GENERAL QUESTIONS OF THERMODYNAMICS, STATISTICAL PHYSICS, AND QUANTUM MECHANICS

SELF-TRAPPING AND DYNAMICS OF A QUASI-PARTICLE IN A ONE-DIMENSIONAL MOLECULAR CHAIN UNDER INTERACTION WITH OPTICAL PHONONS

YU.E. NATANZON, L.S. BRIZHIK[1], A.A. EREMKO[1]

UDC 539

National University of Kyiv-Mohyla Academy
(2, Skovoroda Str., Kyiv 04170, Ukraine; e-mail: yurko.natanzon@gmail.com),
[1]**M.M. Bogolyubov Institute for Theoretical Physics, Nat. Acad. Sci. of Ukraine**
(14b, Metrolohichna Str., Kyiv 03143, Ukraine; e-mail: brizhik@bitp.kiev.ua; eremko@bitp.kiev.ua)

This article is dedicated to the brilliant memory of Tetyana O. Davydova (29.09.1941—10.04.2005)

The self-trapping conditions for a quasi-particle in a molecular chain are investigated taking into account the quasi-particle interaction with optical phonons, both dispersive and dispersionless. The dynamic properties of this soliton-like state of a quasi-particle are studied for various parameters of the model. The soliton velocity dependence on the wave vector is calculated and analyzed, and the soliton stability conditions are established. It is shown that the soliton velocity increases with the quasi-momentum to some saturation level. The soliton velocity is shown to be an oscillating function of the quasi-momentum, which is due to the Peierls—Nabarro barrier and the influence of optical phonons generated by the soliton. It is shown that the quasi-particle is self-trapped and dynamically stable for values of the wave vector less than the critical one. It is found that, for certain parameters corresponding to alpha-helical proteins, the quasi-particle can propagate over dozens of nanometers without considerable energy loss and without change of the envelope shape.

The properties of quasi-one-dimensional molecular chains are actively investigated for many years. Such systems include synthesized strongly anisotropic quasi-one-dimensional organic and non-organic compounds, many of which are used in modern technologies, and biopolymers and biological macromolecules which play an important role in the charge transfer and the energy storage and transfer. Such systems can be modeled by one-dimensional molecular chains due to a periodic repetition of certain atomic groups. In particular, alpha-helical proteins contain repeated peptide groups, and DNA chains consist of the groups of amides. These groups can be considered as structural units of a chain. The phonon spectrum of such a chain contains several modes, with which the excessive electrons doped into the chain or the molecular excitations or excitons (which will be called *quasi-particles*) can interact with different intensities. This complete system is described by the Fröhlich Hamiltonian. It is known that even the problem of one particle in a chain with one phonon mode (acoustic or optical) is quite complicated, and its exact solution is not found. This problem is solved only in certain approximations. Else more complicated is the problem of a quasi-particle in a chain with several electron bands and several phonon modes (see, for example, [1—4]). It is known that, under certain conditions, namely at a moderate value of the electron-phonon coupling in soft chains with one acoustic mode, the self-trapped electron states can occur that can be attributed to the soliton class in a certain approximation [see reviews in [3,5,6]). This soliton mechanism ensures the lossless transfer of energy and charges over quite long distances, which is important in bioenergetics, information transfer, etc. In the case of the charge transport (when a quasi-particle is an electron), the self-trapped state is frequently called a polaron. This term was introduced

by Pekar more than 50 years ago for electrons interacting with polarization optical vibrations in ionic crystals. Nowadays this term is used for polarons of large radii (which were studied by Pekar and are called Pekar's polarons) and for polarons of small radii. Polarons include also Fröhlich polarons. The term "polaron" is used in the literature to describe self-trapped electron states, whose localization is a consequence of different interaction mechanisms with different phonon branches (Pekar polaron, Fröhlich polaron, Holstein polaron, acoustic polaron, etc.) For a one-dimensional chain, it is common to use the term "one-dimensional polaron". For different interaction mechanisms, the function describing the electron-phonon interaction reveals different behaviors for small quasi-momenta. In particular, under the interaction through a deformation potential, this function tends to a constant. Namely this case is considered in this work.

While the self-trapping of a quasi-particle under its interaction with acoustic phonons has been intensively investigated analytically and numerically, in particular in the works of Davydov and co-authors (see, for example, [3]) and in the works of Scott [5, 7—8], the interaction with optical phonons has been investigated much less. In particular, in the continual approximation, this problem was studied in [9], where it was shown that the soliton width as a function of its velocity is nonmonotonic. Namely, at small propagation velocities, the width decreases with increase in the velocity (the soliton becomes narrower). But at high velocities, the soliton begins to spread with increase in its velocity. This result was obtained by a variational method, and therefore it is important to check its validity and to find the limits of validity. The goal of this work is to establish the possibility of the self-trapping of a quasi-particle and to study the conditions of the self-trapping of quasi-particles in the chains with optical phonons by using the numerical modeling. We also study the dynamics of self-trapped soliton-like quasi-particles interacting with optical phonons.

1. Basic Equations

In our model, we consider only one optical vibration mode of a one-dimensional chain. The optical phonons are usually called normal vibrations of a lattice, whose frequency $\Omega(k)$ tends to a finite value Ω_0 as a wave vector tends to zero in contrast to acoustic phonons, for which $\Omega(k) \to 0$ as $k \to 0$.

