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1993 J. Phys.: Condens. Matter 5 4467

(http://iopscience.iop.org/0953-8984/5/26/017)

J. Phys.: Condens. Matter 5 (1993) 4467–4474. Printed in the UK

Influence of quantum fluctuations on solitary-wave acoustic polaron motion

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Received 19 February 1993

Abstract. The theory of Wilson's solitary-wave acoustic polaron motion is generalized to include the effects of quantum fluctuations and the non-adiabatic behaviour of the electron–phonon coupling. The polaron dynamics are described quantum mechanically in terms of master equations for the electronic variables. As a final result, it emerges that due to the considered quantum effects for $v \ll c$ (v = polaron velocity, c = sound velocity) the polaron behaviour is determined by the well-known semiclassical non-linear Schrödinger equation, whereas for $v < c$ the polaron motion is overdamped but shows by no means a divergent behaviour as obtained in semiclassical theories. In addition, for $v = c$ the phonon cloud around the electron disappears and the electron motion becomes diffusive.

1. Introduction

In one-dimensional elecron–phonon systems the soliton concept has been successfully applied to explain charge and information transfer processes. Especially in polymers like, e.g., polyacetylene (PA) and polydiacetylene (PDA) solitary excitations as polarons and solitons dominate the transport properties instead of electrons and holes [1, 2, 3, 4, 5]. Within this concept the temperature dependence of the soliton diffusion constant as derived by Maki [6, 7] is in agreement with experimental data obtained for PA [8]. Furthermore, measured ultrahigh mobilities in PDA [2] are explained by the existence of polarons. In these transport models the solitary excitation is always believed to be a stable quantity. The interaction with phonons, however, can lead to a diffusive behaviour of the motion [6, 7, 9]. Results which are similar to the ones obtained in polymer systems can also be found in other soliton bearing systems, like, e.g., information transfer models in biological systems [10] or solitary polaron motion in molecular crystals [11, 12]. Polarons in molecular crystals are found to be stable against interactions with acoustic and optical phonons which was confirmed by solving a Boltzmann equation for polaron phonon interactions which were derived in a microscopic model. On the other hand, damping effects on solitons in biological systems were treated in turns of phenomenological damping constants by Davydov [10]. This model yields reasonable results only in the limit of small soliton velocities compared to the velocity of sound. In the case of large soliton velocities Davydov argued that the soliton solutions become unstable with respect to the decay into an exciton. The same problem was discussed by Wilson [2], where the model of the solitary-wave acoustic polaron was successful in explaining high carrier mobilities at low fields. However, in this model the polaron solution diverges as the polaron velocity approaches the velocity of sound. Therefore one is led to the same conclusion as in Davydov's theory namely that the polaron becomes unstable against the decay into electronic conduction band states.

0953-8984/93/264467+08$07.50

Campbell and Bishop [13] gave a qualitative estimate of the stability of different solitary excitations in PA. The calculations are based on the continuum version of the Su–Schrieffer–Heeger (SSH) model [3, 4] introduced by Takayama, Lin Liu and Maki (TLM) [14]. The kink-like soliton solutions are expected to be stable against quantum fluctuations due to their topological stability. On the other hand, two-particle excitations like polarons and bipolarons do not have this topological stability. Therefore it is argued that the adiabatic mean-field solutions derived from the TLM model might be unstable against quantum fluctuations for the case of polaron excitations also.

In this article we investigate the influence of quantum fluctuations on polaron-like excitations using the discrete SSH Hamiltonian. The basic problem lies in the formulation of equations of motion for the electron–phonon system. The use of adiabatic mean-field equations leads to a divergent polaron solution as the polaron velocity approaches the velocity of sound. Therefore, these equations are not applicable to describe the effect of quantum fluctuations being of importance only in the limit of high velocities.

In section 2 we show, that the polaron solution can be derived from the equations of motion for the first moments of the relevant operators. The fluctuations are described in section 3 by the equations of motion for the second moments. As the polaron velocity approaches the velocity of sound, it turns out that the electronic system can be described by the equations for the second moments alone. In these equations no divergencies appear.

