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Bound States of Envelope and Boussinesq Solitons in Anharmonic Lattices

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Abstract

We investigate a soliton charge and energy transport in anharmonic molecular systems and show that at large enough anharmonicity parameter there are two kinds of envelope solitons, one of which is a Davydov soliton. It has the usual one-bell shape and may exist at any anharmonicity. The other kind has a two-bell shape. The two-bell shape is a bound state of Davydov and Boussinesq solitons. It is caused by excitation (electron) tunnelling in the effective lattice potential.

1. Introduction

In the last few years an interesting branch of nonlinear research has appeared: charge and energy transport in highly anharmonic lattices. This direction is rather new because until recently the main interest was in systems where the interaction of charge or energy carriers with a lattice is so weak or the elasticity of the lattice so strong, that the lattice deformation caused by an electron or exciton may be considered in the harmonic approximation. If the anharmonic terms in the lattice potential are small enough they do not play any esential role in the transport phenomena determined by new nonlinear carriers like polarons, solitons, charge–density waves etc. [1–3]. But if one is interested in transport phenomena in materials with a strong carrier–lattice interaction and does not suppose that the lattice is rigid (high-T_c superconductors, molecular crystals and aggregates, biological systems) or one studies a motion of the lattice under extreme conditions (e.g. at supersonic velocities) deformation can not be considered small and anharmonic terms must be taken into account. For instance, there is strong evidence [4, 5] that there is a correlation between structural instability, high-anharmonicity of oxygen-vibrations in high-T_c superconductors and their phase transition temperature. Anharmonic interactions play a role in the dynamics of DNA and the possibility that they might concentrate vibrational energy in DNA into soliton-like objects was developed by several authors [6–11]. In particular, modelling DNA as a Toda lattice with a transversal degree of freedom the importance of nonlinear coupling between longitudinal and transversal motion was demonstrated [12–14].

Nonlinear lattice interactions also play an important role in the supersonic soliton energy and charge transport in molecular systems. As it is well known, the Davydov soliton is a nonlinear excitation which is a result of interaction of charge or energy carrier with acoustic phonons and its velocity can not exceed the sound velocity of the crystal. To overcome the velocity barrier one should take into account an anharmonicity of the lattice. Recently this was done in Ref. [15, 16] where the experiments on energy transfer in Langmuir–Blodgett–Scheibe aggregates [17, 18], were discussed in terms of supersonic electronic excitations which interact with Toda lattice solitons.

Anharmonic terms in the lattice potential as well as effects of the acoustic phonon phase velocity dispersion were taken into account in our recent paper [19], where we have shown that the ultrasonic Davydov model reduces to the Hénon-Heiles system [20]. We found a new family of elliptic solitons which carry energy with a velocity exceeding the sound velocity.

In the present paper we investigate envelope solitons in an anharmonic lattice for arbitrary velocities. In the following section we develop the dynamic equations for a quantum particle (excitation or electron) interacting with deformations of the crystal. The travelling wave assumption leads to a generalized Hénon–Heiles system, which represents an effective mechanical system with two degrees of freedom, but the kinetic energy of one of the degrees of freedom is negative.

In Section 3 we investigate soliton solutions of the completely integrable case of the generalized Hénon–Heiles system. We study the shape of the solutions and discuss their physical meaning. We show that a new soliton state may exist in anharmonic lattices: a bound state of Davydov and Boussinesq solitons. It is caused by the excitation (electron) tunneling in the effective two-well potential which is created by the exciton (electron)–phonon interaction and anharmonic terms in the lattice potential.

In Section 4 our calculations of soliton energies for the completely integrable case are presented.

In Section 5 a variational approach is developed to study the solitons in anharmonic lattices far from the completely integrable case.

In Section 6 the dynamical stability of the new two-soliton state is tested by means of numerical simulations. We show that a breather-like motion takes place in the second kind of soliton state.