The total energy of the chain with an excess quasi-particle in it includes the quasi-particle energy, the phonon energy, and the energy of their interaction:

$$H = H_{\rm el} + H_{\rm ph} + H_{\rm int}.$$

The self-trapping of quasi-particles occurs in the systems that satisfy the conditions of the adiabatic approximation. This approximation is equivalent to the so-called semi-classical approach, in which a quasi-particle is described by a quantum equation, and the vibrations of the lattice are treated as classical. In our case, the explicit Hamiltonian in the node representation takes the form:

$$H = \sum_n \{E_0\psi_n^*\psi_n - J[\psi_n^*\psi_{n+1} + \psi_n^*\psi_{n-1}] + \frac{p_n^2}{2M} +$$

$$+\frac{M}{2}v_0(u_{n+1}-u_n)^2 + \frac{M}{2}\Omega_0^2 u_n^2 + \chi_{\rm opt}\psi_n^*\psi_n u_n\}. \qquad (1)$$

Here, ψ_n is the probability amplitude of the location of a quasi-particle at the n-th molecule, E_0 is the energy of a quasi-particle localized at an isolated molecule, J is the exchange interaction energy between the chain molecules, u_n is the normal coordinate corresponding to the frequency Ω_0 of the natural vibrations of a molecule with mass coefficient M; p_n is the canonically conjugated momentum, ν_0 is the dispersion parameter of phonons, and $\chi_{\rm opt}$ is the constant of the electron-phonon interaction.

From this Hamiltonian, we can obtain the Hamilton equations for the generalized coordinates ψ_n and u_n and for the generalized momenta $i\hbar\psi_n^*$ and p_n. Thus, we obtain the system of non-linear differential equations

$$i\hbar\frac{\partial\psi_n}{\partial t} = E_0\psi_n - J(\psi_{n-1}+\psi_{n+1}) + \chi_{\rm opt}u_n\psi_n, \qquad (2)$$

$$\frac{1}{M}\frac{dp_n}{dt} = \frac{v_0}{a^2}(u_{n+1}+u_{n-1}-2u_n) - \Omega_0^2 u_n - \frac{\chi_{\rm opt}}{M}\psi_n^*\psi_n, \qquad (3)$$

$$\frac{du_n}{dt} = \frac{p_n}{M}. \qquad (4)$$

In our case, the dispersion of optical phonons is described by the law

$$\Omega^2(k) = \Omega_0^2 + 4v_0\sin^2\frac{ka}{2} \approx \Omega_0^2 + v_0(ka)^2, \qquad (5)$$

where a is the lattice constant, and the dispersion of a quasi-particle is described as

$$E(k) = E_0 - 2J\cos(ka) =$$

$$= E_0 - 2J + 4J\sin^2\frac{ka}{2} \approx E(0) + J(ka)^2, \qquad (6)$$

where $E(0) = E_0 - 2J$ is the band bottom.

Replacing $\psi_n \to \psi_n e^{-\frac{iE_0 t}{\hbar}}$, we can eliminate the first term on the right-hand side of the first equation of the system.

In the general case, the exact analytical solution of this system is not known even in the continual approximation. Therefore, we applied numerical methods in order to find specific localized solutions.

To do that, we introduce dimensionless functions, variables, and coefficients:

$$u_n \to \frac{u_n}{a}, \quad p_n \to \frac{p_n}{M\Omega_0 a}, \quad t \to t\Omega_0,$$

$$j = \frac{J}{\hbar\Omega_0}, \quad g_0 = \frac{\chi_{\rm opt} a}{\hbar\Omega_0}, \quad c_0 = \frac{M\Omega_0 a^2}{\hbar}, \quad v = \frac{v_0}{\Omega_0^2}. \quad (7)$$

It is convenient to separate the real and imaginary parts of the quasi-particle wave function by setting $\psi_n = f_n + i\varphi_n$. Thus from (2)—(4), we obtain the system of equations in the form suitable for numerical integration:

$$\frac{\partial f_n}{\partial t} = -j(\varphi_{n-1} + \varphi_{n+1}) + g_0 u_n \varphi_n, \quad (8)$$

$$\frac{\partial \varphi_n}{\partial t} = j(f_{n-1} + f_{n+1}) - g_0 u_n f_n, \quad (9)$$

$$\frac{dp_n}{dt} = v(u_{n+1} + u_{n-1} - 2u_n) - u_n - \frac{g_0}{c_0}(f_n^2 + \varphi_n^2), \quad (10)$$

$$\frac{du_n}{dt} = p_n. \quad (11)$$

2. Initial and Boundary Conditions. Dependence of a Steady-State Solution on Dispersion

2.1. Periodic boundary conditions

In the case of a sufficiently long chain, we can use the Born—Karman periodic boundary conditions:

$$u_{n+N} = u_n, \quad \psi_{n+N} = \psi_n,$$

where N is the number of molecules in the chain, $N >> 1$).

2.2. Steady-state solutions. Initial conditions for obtaining steady-state solutions

Let us find a steady-state solution to system (8)—(11). To do that, we use an ansatz which coincides with the analytical solution of the system in the continuum approximation at the zero velocity.

In the continual approximation, $n \to x$, the system of equations (2)—(4) takes the form

$$i\hbar\frac{\partial\Psi}{\partial t} + J\frac{\partial^2\Psi}{\partial x^2} - \chi_{\rm opt} u\Psi = 0,$$

$$\frac{\partial^2 u}{\partial t^2} + \Omega_0^2 u - \nu_0 \frac{\partial^2 u}{\partial x^2} + \frac{\chi_{\rm opt}}{M}|\Psi|^2 = 0. \quad (12)$$

In the class of functions that depend on the variable $\xi = x - \nu t$ ($\nu = V/a$, V is the velocity of a wave packet), that is $u(x,t) = u(\xi)$ and $|\psi(x,t)|^2 = \varphi^2(\xi)$, the solution of the last equation takes the form

$$u(\xi) = -\frac{\chi_{\rm opt}}{M\Omega_0^2}\int\limits_{-\infty}^{\xi} dz w(z-\xi)\varphi^2(z), \quad (13)$$

where the integral kernel

$$w(\xi) = \frac{1}{2\pi}\int \frac{\exp(iq\xi)}{1+\sigma q^2} \quad (14)$$

takes different values depending on the parameter

$$\sigma = \frac{v_0^2 - \nu^2}{\Omega_0^2}, \quad (15)$$

Namely,

$$w(\xi) = \frac{1}{2\sqrt{\sigma}}\exp\left(-\frac{|\xi|}{\sqrt{\sigma}}\right) \text{ for } \sigma > 0, \quad (16)$$

$$w(\xi) = \frac{1}{\sqrt{\sigma}}\sin\left(\frac{|\xi|}{\sqrt{\sigma}}\right) \text{ for } \sigma < 0, \quad (17)$$

$$and w(\xi) = \delta(\xi) \text{ for } \sigma = 0. \quad (18)$$

Here, $\delta(\xi)$ is the δ-function.

