IOP Conf. Series: Journal of Physics: Conf. Series **833** (2017) 012021 doi:10.1088/1742-6596/833/1/012021

Charged ultradiscrete supersonic kinks and discrete breathers in nonlinear molecular chains with realistic interatomic potentials and electron-phonon interactions

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Abstract.

The problem of electron or hole trapping by supersonic lattice kink is revisited. Supersonic kinks in molecular chains with realistic interatomic potential produce local compression of the lattice. Lattice compression enhances electron Fermi energy and therefore produces for the electron a local potential hill, rather than a potential well, through the deformation potential of the proper sign. Here we discuss the possibility of electron trapping above the top of its tight-binding conduction band, where it possesses negative effective mass, by supersonic kink in a molecular chain with realistic interatomic potentials and electron-phonon interactions. The localization length of the electron wave function is much larger than lattice period in the case of adiabatic electron dynamics and decreases with the velocity of the ultradiscrete supersonic kink with the approximately sinusoidal envelope with the "magic" wave number. Such kinks were revealed in lattices with different interatomic potentials with hardening anharmonicity. Electron or hole can also be trapped by discrete breather (intrinsic localized mode) in the lattice with realistic asymmetric anharmonic potential. The local quasi-static strain, produced by the stationary or slowly-moving discrete breather in the lattice, can trap the electron (or hole) with its localization below the lower edge of the conduction (or above the upper edge of the valence) band.

1. Introduction

Plane one-dimensional shock waves can be considered as an example of supersonic propagation of locally enhanced density in macroscopic condensed matter systems [1, 2]. One the other hand, macromolecules in polymers present an example of nanoscale quasi-one-dimensional systems. Electron-phonon interaction in quasi-one-dimensional macromolecules like polyacetylene can result in the Pierles lattice dimerization and the formation of the gap at the Fermi level, which strongly affect transport properties of such low-dimensional materials [3]. Essentially the Pierles lattice dimerization in a quasi-one-dimensional system can be considered as the *band* $Jahn\text{-}Teller\ effect$ [4].

Supersonic kinks with local lattice compression can also propagate in quasi-one-dimensional macromolecules of the polyacetilene type [5]. In this paper we discuss the scenario of electron trapping above the top of its tight-binding conduction band, where it possesses negative effective

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mass, by supersonic kink in a molecular chain with realistic interatomic potentials and electron-phonon interactions. The reason of such kind of electron trapping is related with the property that lattice compression enhances electron Fermi energy and therefore produces for the electron a local potential hill, rather than a potential well, through the deformation potential of the proper sign. Electron trapping by the potential hill is different from the previously considered electron trapping by the effective potential well, produced by supersonic kink [6, 7, 8, 9, 10]. We consider electron trapping by ultradiscrete supersonic kinks with the approximately sinusoidal envelope with the "magic" wave number, which were revealed in lattices with different interatomic potentials with hardening anharmonicity [11, 12, 13]. It is worth mentioning that the trapping by *potential hill* of the quasiparticle with negative effective mass is similar to the formation of intrinsic localized mode (discrete breather) above the phonon band in a crystal with *repulsive* anharmonicity [14].

Electron, exciton or hole can also be localized by the discrete breather in the lattice with realistic asymmetric anharmonic potential. In the case of stationary or slowly moving discrete breather (DB), there is a kink-like distribution of static or quasi-static lattice displacements, caused by the asymmetry of the interparticle potential [15] (see also [16]). In the lattice with realistic interatomic potentials, these displacements cause local lattice stretching and the formation of local potential well for the electron (or exciton), produced by the discrete breather. This in turn results in the trapping of slowly-moving electron (or exciton) by DB with its localization below the lower edge of the conduction (or exciton) band. The hole can be trapped by the stationary or slowly-moving DB above the valence band, below the Fermi level. The papers [17, 18] consider different mechanisms of electron localization by DB, not related with static stretching of the anharmonic lattice.

2. The model

We consider the following semiclassical Hamiltonian, which describes the interaction of classical longitudinal phonons with a quantum quasiparticle (electron, exciton or hole) in 1D lattice with nearest-neighbor interactions between atoms (nuclei) and between corresponding quasiparticles (the tight-binding model):

$$
\begin{aligned}
H &= H_{lat} + H_{el} + H_{el-ph}, && (1)\\
H_{lat} &= \sum_n [\frac{1}{2M} p_n^2 + U(u_n - u_{n-1})], && (2)\\
H_{el} &= \sum_n [E_0 a_n^* a_n - J a_n^* (a_{n+1} + a_{n-1})], && (3)\\
H_{el-ph} &= -\sum_n (u_n - u_{n-1})[g_1 a_n^* a_n - g_2 a_n^* (a_{n+1} + a_{n-1})], && (4)
\end{aligned}
$$