2. Davydov solitons in anharmonic lattice

Let us consider excitation energy transport in anharmonic molecular crystals. Note that although we shall mainly talk about energy transport, all our conclusions are also valid for the transport of an excess electron [1]. The Hamiltonian of the system has the form

$$H = -J \sum_n (\Psi_n^*(\Psi_{n+1} + \Psi_{n-1}) - 2|\Psi_n|^2) + \chi \sum_n |\Psi_n|^2(\beta_{n+1} - \beta_{n-1}) + \frac{1}{2}\sum_n \left(M\left(\frac{d\beta_n}{dt}\right)^2 + w(\beta_{n+1} - \beta_n)^2 - \frac{2}{3}\alpha w(\beta_{n+1} - \beta_n)^2 \right). \quad (2.1)$$

Here $\Psi_n(t)$ is the excitation function of the molecule at site n, $\beta_n(t)$ is the displacement of the nth molecule, J is the matrix element of the excitation transition, the constant χ characterizes the exciton-displacement interaction, M is the mass of a molecule, the parameters w and α characterize the elasticity and anharmonicity of the lattice correspondingly.

The equations of motion for $\Psi_n(t)$ and $\beta_n(t)$ are

$$i\hbar \frac{d}{dt}\Psi_n(t) = -J(\Psi_{n+1} + \Psi_{n-1} - 2\Psi_n) + \chi(\delta\beta_{n+1} - \beta_{n-1})\Psi_n, \quad (2.2)$$

$$M\frac{d^2\beta_n}{dt^2} = w(\beta_{n+1} + \beta_{n-1} - 2\beta_n)(1 - \alpha(\beta_{n+1} - \beta_{n-1})) + \chi(|\Psi_{n+1}|^2 - |\Psi_{n-1}|^2). \quad (2.3)$$

We shall seek solutions of eqs (2.2) and (2.3) in the form of envelope solitons:

$$\Psi_n(t) = e^{iKnl}\Psi(nl, t), \quad \beta_n(t) = \beta(nl, t)$$

where K is the carrier wave vector, l denotes the lattice constant and $\Psi(nl, t)$ as well as $\beta(nl, t)$ are smooth functions of the continuous variable $x = nl$. In this case eqs (2.2) and (2.3) take the form

$$i\hbar\frac{\partial}{\partial t}\Psi = E(K)\Psi - i\hbar v_g(K)\frac{\partial}{\partial x}\Psi - J(K)l^2\frac{\partial^2}{\partial x^2}\Psi + 2\chi l\frac{\partial\beta}{\partial x}\Psi, \quad (2.4)$$

$$M\frac{\partial^2}{\partial t^2}\beta = l\frac{\partial}{\partial x}\left\{ w\left(1 + \frac{1}{12}l^2\frac{\partial^2}{\partial x^2}\right) l\frac{\partial\beta}{\partial x} - \alpha w\left(l\frac{\partial\beta}{\partial x}\right)^2 + 2\chi|\Psi|^2 \right\}. \quad (2.5)$$

Here $J(K) = J\cos(Kl)$, $E(K) = 2(J(0) - J(K))$ is the excitation energy, $v_g(K) = (1/\hbar)(dE(K)/dK)$ is the group velocity. The term $(l^2/12)(\partial^2/\partial X^2)$ in the r.h.s. of the eq. (2.5) takes into account a dispersion of the acoustic phonon group velocity.

The Hamiltonian (2.1) conserves the number of excitations in the crystal. We shall assume that there is only one excitation. Thus the normalization condition for the wave function $\Psi(x, t)$ becomes

$$\frac{1}{l}\int_{-\infty}^{\infty} dx\,|\Psi(x, t)|^2 = 1. \quad (2.6)$$

We shall consider solutions of eqs (2.4) and (2.5) in the form of travelling waves

$$\Psi(x, t) = \left(\frac{J(K)w}{24\chi^2}\right)^{1/2} e^{i(QX - \Omega t)}\phi(\theta),$$