Substituting solution (13) into the first equation of system (12), we obtain a non-linear integro-differential equation in the general case of an arbitrary velocity:

$$i\hbar\frac{\partial\Psi}{\partial t} + J\frac{\partial^2\Psi}{\partial x^2} + \frac{\chi_{\rm opt}^2}{M\Omega_0^2}\int\limits_{-\infty}^{\xi} dz w(z-\xi)|\Psi(z)|^2 = 0. \quad (19)$$

Thus, at the zero parameter σ, the last equation becomes, according to (18), a non-linear Schrödinger equation

$$i\hbar\frac{\partial\Psi}{\partial t} + J\frac{\partial^2\Psi}{\partial x^2} + 2G_{\rm opt}|\Psi|^2\Psi = 0 \quad (20)$$

that has a well-known soliton solution. Here, we denote

$$G_{\rm opt} = \frac{\chi_{\rm opt}^2}{2M\Omega_0^2} = J\frac{g_0}{2jc_0}. \quad (21)$$

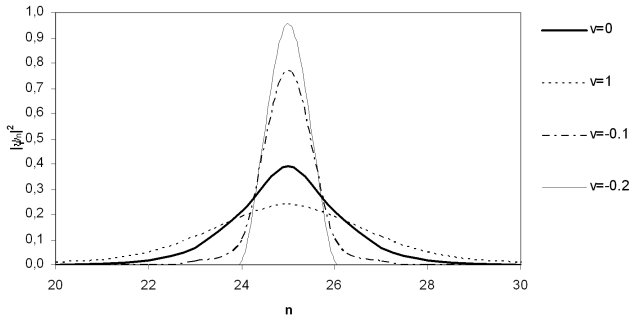

Fig. 1. Dependence of the square amplitude of the steady localized state on the velocity for various parameters v at j=1

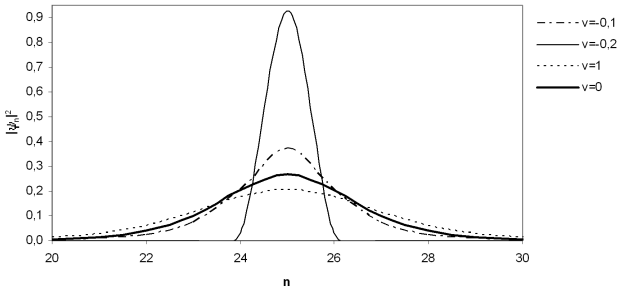

Fig. 2. Dependence of the square amplitude of the steady localized state on the phonon dispersion v at $j = 1.2$

As was shown in [9], for a non-zero small parameter σ, Eq. (19) becomes a modified non-linear Schrödinger equation. It is known that this equation has a soliton solution. We expect that a steady-state solution of the discrete system of equations (2)—(4) has the same properties. Therefore, we take the following initial conditions while seeking for the steady-state solution of system (8)—(11):

$$f_n(0) = \frac{\sqrt{g_{\rm opt}}}{2}\cosh^{-1}\left[\frac{g_{\rm opt}(n-N/2)}{2}\right],$$

$$\varphi_n(0) = 0,$$

$$u_n(0) = -\frac{g_0}{c_0}|\psi_n(0)|^2,$$

$$p_n(0) = 0.$$

Here, $g_{\rm opt} = \frac{g_0^2}{2jc_0}$. As these initial conditions are only an approximation to the steady-state solution for a non-zero velocity, we introduce a small friction to Eq. (10) which will suppress phonons that are radiated during the transition to a lower energy level that corresponds to the steady-state solution:

$$\frac{dp_n}{dt} = v(u_{n+1}+u_{n-1}-2u_n)-u_n-\frac{g_0}{c_0}(f_n^2+\varphi_n^2)-\gamma p_n. \quad (22)$$

In this manner, we obtained quasi-steady-state solutions (which do not change in time, but are not real functions of n) for various values of the parameter v for dispersionless phonons and phonons with positive or negative dispersion (that is, for $v > 0$ and $v < 0$, respectively). Next we will use these solutions to obtain moving localized wave packets. Fig. 1 shows the square amplitude of the steady-state solution $|\psi_n|^2$ at various values of the dispersion parameter v.

In the calculation, we used the following parameters:

$$j = 1, \quad g_0 = 1.43, \quad c_0 = 0.8, \quad \gamma = 5.$$

We can see from Fig. 1 that the phonon dispersion affects the packet width. In particular, the positive dispersion spreads the packet, whereas the negative one localizes the packet. At the negative dispersion, the effective frequency of phonons decreases, which leads to an increase of the nonlinearity parameter $G_{\rm opt}$ and, as a consequence, to a decrease of the localization region of a quasi-particle. Already at $v = -0.2$, a quasi-particle is localized at one node. This is why, we did not consider the dispersion at $v < -0.2$.

In addition, we obtained steady-state solutions at $j = 1.2$ for the negative dispersion (Fig. 2). It can be seen that a change in the exchange energy does not affect the packet shape, but, at bigger j, the amplitude becomes sufficiently smaller. Namely, when the intermolecular repulsion energy is bigger than the energy of intramolecular vibrations, the quasi-particle losses its energy to compensate the difference, and therefore the wave packet amplitude is reduced.

2.3. Initial conditions for a nonstationary solution

To find the quasi-steady-state solutions for moving solitons, we use the method of adiabatic acceleration of a soliton which was proposed in [10].