2. Equations of motion for the first moments

We start from the SSH Hamiltonian [4]

$$H = \sum_n (J - \alpha(u_{n+1} - u_n))\,[c_{n+1}^+ c_n + \mathrm{HC}] + \frac{K}{2}\sum_n (u_{n+1} - u_n)^2 + \frac{1}{2M}\sum_n p_n^2 \tag{1}$$

which, as shown by Wilson [2], is also suited to describe acoustic polarons in PDA, although the SSH Hamiltonian was originally formulated for trans-PA. When applying (1) to PDA the definition of the unit cell changes. In PA the unit cell consits of two C–H groups whereas in the case of PDA four carbon atoms form the unit cell.

The displacements u_n and momenta p_n obey the commutation rule ($\hbar = 1$)

$$[u_n, p_m]_- = \mathrm{i}\delta_{n,m} \tag{2}$$

and c_n^+ (c_n) creates (annihilates) an electron at site n. The Fermi commutation rule reads

$$\{c_n^+, c_m\}_+ = \delta_{n,m}. \tag{3}$$

Using the Heisenberg equation of motion

$$-\mathrm{i}\partial_t \hat{A} = [H, \hat{A}] \tag{4}$$

the following master equations for the expection values of phonon and electron operators (denoted by $\langle c_n \rangle$) are obtained

$$\partial_t u_n = (1/M) p_n \tag{5}$$

$$\partial_t p_n = K[u_{n+1} + u_{n-1} - 2u_n] + \alpha[\langle c_n^+ c_{n-1}\rangle - \langle c_{n+1}^+ c_n\rangle + \mathrm{HC}] \tag{6}$$

$$\partial_t \langle c_n \rangle = -\mathrm{i}\,\{[J - \alpha(u_n - u_{n-1})]\langle c_{n-1}\rangle + [J - \alpha(u_{n+1} - u_n)]\langle c_{n-1}\rangle\}. \tag{7}$$

We now solve equations (5)–(7) in a first step. Therefore we change the spacial difference equations into differential equations by applying the continuum approximation up to second order in the derivatives, e.g.

$$u_{n\pm 1} = u_n \pm \partial_n u_n + \tfrac{1}{2}\partial_{nn} u_n. \tag{8}$$

Further we assume the electronic expectation values $\langle c_n^+ c_{n+1}\rangle$ to factorize into

$$\langle c_n^+ c_m\rangle = \langle c_n^+\rangle\langle c_m\rangle. \tag{9}$$

This implies that the electron dynamics has coherent character. As long as the fluctuations are small the approximation (9) is justified.

From (5)–(7) we obtain

$$\left(\partial_{nn} - (1/c^2)\partial_{tt}\right) u_n = (2\alpha/K)\partial_n|\langle c_n\rangle|^2 \tag{10}$$

$$\partial_t\langle c_n\rangle = -\mathrm{i}J\left(2c_n + \partial_{nn}\langle c_n\rangle\right) + 2\mathrm{i}\alpha\langle c_n\rangle\partial_n u_n \tag{11}$$

where

$$c = \frac{K}{M}$$

is the velocity of sound. As an *ansatz* we now assume all variables in (10) and (11) to depend on t and n in the form

$$\tau = t - n/v \tag{12}$$

which means that we look for pulse-like solutions of (10) and (11), where v is the pulse velocity. This yields

$$\left(1 - v^2/c^2\right) q_n = (2\alpha/K)|\langle c_n\rangle|^2 \tag{13}$$

$$\partial_t\langle c_n\rangle = -\mathrm{i}J\left(2c_n + \partial_{nn}\langle c_n\rangle\right) + 2\mathrm{i}\alpha\langle c_n\rangle q_n \tag{14}$$

where q_n is defined as

$$q_n = \partial_n u_n. \tag{15}$$

Inserting (13) into (14) leads to

$$\partial_t\langle c_n\rangle = -\mathrm{i}J\left(2c_n + \partial_{nn} c_n\right) + 2\mathrm{i}A(v)\langle c_n\rangle|\langle c_n\rangle|^2 \tag{16}$$

