1,2), i.e. a dimer. The kernel (13) is convenient for the discussion of the different time dependences following from a map, because of the simple connection to the vibration via $\Delta_k(t)$. In (13) $\mathcal{K}_{km}$ is still a function of the separate time arguments, transforming into the stationary form as a function of $t-\tau$ after an appropriate ensemble average is performed.

3. Memory Function for Different Vibrational Solutions

We now establish the connection between the memory function and the map following from eqs. (9), (10) for the action- angle variables of the vibration. Inserting eqs. (2),(3) and (6) into (13) one obtains $(\varepsilon_k = \varepsilon_m)$

$$\mathcal{K}_{mm\pm1}(t,\tau) = |V_{mm\pm1}|^2 e^{i[f_m^\pm(q)S(t,\tau) + (c.c.)]} + (c.c.), \tag{14}$$

where

$$f_m^\pm(q) = C e^{iqx_m}\left(e^{\pm iqa} - 1\right), \tag{15}$$

$$S(t,\tau) = \int_\tau^t dt' \sqrt{I(t')}\, e^{i\theta(t')} \tag{16}$$

and a is the distance between the molecules. According to (9) and (10) in the time interval between two successive kicks, $\nu T + 0 < t < (\nu+1)T + 0$ the evolution of the action and phase is given by

$$I(t) = I_0 + \left(I_\nu - I_0 + \varepsilon I_0 \cos(\theta + \delta)\right) e^{-2|A_1|(t-\nu T)} \tag{17}$$

and

$$\theta(t) = \theta_\nu + \omega_0(t-\nu T) + \frac{B_2}{2|A_1|}\left(I_\nu - I_0 + \varepsilon I_0 \cos(\theta_\nu + \delta)\right) \times \left(1 - e^{-2|A_1|(t-\nu T)}\right), \tag{18}$$

where $I_\nu = I(\nu T - 0)$ and $\theta = \theta(\nu T - 0)$ refer to the values of $I(t), \theta(t)$ immediately before the ν th kick, respectively, $\nu = 1, 2, ..$. Setting $t = (\nu+1)T - 0$ in (17),(18) one obtains the dissipative standard map /9/ . We consider a further simplification reducing the dynamics of the two dimensional system (17),(18) to a one dimensional for the phase evolution θ . Assuming $\varepsilon \ll 1$ and the following relations between the parameters of the model

$$|A_1| \gg \frac{1}{T} \tag{19}$$

$$\frac{B_2}{B_1} > \frac{1}{\varepsilon} \gg 1 \tag{20}$$

it follows from (9) that the action change due to a single kick is small compared to I_0. Then, according to (19), action changes cannot accumulate because the interval between the kicks T is large compared to the action relaxation time $|A_1|^{-1}$ in (17), i.e. the action completely relaxes to its stationary value I_0 in a time of order $|A_1|^{-1}$ after each kick. Then we have $I_{\nu+1} \cong I_\nu \cong I_0$. However, the influence of the action changes on the phase evolution is not small because of the second inequality (20), which is equivalent to $(\varepsilon B_2 I_0 / |A_1|) \gg 1$ in (18). Now inserting (17), (18) into (16) and neglecting the action changes one obtains

$$S(t,\tau) = \sum_{\nu=\nu_1}^{\nu_2} S'_\nu + \Delta S'(t,\tau), \tag{21}$$

where

$$S'_\nu = \sqrt{I_0} \int_{\nu T - 0}^{(\nu+1)T - 0} dt'\, e^{i\theta(t')} . \tag{22}$$

Here the t' - integration was divided in intervals between the kicks and $\nu_1 = ([\tau/T]+1)T-0$, $\nu_2=[t/T]-0$ with [ ] denoting the integer part, indicate the kick numbers at the beginning and the end of the (τ,t) interval. The quantity $\Delta S'(t,\tau)$ contains the rest of the integral of (16) which is not covered by the sum in (21). The phase evolution in the integration interval of (22) is

$$\Theta(t) = \Theta_\nu + \omega_0(t-\nu T) + \varepsilon \frac{B_2}{2B_1}\left(1-e^{-2|A_1|(t-\nu T)}\right)\cos(\Theta_\nu+\delta) \qquad (23)$$

For $t=(\nu+1)T-0$ and the choice $\delta=-\pi/2$ one obtains from (23)

$$\Theta_{\nu+1} = \Theta_\nu + \omega_0 T + \lambda\sin\Theta_\nu , \qquad (24)$$

where

$$\lambda = \varepsilon\frac{B_2}{2B_1}\left(1-e^{-2|A_1|T}\right) . \qquad (25)$$