We use the fact that a steady-state moving soliton is described by the function

$$\psi_n(t) = \Phi_n(t)\exp(ikn),$$

where k is the soliton wave vector that is related to its velocity as $k = \frac{\hbar v}{2J}$ (k is measured in the units of lattice constant). Having obtained the steady-state functions f_n, φ_n, u_n, and p_n that correspond to the zero quasi-momentum, we can find quasi-steady-state solutions by gradually accelerating the wave packet, namely, by

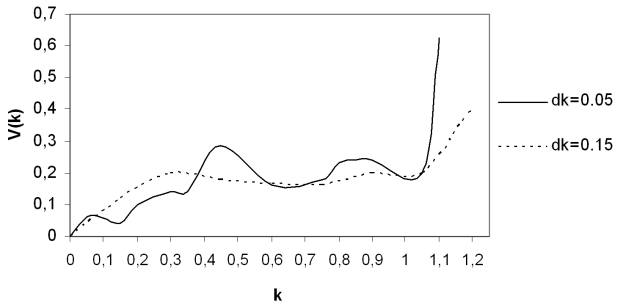

Fig. 3. Packet velocity versus the wave vector for different acceleration increments Δk

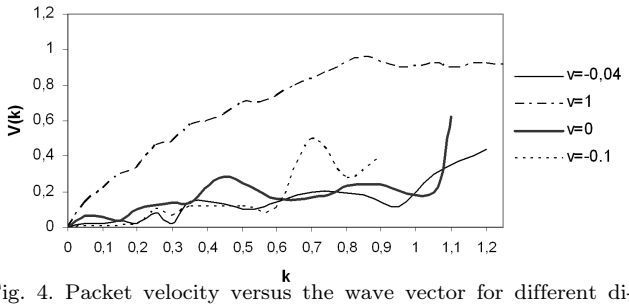

Fig. 4. Packet velocity versus the wave vector for different dispersion values v

increasing its quasi-momentum by a small increment Δk starting from $k = 0$.

Thus, separating the real and imaginary parts of the wave function and taking a nonzero momentum p_n, we obtain

$$f_n(0, k + \Delta k) = f_n(k) \cos \Delta kn - \varphi_n(k) \sin \Delta kn, \quad (23)$$

$$\varphi_n(0, k + \Delta k) = f_n(k) \sin \Delta kn + \varphi_n(k) \cos \Delta kn, \quad (24)$$

$$p_n(0, k + \Delta k) = -j[u_n(k) - u_{n-1}(k)] \sin(k + \Delta k), \quad (25)$$

$$u_n(0, k + \Delta k) = u_n(k). \quad (26)$$

Thus, firstly, we put $k = 0$ and take the earlier obtained steady-state solution as an initial condition. Applying conditions (23)—(26), we obtain the quasi-steady-state solutions that move with the velocity corresponding to the quasi-momentum Δk. Applying again conditions (23—26), we obtain the quasi-steady-state solutions that move with the velocity corresponding to $2\Delta k$, etc. We try to investigate how the wave-packet velocity changes with a gradual increase in k and what will happen to a quasi-particle when k approaches the critical value. We have done this in the cases $v = 0$ (dispersionless phonons), $v > 0$ (positive dispersion), and $v < 0$ (negative dispersion). In what follows, we consider and analyze these three cases.

3. Soliton Dynamics

3.1. Dispersionless optical phonons

Putting $v = 0$, we obtain the case of dispersionless phonons. We investigated the wave packet motion in the interval $k = [0; 1.35]$ with various steps of acceleration. As was expected, the packet velocity increases with k in a certain interval. But, in contrast to the dynamics of a soliton in a chain with acoustic phonons [10,11], it turned out that, at the same value of k, the packet velocity is different for different types of acceleration (namely, it depends on the initial velocity and the momentum increment Δk). This can be explained by the fact that the essential part of the initial energy is spent to surmount the Peierls—Nabarro barrier which is created for a soliton due to the chain discreteness [see, for example, [12—19]). Therefore, if the packet initially moved quickly enough, all the added energy is spent for the velocity increase. But if the packet was decelerated or it oscillates in the scope of one or two nodes (the so-called pinning), the additional energy is spent to overcome the barrier, and only the rest of the energy is used to increase the packet velocity. Thus, the packet velocity depends on the history of acceleration (Fig. 3).

In addition, one can observe that the velocity increases with k (with the correction on overcoming the Peierles—Nabarro barrier) and reaches a critical value. After that, the velocity remains almost permanent with oscillations in insignificant limits. At $k > 1$, one can observe a time moment, at which the packet suddenly accelerates to the speed which is maximum for the time of its existence and then delocalizes by decaying into small-amplitude perturbations. This happens because the total momentum of the packet reaches a value, at which the Peierls–Nabarro barrier becomes "invisible". Such a soliton starts to move quickly by causing the intense radiation of phonons in the chain and by loosing its "soliton" properties. These radiated phonons interact, in turn, with the quasi-particle and ruin the packet. In our case, the delocalization was observed at $k = 1.35$ (with the increment $\delta k = 0.15$) and at $k = 1.1$ (with the increment $\delta k = 0.05$). The more detailed analysis of the dependence of the critical k (and the soliton life-time) on the acceleration conditions and the parameters of the model will be given later on.

All these properties are illustrated in the graphs that were obtained in numerical experiments.