where u_n is atomic displacement from the equilibrium position in the lattice site n, M is atomic mass, p_n is the momentum conjugate to u_n, $U(r)$ is the (nonlinear in general) interparticle potential, where $r = u_n - u_{n-1}$ is relative particles displacement, a_n is the complex amplitude of the quasiparticle in the lattice site n such that $|a_n|^2$ gives the probability to find the quasiparticle at this site, E_0 is energy in the center of the conduction band, $4J$ gives the width of the conduction band, g_1 and g_2 are (positive) constants of the electron-phonon interaction, which determine the shift of the center and the change of the width of the conduction band caused by lattice strain (1D deformation) $u_n - u_{n-1} = d\partial u/\partial x$, d is lattice period. The model of the electron-phonon interaction with the two parameters g_1 and g_2, eq. (4), combines the deformation-potential model for nonpolar semiconductors [19] with the Su-Schriffer-Heeger (SSH) model for quasi-1D conducting systems [20] (with the parameters g_1 and g_2, respectively).

From equations (1)-(4) we obtain the corresponding equations of motion for a_n and u_n:

$$\begin{aligned} i\hbar\dot{a}_n &= E_0 a_n - J(a_{n+1}+a_{n-1}) - (u_n - u_{n-1})[g_1 a_n - g_2(a_{n+1}+a_{n-1})], \quad (5) \\ M\ddot{u}_n &= -\frac{\partial}{\partial u_n}[U(u_n-u_{n-1}) - U(u_{n+1}-u_n)] + [g_1(|a_n|^2 - |a_{n-1}|)^2 \\ & -g_2(a_n^*(a_{n+1}+a_{n-1}) - a_{n-1}^*(a_n + a_{n-2}))]. \quad (6) \end{aligned}$$

Both at the lower and upper edges of the quasiparticle band, one has $|a_n| \approx |a_{n+1}|$ and the amplitudes a_n at the nearest-neighbour sites are in phase at the lower edge and are anti-phase at the upper edge of the band. Therefore at both edges the effective Hamiltonian of the electron-phonon interaction H_{el-ph}^{eff} can be written in the following universal form (cf. eq. (4)):

$$H_{el-ph}^{eff} = -g_{\pm}^{eff}\sum_n (u_n - u_{n-1})a_n^* a_n, \quad (7)$$

where $g_{\pm}^{eff} = g_1 \pm 2g_2$, and sign plus (minus) corresponds to the upper (lower) edge of the quasiparticle band. The corresponding equations of motion for a_n and u_n take the following form:

$$\begin{aligned} i\hbar\dot{a}_n &= E_0 a_n - J(a_{n+1}+a_{n-1}) - g_{\pm}^{eff}(u_n - u_{n-1})a_n, \quad (8) \\ M\ddot{u}_n &= -\frac{\partial}{\partial u_n}[U(u_n-u_{n-1}) - U(u_{n+1}-u_n)] + g_{\pm}^{eff}(|a_n|^2 - |a_{n-1}|)^2. \quad (9) \end{aligned}$$

In the continuum approximation with respect to the quasiparticle wave function $\psi = \psi(x,t)$, equations (8) and (9) can be written as:

$$\begin{aligned} i\hbar\dot{\psi} &= E_{\pm}\psi \pm Jd^2\frac{\partial^2\psi}{\partial x^2} - g_{\pm}^{eff}(u_n - u_{n-1})\psi, \quad (10) \\ M\ddot{u}_n &= -\frac{\partial}{\partial u_n}[U(u_n-u_{n-1}) - U(u_{n+1}-u_n)] + g_{\pm}^{eff} d\frac{\partial|\psi|^2}{\partial x}, \quad (11) \end{aligned}$$

where $\psi(x) = a_n$ and $\psi(x) = (-1)^n a_n$ at the lower and upper edges of the quasiparticle band, respectively, $x = nd$, $E_{\pm} = E_0 \pm 2J$. Equation (10) for the quasiparticle wave function close to the upper edge of the band corresponds to the anti-continuum limit, which is known in the envelope-function approach to the short-wavelength lattice and spin dynamics, both linear and nonlinear, see, e.g., Refs. [21, 22].