The map (24) is known as the sine transformation /9/ or in an extended Θ-scheme (dividing the Θ-line into cells $2\pi\nu<\Theta<2\pi(\nu+1)$, $-\infty<\nu<+\infty$) as the climbing sine map /10/. The choice $\delta=-\pi/2$ was taken to obtain the connection of S_ν with this map the solution structure of which is well investigated. Inserting (23) into (22) one obtains

$$S_\nu = \sqrt{I_0'}\, e^{i\Theta_\nu}\int_0^T dt\, e^{i\omega_0 t + i\lambda\alpha(t)\sin\Theta_\nu} \quad , \qquad (26)$$

where

$$\alpha(t) = \frac{1-e^{-2|A_1|t}}{1-e^{-2|A_1|T}} . \qquad (27)$$

Eqs. (26),(27) express the quantities S'_ν by the solutions of the map equation (24). The different forms of the solutions of (24) are connected with the kernel of the GME (14) via $S'(t,\tau)$. In order to discuss this connection it is sufficient to consider K_{km} at the discrete times $t=\nu_1 T-0$ and $\tau=\nu_2 T-0$ whereby $\Delta S'=0$ in the exponential of (21).

The solution structure of the map (24) is characterized by periodic and chaotic solutions /9,10/. The two cases are discussed separately.

A Periodic solutions

Setting $\lambda\sin\Theta_1=2\pi m$ and assuming $\omega_0 T=2\pi k$ in (24), m and k being integers, one has for all ν, $\Theta_\nu=\Theta_1=\Theta_f$ (taking Θ mod 2π) i.e. a period 1 solution[1]. The region of stability of this solution is indicated in /10/. The corresponding value of is a complex constant independent of ν

$$S_\nu = S'(\Theta_f) = S_f \quad . \qquad (28)$$

Inserting (28) into (21) one obtains from (14)

$$K(t=\nu_2 T, \tau=\nu_1 T) = 2|V|^2 \,\mathrm{Re}\, e^{i(\nu_2-\nu_1)\delta(q)} , \qquad (29)$$

where

$$\delta(q) = f(q)S'_f + (c.c.) \quad . \qquad (30)$$

Eqs. (29) and (30) express the kernel as the projection on the real axis of a vector rotating in the complex plane (unnecessary indices at K are suppressed in what follows). Each interval T is connected with the rotation angle $\delta(q)$ and the total angle of rotation is proportional to the number of kicks in the (τ,t) interval.

The behaviour of the kernel for a period p solution $\Theta_1,\Theta_2\ldots\Theta_p$ of the map (24) follows from a straightforward generalization: Instead of one S'_f in (28) one has to take account of p different values $S'_1, S'_2 \ldots S'_p$ and corresponding rotation angles $\delta_1,\delta_2\ldots\delta_p$. The rotation of the vector connected with the kernel proceeds through $\delta_1,\delta_2\ldots\delta_p$ and is repeated after p steps.

B Chaotic solutions

According to (20) the nonlinearity parameter of the map $\lambda > 1$ and λ increases with an increasing ratio B_2/B_1 in the left hand side of (20). Then on the Θ-line the periodic solutions of (24)

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1) In the extended scheme this solution is referred to as a period 1 running solution /10/, because the iterates Θ_ν run over different cells. Here the relevant quantities are S_ν, eq. (26), and depend on trigonometric functions of Θ_ν, i.e. the running solutions are automatically projected on the reduced scheme and can be taken modulo 2π .

can be viewed as contained in small islands surrounded by a "stochastic sea" of chaotic solutions, the region occupied by the chaotic solutions increasing with increasing λ. The decay of the phase correlations in the chaotic solutions is given by the correlation function

$$\langle e^{i(r\theta_{\nu_2}-s\theta_{\nu_1})}\rangle_\theta \sim e^{i(\nu_2-\nu_1)r\omega_0 T-(\nu_2-\nu_1)T/\tau_c} \tag{31}$$

with the correlation time

$$\tau_c = T/\ln\lambda, \tag{32}$$

where $\langle\ldots\rangle_\theta$ denotes the average over a region of initial conditions in the "chaotic sea". The relation (31) is derived by repeatedly using the map equation (24) and applying expansions into Bessel functions (see /9/).

The kernel is again representable as a vector rotating in the complex plane, however, now one has an infinite sequence of S_1, S_2,... and corresponding angles $\delta_1, \delta_2 \ldots$. The rotations become uncorrelated after a few steps and considering an ensemble of starting positions of the rotating vector corresponding to the initial conditions of the chaotic trajectories one gets a decaying memory by averaging over different rotation histories.

Summarizing both cases and taking account of the general relation between the memory function and the character of exciton motion /1/ one finds that for periodic vibrational solutions the kernel represents a non-decaying oscillating memory and correspondingly coherent exciton propagation results. On the other hand for chaotic solutions and averaging over different vibrational trajectories a decaying memory is obtained, i.e. in the long time limit incoherent exciton propagation is expected. Hence by changing the control parameter and/or initial conditions a transition from incoherent to coherent exciton propagation is possible. It must be stressed, however, that at the microscopic level the kernel is purely oscillating in both cases, i.e. a summation over many kernels containing chaotic vibrational trajectories is necessary to obtain a decaying memory. This summation is just the familiar coarsegraining procedure by which many vibrational states are attached to a given exciton state.