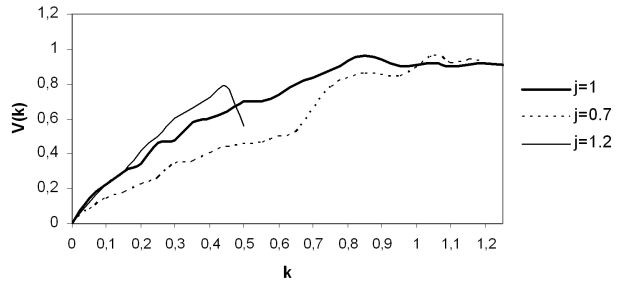

Fig. 5. Dependence of the packet velocity on the wave vector for different parameters j at $v = 1$

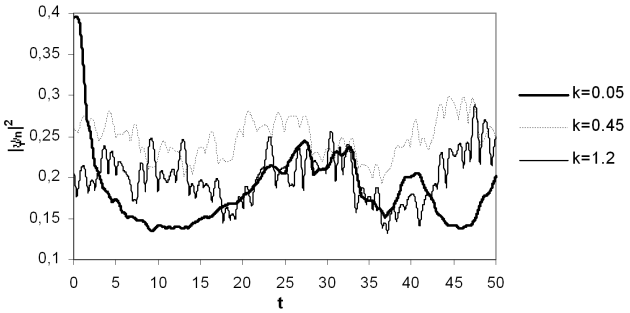

Fig. 6. Square of the maximum amplitude versus time for different values of k and $v = 1$

3.2. Phonons with positive dispersion

In this case, the velocity as a function of k resembles that of a soliton created in the presence of acoustic phonons [10,11]. We have chosen quite a large value of the dispersion parameter ($v = 1$). For this reason, the main part of phonons radiated during the movement of a packet along the chain is separated from the soliton and, as a consequence, has a little influence on it. Thus, the movement velocity increases almost linearly with k and reaches its saturation (in reality, there are velocity oscillations even at small k that can be approximated, nevertheless, by a straight line). After that, the increase in k has almost no influence on the velocity, which is oscillating around the maximum value. Obviously, the packet must be destroyed at large k, but the observation of this process was not our goal, and the calculation was truncated prior to the packet begins to spread.

We have performed 3 circles of calculations for j=0.7, 1, and 1.2. The results are shown in Figs. 4 and 5. Fig. 4 presents the velocity versus the dispersion v, and Fig. 5 demonstrates the velocity dependence on the quasi-particle dispersion j for the steady dispersion of optical phonons $v = 1$.

A sudden jump at $k = 0.65$ seen in Fig.5 ($j = 0.7$) is due to the twice larger increment Δk taken in calculations, which created an essential energy excess. If the increment was not increased, the graphs for $j = 1$ and $j = 0.7$ would be almost identical and would differ only in their slop. The soliton velocity is proportional to the wave vector for relatively small values of this vector, i.e. for a small velocity. The proportion coefficient depends on the effective mass of the quasi-particle which depends on the resonant interaction energy J. This can be observed as different slopes of the curves in Fig. 5.

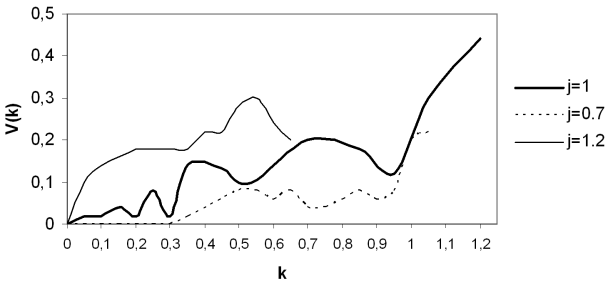

Fig. 7. Packet velocity versus the wave vector at $v = -0,04$ for various values of the parameter j

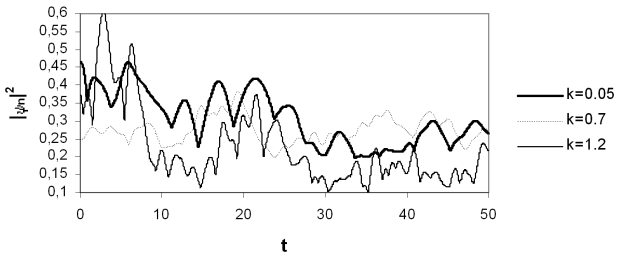

Fig. 8. Maximum wave-packet amplitude versus time for various wave vectors k at $v = -0.04$

Fig. 6 shows the maximum packet amplitude versus time for different values of k. Here, we have two periodic movements superimposed. The great period of the amplitude vibrations is related to the influence of the Peierls—Nabarro potential and the internode transitions of the packet. For a small dispersion, this period is inversely proportional to the quasi-particle velocity which is proportional to k (for small k).

The small period of the amplitude oscillations is due to the electron-phonon interaction. The period of these oscillations is related, to a significant extent, to the frequency of radiated phonons. In particular, for a positive dispersion, the frequency increases with k, whereas the period of oscillations decreases.

3.3. Phonons with negative dispersion

For phonons with a negative dispersion, we have chosen $v = -0.04$ and $v = -0.1$ at $j = 1$. The corresponding steady-state solutions were taken as the initial conditions (see Fig. 1)

Fig. 4 shows that the packet behaves itself almost as in the case of non-dispersive phonons. When the dispersion is small, the packet practically does not feel it. But, at $v = -0.1$, the packet delocalizes sooner due to the influence of the phonons created by it.

For a negative dispersion and different values of the parameter j, the packet behaves itself as in the case of a positive dispersion, but with the other behavior of the velocity (Fig. 7).

In this case, it can be seen that the dependence of the velocity on k has the oscillating character, which is characteristic of optical phonons. The jumps in the graphs correspond to a sudden increase in Δk, which is necessary for the calculations of this system which is very sensitive to phonons. This system requires the energy injections which prevent both the deceleration of a soliton and the appearance of oscillations (it is well seen in Fig. 4).

In addition, Fig. 8 shows the change of the wave-packet amplitude in time for a small velocity, the velocity in the local saturation region, and the critical velocity. As in the case of positive dispersion, we have the superposition of two periodic movements. The period of small vibrations related to the motion in the field of optical phonons decreases with the increase in k because, according to (5), the frequency of radiated phonons decreases. Because the total dispersion is smaller in this case than in the case of positive dispersion, the amplitude increases significantly and, at the same time, the influence of phonons also increases. The motion period in the Peierls—Nabarro potential is smaller than that in the case of positive dispersion.