$$\beta(x, t) = \beta(\theta), \quad \frac{\partial\beta}{\partial x} = -\frac{J(K)}{\chi}u(\theta), \quad (2.7)$$

where $\theta = (1/l)(x - vt)$, v is the wave velocity, $Q = (\hbar/2J(K)l^2)(v - v_g(K))$ is the wave vector and Ω is the carrier frequency, $\phi(\theta)$ is the envelope function, and $u(\theta)$ is a strain function. Inserting (2.7) into eqs (2.4) and (2.5) gives

$$\ddot{\phi} + 2u\phi - A\phi = 0, \quad (2.8)$$

$$\frac{d^2}{d\theta^2}(\ddot{u} - 4cu + gu^2 - \phi^2) = 0, \quad (2.9)$$

where the parameters A, c and g are given by

$$A = \frac{1}{J(K)}\left(E(K) + \frac{\hbar^2(v^2 - v_g^2(K))}{4l^2J(K)} - \hbar\Omega\right),$$

$$c = 3\left(\frac{v^2}{v_0^2} - 1\right), \quad g = \frac{12\alpha J(K)}{\chi}, \quad (2.10)$$

$v_0 = l(w/M)^{1/2}$ is the sound velocity and the dots denote differentiation with respect to θ. We want to consider both supersonic and subsonic solitons. So, the sign of c may change: for supersonic solitons ($v > v_0$) the parameter c is positive and in the case of subsonic solitons ($v > v_0$) it is negative. We shall assume that the effective mass of excitation is positive, i.e. $J > 0$ and consider the carrier wave vectors K in the interval $0 \leqslant Kl < \Pi/2$.

Under the boundary conditions

$$\dot{u}(\pm\infty) = \ddot{u}(\pm\infty) = \dddot{u}(\pm\infty) = \phi(\pm\infty) = \dot{\phi}(\pm\infty) = 0$$

integrating eq. (2.9) twice with respect to θ yields

$$\ddot{u} - 4cu + gu^2 - \phi^2 = U, \quad (2.11)$$

where $U = gu^2(-\infty) - 4cu(-\infty)$ is the integration constant. $U = 0$ if the boundaries of the crystal are free. $U \neq 0$ if an external force is applied at one of boundaries of the crystal. We consider the case $U = 0$.

It is interesting to note that the set of equations

$$\ddot{\phi} + 2u\phi - A\phi = 0, \quad -\ddot{u} + 4cu - gu^2 + \phi^2 = 0, \quad (2.12)$$

corresponds to a mechanical system with the Lagrange function

$$L = T - V \quad (2.13)$$

where

$$T = \frac{1}{2}(\dot{\phi}^2 - \dot{u}^2) \quad (2.14)$$

is the effective kinetic energy and

$$V = -\frac{1}{2}A\phi^2 + 2cu^2 + \phi^2 u - \frac{1}{3}gu^3 \quad (2.15)$$

is the potential function. We see from eqs (2.13)–(2.15) that Davydov solitons in an anharmonic lattice are described by the Hénon–Heiles like Lagrangian. But in contrast to the ordinary Hénon–Heiles system [20] the mass of one of the degrees of freedom is negative in our case.

It is worth noting that eqs (2.4) and (2.5) as well as their reduced form (2.8) and (2.9) have arisen already in the study of nonlinear wave propagation in a plasma [21] and diatomic chains [22]. In plasma ψ denotes the amplitude of the Langmuir waves and β is the ion–density perturbation. But in contrast with our case in plasma the parameter g has a unique value: $g = -6$ [21]. In diatomic chains Ψ denotes the amplitude of the optical vibrations and coupled nonlinear equations for optical and acoustical degrees of freedom coincide with eqs (2.4) and (2.5) except when the mass of both particles in the effective kinetic energy is positive. We shall show that this peculiarity: different signs of masses and $g > 0$, influences the character of solitons in an essential manner.