where

$$A(v) = 2(\alpha^2/K)/(1 - v^2/c^2). \tag{17}$$

This equation corresponds exactly to the non-linear Schrödinger equation obtained by Wilson [2] for the description of the polaron motion in PDA and to the equation for the excitation transfer in biological systems as derived by Davydov [10]. The solution of (16) is the so-called Davydov soliton which is given by

$$\langle c(n-vt)\rangle = \sqrt{A(v)/2J}\exp[\mathrm{i}(kn-(\Omega-kv-2J)t)] \times \operatorname{sech}[(A(v)/2J)(n-vt)] \tag{18}$$

with

$$\Omega = -J(k^2 - A^2(v)/J^2) \tag{19}$$

$$k = v/2J. \tag{20}$$

In the limiting case $v \to c$ the solitary-wave solution (18) diverges. This divergent behaviour was used by Wilson [2] for an estimate of the maximum mobility in PDA. He claimed that when the polaron is accelerated by an electric field its spatial extension can shrink with increasing velocity but only up to the extension of one lattice constant. This argumentation leads to a maximum mobility of 735 $\mathrm{m^2\ V^{-1}\ s^{-1}}$. In this limit, however, the continuum approximation (8) is not valid. Furthermore, the factorization procedure (9) can no longer be applied to the electronic variables because, for fast solitons, quantum fluctuations, which are reponsible for the change to an incoherent behaviour, cannot be neglected. Therefore the equations of motion for the first moments are no longer suited to describe the electron–phonon dynamics and the equations of motion for the second moments have to be taken into account.

3. Equations of motion for the second moments

The divergent behaviour of (16) arises due to the factorization procedure (9) of the electronic expection values and the subsequent elimination of the lattice degrees of freedom by inserting (13) into (14). To overcome this difficulty we do not apply the factorization of (9) to (6). Instead we derive the master equations for the second moments of the electronic variables. Since the polaron solution (18) for the amplitudes diverges as v approaches c, we assume in the following the first moments $\langle c_n^+\rangle$ and $\langle c_n\rangle$ to be zero and describe the electron dynamics by the second moments $\langle c_n^+ c_n\rangle$. The resulting equations are rather complex since, e.g. equations of motion for the variable $\langle c_n^+ c_n\rangle$ contain terms of the form $\langle c_n^+ c_{n+i}\rangle$, $i = \pm 1, \pm 2$ and also second-order moments of the phonon variables. Evaluating these equations leads to higher-order terms in the electron coordinates and so on. In order to find a solution for this set of equations we truncate the hierarchy by only considering nearest- and next-nearest-neighbour interactions in the electron system. Due to the complexity of the equations on a first view, an analytical approach seems to be impossible. However, as seen from (5) and (6), in the equations of motion for the first moments of the phonon variables no dissipative or fluctuation terms appear. This offers the possibility to describe the phonons by coherent states which means that the phonon system is determined by the first-moment equations, whereas the electrons are described by second-moment equations. Using (4) and defining

$$N_n = \langle c_n^+ c_n\rangle \tag{21}$$

$$D_n^\pm = \langle c_n^+ c_{n+1}\rangle \pm \mathrm{HC} \tag{22}$$

$$T_n^\pm = \langle c_{n-1}^+ c_{n+1}\rangle \pm \mathrm{HC} \tag{23}$$

we obtain

$$i\partial_t N_n = [J - \alpha(u_{n+1} - u_n)]D_n^- - [J - \alpha(u_n - u_{n-1})]D_{n-1}^- \tag{24}$$

$$\begin{aligned} i\partial_t D_n^{\mp} &= [J - \alpha(u_{n+2} - u_{n+1})]T_{n+1}^{\pm} - [J - \alpha(u_n - u_{n-1})]T_n^{\pm} \\ &\quad - [J - \alpha(u_{n+1} - u_n)][N_{n+1} - N_n \pm \text{HC}]. \end{aligned} \tag{25}$$