3.4. Dependence of the critical value of the wave vector on dispersion

The numerical calculations show that, for different parameters v and j, the critical values of the wave vector k that correspond to the final delocalization of the wave packet are different. It is worth noting that the packet delocalizes much sooner at $j = 1.2$ than at $j \leq 1$ (Figs. 5 and 7). Moreover, one can see from Fig.6 that the critical value of k depends on the phonon dispersion parameter v. The determination of this dependence requires an additional analysis.

It should be noted that Hamiltonian (1) conserves the total wave vector (quasi-momentum) of the system which is a sum of the wave vectors of a quasi-particle and phonons. Therefore, the steady states of the Schrödinger equation with Hamiltonian (1) will correspond to a certain value of the total wave vector k with the energy $E(k)$. The steady-state solutions of Eqs. (2)—(4) [or their continual approximation (12)] with non-zero k correspond to the soliton states that move with the velocity $V = \frac{dE(k)}{dP}$, where $P = \hbar k$ is the total quasi-momentum. Knowing the function $E(k)$, one can analyze the soliton behavior upon the increase of its wave vector. For example, in the case of the soliton interaction with acoustic phonons, the continual approximation provides the exact solution which yields that, at small momenta, $E(P) \approx E(0) + P^2/2M_{\rm sol}$, while $E(P) \approx E^* + V_{\rm ac}P$ at large momenta, where V_{ac} is the velocity of acoustic waves. That is, the soliton velocity tends to the acoustic wave velocity with increase in the momentum and does not exceed it [20]. In addition, we can conclude that the increase in the wave vector shifts the balance between the dispersion and the nonlinearity towards the nonlinearity. Therefore, with increase in k, the soliton localization region will narrow, which also follows from the analytical solution in the continual approximation.

Unfortunately, we have no general analytical solution of Eqs. (12) in the case of optical phonons. But we can, nevertheless, make some conclusions about the dependence of E on k. We start from the qualitative considerations of Haken, which are presented in [21]. In the general case, one-particle steady states of the Fröhlich Hamiltonian can be decomposed over the full system of eigenfunctions of the non-interactive Hamiltonian. Every term of this decomposition corresponds to the eigenvalue of the non-interactive Hamiltonian with a certain number of phonons,

$$E(k, \{n_q\}) = E(p) + \sum_q \hbar\Omega(q) n_q. \tag{27}$$

Here, due to the conservation of the total momentum, the wave vectors of the quasi-particle, p, and the phonons, q, satisfy the condition

$$k = p + \sum_q q n_q. \tag{28}$$

Here, n_q is the number of phonons with the wave vector q.

It can be seen that, at $E - E(0) < \hbar\Omega_{\rm min}$, there is only one phononless state $E_0(k, 0) = E(k)$ for each k. Buut, at $E - E(0) \geq \hbar\Omega_{\rm min}$, there are many states

(a quasi-continuum) starting from one-phonon states $E_1(k,1_q) = E(k-q) + \hbar\Omega(q)$ with different q. The interaction operator in (1) links unperturbed states with the same total wave vector. The term $H_{\rm int}$ will shift unperturbed energy levels and will split them at the points of their intersection.

In order to apply these considerations, it is convenient to pass in Eqs. (2)—(4) to the quasi-momentum representation: $f_n = (1/\sqrt{N})\sum\limits_p \exp(ipna)f(p)$. In addition, using the transformation

$$u(q) = \sqrt{\frac{\hbar}{2M\Omega(q)}}[\beta(q) + \beta^*(q)],$$

$$p(q) = -i\sqrt{\frac{\hbar M\Omega(q)}{2}}[\beta(q) - \beta^*(-q)] \qquad (29)$$

we introduce new phonon variables $\beta(q)$. Thus, Eqs. (2)—(4) take the form

$$i\hbar\frac{d\psi(p)}{dt} = E(p)\psi(p) + \frac{1}{\sqrt{N}}\sum_q G(q)[\beta(q)+$$

$$+\beta^*(-q)]\psi(p-q),$$

$$i\hbar\frac{d\beta(q)}{dt} = \hbar\Omega(q)\beta(q) + \frac{G(q)}{\sqrt{N}}\sum_{p'}\psi^*(p'-q)\psi(p'), \qquad (30)$$

where $E(p)$ and $\Omega(q)$ are determined by formulas (5) and (6), and

$$G(q) = \chi\sqrt{\frac{\hbar}{2M\Omega(q)}}. \qquad (31)$$

In the absence of the interaction ($G = 0$), the function $\psi_0(p) = \exp -iE(p)t/\hbar$ corresponds to the phononless state, and the functions $\psi_1 = \beta(q)\psi_0(p) = \exp\{-i[E(p) + \hbar\Omega(q)]t/\hbar\}$ to one-phonon states. Let us reduce the problem to the problem of the effective interaction of these states. Consider $\psi_0(k)$ that corresponds to the phononless state with a total wave vector k. The first equation in (30) yields that the interaction generates the appearance of one-phonon states $\psi_1(k,q) = \beta(q)\psi_0(k-q)$. Among all these states, the main contribution to the interaction with a phononless state is given by the state with the nearest energy. Thus, the sum over all one-phonon states in the equation for $\psi_0(k)$ is approximated by the effective interaction with only one state $\psi_1(k) = \beta(q_0)\psi_0(k-q_0)$ with q_0, which corresponds to the minimal energy of the one-phonon state for a given k. Then we can retain only functions $\psi_0(k)$ and $\psi_0(k-q_0)$ in the equations. It follows from the second equation in (30) that $\beta(-q_0) = 0$. In the equation for $\psi_1(k)$ which follows from (30), we neglect the terms quadratic in $\beta(q)$, which correspond to two-photon states. We also take into account that, in the zero approximation, $|\psi_0(k-q_0)|^2 = 1$. Thus, we obtain the following system of equations:

$$i\hbar\frac{d\psi_0(k)}{dt} = E(k)\psi_0(k) + G\psi_1(k),$$

$$i\hbar\frac{d\psi_1(k)}{dt} = [E(k-q_0) + \hbar\Omega(q_0)]\psi_1(k) + G\psi_0(k). \qquad (32)$$

This system of equation corresponds to the effective Hamiltonian

$$H = E_0\psi_0^*\psi_0 + E_1\psi_1^*\psi_1 + G(\psi_0^*\psi_1 + \psi_1^*\psi_0),$$

where $G = G(q_0)$, $E_0 = E(k)$ and $E_1 = E(k-q_0) + \hbar\Omega(q_0)$.