3. Results and Discussion

Below we list the realistic nonlinear interatomic potentials $U(r)$, which are known to support the propagation of supersonic kinks:

$$\begin{aligned} U(r) &= \frac{1}{2}K_2 r^2 - \frac{1}{3}K_3 r^3, \quad K_3 > 0, \quad (12) \\ U(r) &= \frac{1}{2}K_2 r^2 - \frac{1}{3}K_3 r^3 + \frac{1}{4}K_4 r^4, \quad K_3 \geq 0, \quad K_4 > 0, \quad (13) \\ U(r) &= \epsilon(\frac{1}{(1+r)^{12}} - \frac{2}{(1+r)^6}), \quad (14) \\ U(r) &= \frac{1}{1+r}, \quad (15) \end{aligned}$$

which are the α-Fermi-Pasta-Ulam (α-FPU), α-β-FPU, Lennard-Jones (LJ) and repulsive Coulomb (RC) potentials, respectively. In all these interparticle potentials, the part of the potential, which describes *contraction* of the lattice, is always more steep than the part, describing *stretching* of the lattice, which ensures the possibility of propagation of the *compression* supersonic kinks. It is worth mentioning that the α-β-FPU potential is also realized for the intermediate relative displacements r in the Lennard-Jones and repulsive Coulomb potentials.

3.1. Trapping of quasiparticle by supersonic kink

To describe a supersonic kink traveling to the right in the one-dimensional chain with the α-β-FPU interatomic potential, we use the following *ansatz* with the "magic" wave number $2\pi/3d$, which was introduced in Refs. [11, 12] and was successfully applied for the description of ultradiscrete supersonic kinks in repulsive Coulomb lattice in Ref. [13]:

$$u_n - u_{n-1} = -\frac{A}{2}(1 + \cos(\frac{2\pi}{3d}(nd - Vt)) \tag{16}$$

for $-\pi \leq (2\pi/3d)(n - Vt) < \pi$, and $u_n - u_{n-1} = 0$ otherwise, where $A > 0$ is the kink amplitude of relative particle displacements, $V > \sqrt{K_2/M}d$ is supersonic velocity of the kink, $\sqrt{K_2/M}d$ is a speed of sound in the system. Localization of such nonlinear excitations increases with its velocity V, when the inverse localization length κ_{lat} of the lattice excitation is determined by its velocity and follows the equation [11]:

$$MV^2\kappa_{lat}^2 = 4K_2 \sinh^2(\kappa_{lat}d/2). \tag{17}$$

The kink velocity V grows in the large-amplitude limit (in β-FPU lattice) as [12]

$$V = \frac{3d}{2\pi}\sqrt{\frac{3K_2 + (45/16)K_4A^2}{M}}. \tag{18}$$

Supersonic kink with the pattern of relative displacements (16) can be considered as a discrete limit of the kink in the Korteweg - de Vries or modified Korteweg - de Vries equation.

Following the known solution of Schrödinger equation for localization in the 1D potential well which can be considered as perturbation [23], with the use of equation (10) we obtain the quasiparticle inverse localization length $\kappa_{qp} > 0$, given by the integral over the discrete breather width of the deformation potential (7), in which we substitute $u_n - u_{n-1}$=$d\partial u/\partial x$:

$$\kappa_{qp} = \frac{|m_{qp}|}{\hbar^2}\int_{-\infty}^{+\infty} g_+^{eff}(d\partial u/\partial x)dx = \frac{|m_{qp}|}{\hbar^2}g_+^{eff}dA \tag{19}$$

for $g_+^{eff} > 0$, where $|m_{qp}| = \hbar^2/(2d^2J)$ is the modulus of the negative quasiparticle effective mass at the top of the band. From equation (19) follows that quasiparticle localization length decreases with the increase of kink amplitude and velocity, and the localization length is much larger than lattice period in the case of adiabatic electron dynamics, for $V \ll 2Jd/\hbar$.

With the use of equations (10) and (19), we obtain the energy E of the moving with group velocity V quasiparticle, localized above the upper edge of the band E_+:

$$E = E_+ + \frac{|m_{qp}|}{2\hbar^2}(g_+^{eff}dA)^2 - \frac{|m_{qp}|}{2}V^2\ , \tag{20}$$

where $V = \partial E/(\hbar\partial q) = 2Jd\sin(qd)/\hbar = 2Jd(\pi - qd)/\hbar$ is the group velocity of the quasiparticle with the wavenumber q close to the Brillouin zone edge π/d, which coincides with the supersonic kink velocity V in eq. (16). It is worth mentioning that the shift $-|m_{qp}|V^2/2$ of the energy of the moving quasiparticle in equation (20) is consistent with the transformation of wave function of the particle with a given mass, moving with respect to laboratory frame [23]: the mass is effective and negative in equation (20). According to equation (19), the finite quasiparticle velocity V does not affect the localization condition, and the energy of the moving localized quasiparticle can enter the band, for $\Delta E < 0$ and $E < E_+$, since the latter is determined in the laboratory frame.