From (5) and (6) we obtain for the phonon variable $q_n = \partial_n u_n$:

$$\partial_n \langle q_n \rangle = (A(v)/\alpha)[D_n^+ - D_{n-1}^+]. \tag{26}$$

In order to get a closed set of equations we expand the next-nearest-neighbour terms T_n with respect to the nearest-neighbour terms D_n which yields

$$\begin{aligned} T_n &= \tfrac{1}{2}[\langle c_{n-1}^+ c_{n+1}\rangle + \langle c_{n-1}^+ c_{n+1}\rangle] \approx \tfrac{1}{2}[\langle c_n^+ c_{n+1}\rangle + \langle c_{n-1}^+ c_n\rangle] \\ &= \tfrac{1}{2}[D_n + D_{n-1}]. \end{aligned} \tag{27}$$

In a first step we solve equations (24)–(26) by performing again the continuum approximation (8). It is important to note, that D_n itself is non-local. Therefore, in spite of applying the continum approximation, the discrete structure of the equations of motion is not lost. Retaining nearest-neighbour interactions we obtain

$$\partial_t N_n = i(J/2)\partial_{nn} D_n^- - i[J - \alpha\langle q_n\rangle]\partial_n D_n^- \tag{28}$$

$$\langle q_n \rangle = (A(v)/\alpha) D_n^+ \tag{29}$$

$$\partial_t D_n^{\mp} = -J\partial_n D_n^{\pm} - iA(v) D_n^+ D_n^{\pm} + i[J - A(v) D_n^+][\partial_n N_n \pm \text{HC}]. \tag{30}$$

In the following procedure we have to express the second moments $D_n^{\pm}$ in terms of the occupation numbers N_n. Therefore we apply the *ansatz* (12) to (30) which yields

$$i\partial_n D_n^- + i\frac{A(v)}{J} D_n^+ D_n^- = \frac{v}{J}\partial_n D_n^+ \tag{31}$$

$$\partial_n D_n^+ + 2\frac{A(v)}{J}\partial_n N_n D_n^+ = 2\partial_n N_n - i\frac{v}{J}\partial_n D_n^- \tag{32}$$

where we have neglected quadratic terms of D_n^+. The inhomogenities of (31)–(32) can be taken as small quantities and substituted by their linearized expressions.

We obtain

$$i\partial_n D_n^- + \frac{i}{J}\frac{A(v)}{1 + v^2/J^2} D_n^+ D_n^- = \frac{2}{J}\frac{v}{1 + v^2/J^2}\partial_n N_n \tag{33}$$

$$\partial_n D_n^+ + \frac{2}{J}\frac{A(v)}{1 + v^2/J^2}\partial_n N_n D_n^+ = \frac{2}{1 + v^2/J^2}\partial_n N_n. \tag{34}$$

Equation (34) can be integrated to give

$$D_n^+ = J/A(v) + C\exp\left(-\frac{2}{J}\frac{A(v)}{1 + v^2/J^2} N_n\right). \tag{35}$$

The integration constant in (35) can be determined by the boundary conditions

$$\lim_{n\to\pm\infty}\langle q_n\rangle = \lim_{n\to\pm\infty} D_n^+ = 0. \tag{36}$$

This yields for C

$$C = -\frac{J}{A(v)} \tag{37}$$

and the second moment D_n^+ is given by

$$D_n^+ = \frac{J}{A(v)}\left[1 - \exp\left(-\frac{2}{J}\frac{A(v)}{1+v^2/J^2}N_n\right)\right]. \tag{38}$$

We note that for small velocities the exponential function can be expanded in a Taylor series which, with equation (26), yields

$$\langle q_n\rangle = 2\frac{A(v)}{\alpha}N_n. \tag{39}$$

This is, except for the factorization, the same relation between electron and phonon coordinates as in equation (13), which means that our calculations up to now give the correct results in the limit of small soliton velocities.