Let us reduce this quadratic form to the diagonal representation in order to obtain the energies corresponding to the new states ϕ_0 and ϕ_1 of the bound system. To this end, we carry out the unitary transformation

$$\psi_0 = \phi_0\cos\theta + \phi_1\sin\theta,$$

$$\psi_1 = -\phi_0\sin\theta + \phi_1\cos\theta$$

which reduces the Hamiltonian to the diagonal form for values of the transformation variable θ that obey the condition

$$\mathrm{tg}2\theta = \frac{2g}{E_1 - E_0}$$

Thus, we have

$$H = \varepsilon_0\phi_0^*\phi_0 + \varepsilon_1\phi_1^*\phi_1.$$

If the energy is reckoned from the band bottom and is measured in the units of $\hbar\Omega_0$, the corresponding dimensionless energies are expressed as

$$\varepsilon_0 = \frac{1}{2}\left[E_0 + E_1 - \sqrt{4g^2 + (E_1 - E_0)^2}\right], \qquad (33)$$

$$\varepsilon_1 = \frac{1}{2}\left[E_0 + E_1 + \sqrt{4g^2 + (E_1 - E_0)^2}\right], \qquad (34)$$

where $E_0 = 4j\sin^2(\frac{k}{2}) \approx jk^2$,

$$E_1 = 4j\sin^2(\frac{k-q_0}{2}) + \sqrt{1 + 4v\sin^2(\frac{q_0}{2})} \approx$$

$$\approx j(k-q_0)^2+\sqrt{1+vq_0^2}, \tag{35}$$

$$g=\frac{g_0}{\sqrt{2c_0\sqrt{1+vq_0^2}}}.$$

Namely ε_0 is the required energy which defines the qualitative dependence of the ground state energy of the quasi-particle on the total momentum.

The value of q_0 is found from the condition that $E_1 \to \min$, i.e. $\frac{\partial E_1}{\partial q}=0$. For non-dispersive phonons, $q_0=k$, and we obtain that the ground state energy

$$\varepsilon(k)=\frac{1}{2}\left[1+4j\sin^2\frac{k}{2}-\sqrt{(1-4j\sin^2\frac{k}{2})^2+4g^2}\right]. \tag{36}$$

In the case of dispersive phonons, we use a long-wavelength approximation ($k<1$) in (35). For a weak dispersion, we obtain

$$q_0\approx\frac{2jk}{2j+v}, \tag{37}$$

and the energy dependence on the full wave vector will be given by Eq. (33) with

$$E_0=jk^2, E_1=\frac{jv^2}{(2j+v)^2}k^2+\sqrt{1+\frac{4j^2v}{(2j+v)^2}k^2}. \tag{38}$$

The quantity $d\varepsilon/dp$ has the meaning of a quasi-particle velocity and is shown in Fig. 9. It follows from this figure that the soliton velocity reaches the maximum value at a certain wave vector. Namely this value of the quasi-momentum is the critical value of the wave vector that corresponds to the soliton delocalization. It is seen that, for the positive dispersion, the delocalization occurs sooner for bigger j. Namely this was observed in the numerical experiment (Fig. 5).

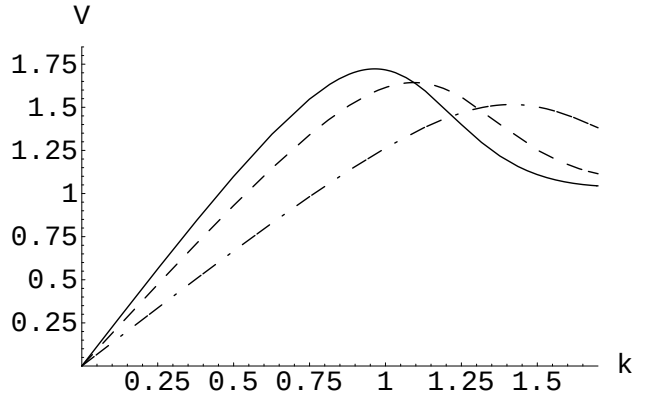

Fig. 9. Wave packet velocity versus k for different values of the parameter j at $v=1$

4. Conclusions

Thus, according to the numerical modeling of the discrete system of equations that describes a molecular chain containing a quasi-particle interacting with optical phonons, the self-trapping of the quasi-particle in a soliton-like state takes place in a wide range of the parameters of the model. Such a soliton can move along the chain with a velocity that increases with the quasi-momentum k, until it reaches a saturation value. This maximum soliton velocity and the value of the corresponding quasi-momentum strongly depend on the system parameters.

During the motion along the chain, the soliton generates the vibrations of the lattice nodes which influence, in turn, the soliton dynamics. The time dependence of the maximum soliton amplitude shows that the soliton motion is a superposition of the two periodic motions which can be interpreted as the motion in the Peierls—Nabarro relief and the motion in the field of optical phonons. Namely for this reason, the soliton velocity dependence on the quasi-momentum is not monotonic, but has the oscillation character that depends on the history of the acceleration of the soliton. For small quasi-momenta, the main mechanism of the motion of a not very narrow soliton is the over-barrier motion in the Peierls—Nabarro relief. In the case of optical phonons, the delocalization region of the soliton always contains vibrations generated by the soliton. But, in the case of a non-zero phonon dispersion, a part of these vibrations can be transferred along the chain. Thus, the vibrations generated by the soliton have an essensial influence on the soliton dynamics. (For comparison: in the case of the interaction of a quasi-particle with acoustic phonons, the vibrations generated by the soliton propagate in the chain with a sound velocity and spread away from the localization region of the soliton. Thus, these vibrations do not influence significantly the soliton dynamics). However, when k increases further, there is a moment when the packet starts to decay because the role of the under-barrier tunnelling of a quasi-particle through the Peierls—Nabarro barrier increases with k. Upon the under-barrier tunnelling, the effective dispersion of the wave packet increases, which leads to the separation of the quasi-particle from the deformation, which results in the destruction of the soliton.