4. Decay of the Stationary Memory Function for Chaotic Solutions

We now consider the calculation of the stationary kernel by averaging over chaotic solutions with different initial phases, i.e. the stationary kernel $\mathcal{K}(t-\tau)$ is given by

$$\mathcal{K}(t-\tau) = \langle \mathcal{K}(t,\tau)\rangle_{\theta_1}, \tag{33}$$

where $\mathcal{K}(t,\tau)$ is represented by (14) and $\langle\ldots\rangle_{\theta_1}$ denotes the average over initial phases of chaotic trajectories. Using a standard expansion into Bessel functions of the exponential of the sine in (26) one obtains

$$S_\nu = \sum_{\ell=-\infty}^{+\infty} b_\ell e^{i\ell\theta_\nu}, \tag{34}$$

where

$$b_\ell = \sqrt{I_0}\int_0^T dt\, e^{i\omega_0 T} J_{\ell-1}(\lambda x(t)) \tag{35}$$

and J_ℓ are the expansion coefficients and the Bessel function of lth order, respectively. Inserting (34) into eqs. (14),(21) one finds

$$\mathcal{K}(t-\tau) \sim 2|V|^2 \mathrm{Re}\langle \exp\{i[\sum_{\ell=-\infty}^{+\infty}\sum_{\nu=\nu_1}^{\nu_2}(f(q)b_\ell e^{i\ell\theta_\nu} + (c.c.))]\}\rangle_{\theta_1}. \tag{36}$$

Here the meaning of τ and t is as in eq. (26), i.e., they are taken at the discrete times $\tau=\nu_1 T$ and $t=\nu_2 T$, respectively. The variation of τ and t within the intervals between the kicks is easily seen to result in additional oscillations connected with the ΔS term in (21), which do, however, not contribute to the decay of the memory function due to kicking. In order to indicate that these oscillations were omitted the proportionality sign was set in (36).

The average in (36) is expressed by the correlation function (31) using a cumulant expansion up to second order in (36), i.e.

$$\mathcal{K}(t-\tau) \sim 2|V|^2 \exp\Big\{-\frac{1}{2}\sum_{l,l'}\sum_{\nu,\nu'} \big\langle [f(q) b_l e^{il\theta_\nu} + (c.c.)] \cdot [f(q) b_{l'} e^{il'\theta_{\nu'}} + (c.c.)] \big\rangle_{\theta_1} \Big\}. \tag{37}$$

(The contribution of the first cumulate vanishes, $\langle e^{i\theta_\nu}\rangle_{\theta_1} = 0$). Passing in the ν, ν' sums of (37) to the new variables ν, $\varkappa = \nu - \nu'$ using (31) and assuming a sufficiently large number of kicks $\nu_2 - \nu_1 \gg 1$ between τ and t one finds

$$\mathcal{K}(t-\tau) \sim 2|V|^2 \exp\Big\{-2(\nu_2-\nu_1)\sum_{\varkappa} e^{-\varkappa T/\tau_c} \cdot \sum_{l,l'}\big[A_{ll'} e^{il\omega_0 \varkappa T} + A_{l'l} e^{-il\omega_0\varkappa T}\big]\Big\}, \tag{38}$$

where

$$A_{ll'} = [f(q)]^2 b_l b_{-l'} + [f^*(q)]^2 b^*_{-l} b^*_{l'} + |f(q)|^2 (b_l b^*_{l'} + b^*_{-l} b^*_{-l'}). \tag{39}$$

Now setting $\nu_2 - \nu_1 = (t-\tau)/T$ and performing the $\varkappa$-sum one finally obtains

$$\mathcal{K}(t-\tau) \sim 2|V|^2 \exp[-\Gamma(t-\tau)], \tag{40}$$

where

$$\Gamma = \frac{2}{T}\sum_{l,l'}\left[\frac{A_{ll'}}{1-e^{-(T/\tau_c)+il\omega_0 T}} + (c.c.)\right] . \tag{41}$$

The kernel (40) is of the familiar form of an exponentially decaying memory function, the decay being described by the parameter Γ . The influence of a parameter describing an exponential decay of the kernel on the various characteristics of exciton propagation is discussed in /1/ and need not to be repeated here. In contrast to the standard theory of interaction of excitons with an equilibrium bath of phonons, however, in the present case the "bath" is due to chaotic trajectories of a nonlinear vibration interacting with the

excitons via a noise like modulation of the site energies. The parameter Γ , eq. (41), contains the characteristics of the nonlinear kicked vibration explicitly.

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