To proceed we have to calculate the first derivative of the second moment D_n^-. Therefore we succesively integrate equation (33) up to the first non-linear term. This yields

$$\mathrm{i}\partial_n D_n^- = \frac{2}{J}\frac{v}{1+v^2/J^2}\partial_n N_n - \frac{1}{J}\frac{A(v)}{1+v^2/J^2}D_n^+ N_n. \tag{40}$$

Inserting (38) and (40) into equation (28) we obtain as a final result

$$\partial_t N_n = \frac{v}{1+v^2/J^2}\partial_{nn}N_n - \frac{2v}{1+v^2/J^2}N_n\exp\left(-\frac{2}{J}\frac{A(v)}{1+v^2/J^2}N_n\right) \tag{41}$$

where we have neglected non-linear terms in the first derivatives of N_n.

In the limiting case, $v \to c$, the non-linear term vanishes and we obtain the diffusion equation

$$\partial_t N_n = D\partial_{nn}N_n. \tag{42}$$

The temperature dependence of the diffusion constant can be estimated by averaging the velocities with the Maxwell–Boltzmann distribution which yields

$$D = \langle v/(1+v^2/J^2)\rangle \tag{43}$$

that is

$$D \sim 1/\sqrt{T} - (2k/mJ^2)\sqrt{T}. \tag{44}$$

This temperature dependence is in qualitative agreement with the magnetic resonance experiments of Kume *et al* [15].

We see that for the case of very large fluctuations, e.g. when $A(v)$ diverges, the polaron solution is destroyed. Therefore no coherent lattice distortion exists which could stabilize the polaron. In this case, electronic motion becomes diffusive as can be seen from equation (42).

The destruction of coherent motion in the limit $v \to c$ is also displayed in the degree of coherence defined as

$$K(n-1, n+1) = \langle c_{n-1}^{+} c_{n+1} \rangle \Big/ \sqrt{\langle c_{n-1}^{+} c_{n-1} \rangle \langle c_{n+1}^{+} c_{n+1} \rangle} \tag{45}$$

which vanishes in the case of no coherence and takes on the value $K = 1$ for factorizing variables. Using the abbreviations (21)–(23) we can rewrite K as

$$K = T_n \Big/ \sqrt{N_{n-1} N_{n+1}}. \tag{46}$$

Expanding the next-nearest-neighbour term T_n with respect to D_n (equation (27)) one can immediately see from (38) that the degree of coherence continously reaches zero for v approaching the velocity of sound.

In the case $v < c$ the exponent in (41) can be expanded up to first order in N_n. We obtain

$$\partial_t N_n = \frac{v}{1 + v^2/J^2} \partial_{nn} N_n - \frac{2v}{1 + v^2/J^2} N_n \left(1 - \frac{2}{J} \frac{A(v)}{1 + v^2/J^2} N_n \right). \tag{47}$$

This equation describes an overdamped polaron motion and can be solved by a perturbation calculation [16]. The zeroth-order solution (zero damping) reads

$$N_n = \frac{3J}{4A(v)} (1 + v^2/J^2) \operatorname{sech}^2[(n - n_0)/\sqrt{2}]. \tag{48}$$

Obviously, the sech-behaviour of the classical polaron solution (18) is reproduced in the limit $v < c$. We note that corrections to the zeroth-order solution can be obtained by a perturbative expansion of the variables N_n and v [16]. However, the electronic master equation (47) is a generalization of the classical adiabatic polaron theory of Wilson [2]. It is derived from the master equations (24)–(26) and contains the effects of quantum fluctuations and dissipation.

4. Conclusion

We have shown that the treatment of the dynamics of the electron system (1) in terms of master equations for the second moments leads to quantum mechanical transport equations which describe the polaron dynamics in the presence of quantum fluctuations and under the influence of a non-adiabatic electron–phonon interaction. In contrast to the classical adiabatic polaron solution (18), the master equations are valid for arbitrary polaron velocities. Even for $v = c$ no divergencies occur in the solutions. This enabled us to show analytically the decay of a solitary polaron due to quantum fluctuations into an electron moving diffusively, as postulated by Wilson [2].

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