In the case of dispersionless phonons, the vibrations of lattice nodes do not produce a wave and do not propagate along the chain. Therefore, these vibrations always influence the soliton which generates them. Under the positive phonon dispersion, the influence of phonons is less significant, because the lattice disturbances caused by the soliton motion are separated from the soliton with a certain velocity. Therefore, the soliton velocity after reaching the saturation remains practically the same in a larger interval of k in comparison with the case of dispersionless phonons.

Our calculations show that, independently of the dispersion of optical phonons in the chain, a self-trapped particle can propagate along a chain over distances of the order of few dozens of nanometers without essential delocalization or energy losses for parameters of the model that are close to those of alpha-helical protein molecules. Such a stability of the quasi-particle can ensure the transport processes of the charge or energy in real proteins.

1. *Excitons*/ Ed. by E.I. Rashba, M.D.Sturge. — Amsterdam: North-Holland, 1982.
2. *Alexandrov A.S., Mott N.* Polarons and Bipolarons. — Singapore: World Scientific, 1996.
3. *Davydov A.S.* Solitons in Molecular Systems. — Dordrecht: Reidel, 1985.
4. *Brizhik L.S., Eremko A.A.*//Synth. Met. — 2000. — **109**, N1—3. — P.117—121.
5. *Scott A.C.*//Phys. Repts. — 1992. — **217**. — P.1—67.
6. *Brizhik L.S.*//Ukr. Fiz. Zh. — 2003. — **48**, N.7. — P.611—622.
7. *Hyman J.M., McLaughlin D.W., Scott A.C.*//Physica. — 1981. — **3D**. — P.23—45.
8. *Scott A.C.*//Phys. Rev. A. — 1982. — **26**. — P.578—595.
9. *Davydov A.S., Enolsky V.Z.* //Zh. Eksp. Teor. Fiz. — 1973. — **110**, N 3. — C.453—454.
10. *Brizhik L., Cruzeiro-Hansson L., Eremko A., Olkhovska Yu.* //Phys. Rev. B. — 2000. — **61**, N 2. — P.1129—1141.
11. *Brizhik L., Cruzeiro-Hansson L., Eremko A., Olkhovska Yu.*//Ukr. Fiz. Zh. — 2003. — **48**, N7. — P.667—671.
12. *Peierls R.E.*// Proc. Phys. Soc. (London). — 1940. — **52**. — P.23—34.
13. Nabarro F.R.N.// Ibid. — 1947. — **59**. — P.256—272.
14. Kuprievich V.A.//Physica. — 1985. — **D 14**. — P.395—402.
15. Kuprievich V.A.//Teor. Mat. Fiz. — **64**, N 2. — P.269—276.
16. Kuprievich V. A.//Ukr. Fiz. Zh. — 1985. — **30**, N 7. — C. 972—977.
17. Vakhnenko O.O., Gaididei Yu.B.// Teor. Mat. Fiz. — 1986. — **68**, No. 3. — P.350—359.
18. *Vakhnenko O.O., Vakhnenko V.O.*// Phys. Lett. A. — 1995. — **196**. — P. 307—312.
19. *Kuprievich V.A., Kudritskaya Z.G., Shramko O.V.*// Ukr. Fiz. Zh. — 1984. — **32**, N 4. — P. 498—505.
20. *Davydov A.S., Kislukha N.I.*//Zh. Eksp. Teor. Fiz. — 1976. — **71**, Iss. 9. — P. 1090—1098.
21. *Kislukha N.I.*// Ukr. Fiz. Zh. — 1976. — **21**, N 5. — P. 829—836.
22. *Haken H.*// Z. Phys. — 1954. — **139**. — P. 66.
23. *Polarons* /Ed. by Yu.A. Firsov. — Moscow: Nauka, 1975 (in Russian).

Received 21.04.05.
Translated from Ukrainian by M. Shendeleva

АВТОЛОКАЛІЗАЦІЯ КВАЗІЧАСТИНКИ ТА ЇЇ ДИНАМІКА В ОДНОВИМІРНОМУ МОЛЕКУЛЯРНОМУ ЛАНЦЮЖКУ З УРАХУВАННЯМ ВЗАЄМОДІЇ З ОПТИЧНИМИ ФОНОНАМИ

Ю.Е. Натанзон, Л.С. Брижик, О.О. Єремко

Р е з ю м е

Досліджено умови автолокалізації квазічастинки в молекулярному ланцюжку з урахуванням її взаємодії з оптичними фононами за відсутності та наявності їх дисперсії. Досліджено динамічні властивості такого солітоноподібного стану квазічастинки в залежності від параметрів задачі. Розраховано та проаналізовано залежність швидкості солітона від хвильового вектора та визначено стабільність солітона в залежності від значень параметрів задачі. Показано, що зі збільшенням квазіімпульсу швидкість солітона зростає, досягаючи деякого насичення. Швидкість солітона є осцилюючою функцією квазіімпульсу, що зумовлено наявністю рельєфу Пайєрлса—Набарро та впливом генерованих солітоном оптичних фононів. Показано, що квазічастинка автолокалізується та є динамічно стійкою при значеннях хвильового вектора, менших за деяке критичне. Встановлено, що при відповідних значеннях параметрів для альфа-спіральних білків квазічастинка може ефективно поширюватись на відстань у десятки нанометрів без помітної втрати енергії та зберігаючи форму огинаючої пакета.