We can compare the inverse localization length (19) and energy (20) of the moving localized quasiparticle with the inverse localization length $\kappa_{DB} > 0$ and energy $\hbar\omega_{DB}$ of the moving discrete breather, localized above the phonon band in the α-β-FPU lattice, see, e.g., [14, 16, 24]:

$$\kappa_{DB} = \sqrt{6K_4/K_2 - 8(K_3/K_2)^2}A_{DB}/d, \tag{21}$$

$$\hbar\omega_{DB} = \hbar\omega_{max}(1 + (\frac{3K_4}{4K_2} - \frac{K_3^2}{K_2^2})A_{DB}^2) - \frac{|m_{ph}|}{2}V^2, \tag{22}$$

$$m_{ph} = -\frac{2\hbar}{d^2}\sqrt{\frac{M}{K_2}}, \tag{23}$$

$$\omega_{max} = 2\sqrt{\frac{K_2}{M}}, \tag{24}$$

where A_{DB} is displacement oscillation amplitude in the discrete breather, m_{ph} is effective "phonon mass" at the top of phonon band with the dispersion $\omega = 2\sqrt{K_2/M}\sin(qd/2)$, $1/m_{ph} = \partial^2\omega/\partial q^2/\hbar$, and $V = \partial\omega/\partial q$. Similar to the case of moving quasiparticle, equation (20), frequency of the moving discrete breather can, in principle, enter phonon band, when $\omega_{DB} < \omega_{max}$, see equation (22).

3.2. Trapping of quasiparticle by discrete breather

Discrete breather in the lattice with realistic asymmetric interparticle potential $U(r)$ causes local static deformation (stretching) of the lattice [15]. For instance, in the α-β FPU chain with $3K_4K_2 > 4K_3^2$, we have the following expression for the local static stretching deformation $(\partial u/\partial x)_{st}$ [16]:

$$(\partial u/\partial x)_{st} = \langle\frac{1}{2}\partial(u_n + u_{n-1})/\partial x\rangle = \frac{K_3}{dK_2}\langle(u_n - u_{n-1})^2_{DB}\rangle > 0\,, \tag{25}$$

where $(u_n - u_{n-1})^2_{DB}$ denotes square of relative particle displacements in the discrete breather and angle brackets denote time averaging (one has $\langle(u_n - u_{n-1})^2_{DB}\rangle \sim A_{DB}^2$, cf. equations (21) and (22)). This relation shows that discrete breather produces local *energetic expansion* of the lattice with realistic asymmetric interatomic potential, which is caused by atoms with locally enhanced vibrational energy, forming discrete breather [16].

With the use of equations (10) and (25) with substitution $u_n - u_{n-1}{=}d(\partial u/\partial x)_{st}$, we obtain the inverse localization length $\kappa_{qp} > 0$,

$$\kappa_{qp} = \frac{2m_{qp}}{\hbar^2}\frac{K_3}{K_2}g_-^{eff}\langle(u_n - u_{n-1})^2_{DB}\rangle\lambda_{DB}, \tag{26}$$

and energy E of the quasiparticle trapped below its conduction band where is possesses positive effective mass m_{qp}:

$$E = E_- - \frac{2m_{qp}}{\hbar^2}(\frac{K_3}{K_2}g_-^{eff}\langle(u_n - u_{n-1})^2_{DB}\rangle\lambda_{DB})^2 + \frac{m_{qp}}{2}V^2\ , \tag{27}$$

where $\lambda_{DB} = 1/\kappa_{DB}$ is localization length of the discrete breather, see equation (21). The trapping can be realized for $g_-^{eff}{=}g_1 - 2g_2{>}\ 0$. Since discrete breathers are stationary or slowly-moving nonlinear lattice excitations, kinetic energy of the moving quasiparticle cannot significantly affect the trapping condition (26), but the energy of the moving quasiparticle can, in principle, enter the band, for $E > E_-$, cf. equations (20) and (22).

In p-doped semiconductor, a hole can be trapped by the stationary or slowly-moving discrete breather. Since the sign of the deformation potential (7) for holes is opposite to that for electrons [19], the hole can be trapped above the upper edge of the valence band. This property reflects the particle-hole symmetry in the quasiparticle trapping.

4. Conclusions

We describe the possibility of electron trapping above the top of its tight-binding conduction band, where it possesses negative effective mass, by supersonic kink in a molecular chain with realistic interatomic potentials and electron-phonon interactions. The localization length of the electron wave function is in general much larger than lattice period for adiabatic electron dynamics and decreases with the velocity of the ultradiscrete supersonic kink. We consider electron trapping by ultradiscrete supersonic kinks with the approximately sinusoidal envelope with the "magic" wave number, which were revealed in lattices with different interatomic potentials with hardening anharmonicity. Electron or hole can also be trapped by discrete breather (intrinsic localized mode) in the lattice with realistic asymmetric anharmonic potential. The local quasi-static strain, produced by the stationary or slowly-moving discrete breather in the lattice, can trap the electron (or hole) with its localization below the lower edge of the conduction (or above the upper edge of the valence) band.

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