3. Completely integrable case of the supersonic soliton problem

It is well known that the Hénon–Heiles system is not completely integrable [20]. However, in the following three cases (i) $A = 4c$, $g = 1$ [23], (ii) $4A = c$, $g = 16$ [24] and (iii) $g = 6$ and arbitrary A and c [25], it possesses a second integral of motion and in this way it is Lioville completely integrable.

We consider here the third case, i.e. we shall assume that there is a link $2\alpha J(K) = \chi$ between the anharmonicity constant, α, the exciton–phonon constant, χ, the matrix element of excitation hopping, J and the carrier wave vector, K. Note that for excitations with a large enough bandwidth: $2J > \chi/\alpha$ we can always choose the wave vector K to satisfy the above condition. We intend to investigate how the shape and energy of solitons depend on their velocity. (Conditions 1 and 2 for integrability can only be fulfilled for one velocity because the normalization condition imposes a link between parameters A and c.)

Introducing the parabolic coordinates

$$\phi = 2\sqrt{\mu_1\mu_2}, \quad u = \mu_1 + \mu_2 + c - A \tag{3.1}$$

we obtain for the Lagrange function (2.13)–(2.15) with $g = 6$ the expression

$$L = \frac{1}{2}(\mu_1 - \mu_2)\left(\frac{1}{\mu_2}\dot{\mu}_2^2 - \frac{1}{\mu_1}\dot{\mu}_1^2\right) - \frac{v(\mu_1) - v(\mu_2)}{\mu_1 - \mu_2} \tag{3.2}$$

where

$$v(\mu) = 2\mu(\mu - A + c)^2(A - \mu). \tag{3.3}$$

Using well known methods of analytical dynamics one can obtain that the problem of supersonic Davydov solitons reduces to the set of equations

$$\frac{d\mu_1}{\sqrt{w(\mu_1)}} = \frac{d\mu_2}{\sqrt{w(\mu_2)}} = \frac{d\theta}{2(\mu_1 - \mu_2)}, \tag{3.4}$$

where $w(\mu) \equiv I_1\mu^2 + I_2\mu + 8\mu v(\mu)$, I_1 and I_2 being integration constants.

As mentioned above we are interested in the case where

$$\phi, \quad u \to 0 \quad \text{at} \quad \theta \to \pm\infty. \tag{3.5}$$

In terms of parabolic coordinates (3.1) these boundary conditions become

$$\mu_1 \to 0, \quad \mu_2 \to A - c \quad \text{at} \quad \theta \to \pm\infty \tag{3.6}$$

or vice versa. Taking into account the boundary conditions (3.6) one may conclude that $I_1 = I_2 = 0$ and eqs (3.4) reduce to

$$\frac{d\mu_1}{\mu_1(\mu_1 - A + c)\sqrt{A - \mu_1}} = \frac{d\mu_2}{\mu_2(\mu_2 - A + c)\sqrt{A - \mu_2}} = \frac{2\,d\theta}{(\mu_1 - \mu_2)}. \tag{3.7}$$

Letting $\mu_1 = 0$ in eq. (3.7) (corresponding to a crystal without high frequency excitations, i.e. $\Psi_n = 0$), we obtain the solution

$$\phi = 0, \quad u_{\text{latt}} = c\,\text{sech}^2\sqrt{c}(\theta - \theta_0) \tag{3.8}$$

which corresponds to the so-called Boussinesq-soliton [13]. This exists at supersonic velocities and represents a lattice compression which moves along the chain without changing its shape. θ_0 is an integration constant.

Letting $\mu_2 = A - c$ in eq. (3.7) we obtain the solitonic wave function, $\phi(\theta)$, and deformation function $u(\theta)$ in the form

$$\phi = 2\sqrt{A(A - c)}\,\text{sech}\sqrt{A}(\theta - \theta_0) \tag{3.9}$$

$$u = A\,\text{sech}^2\sqrt{A}(\theta - \theta_0). \tag{3.10}$$

Note that $u = \phi^2/(4(A - c))$ only for $g = 6$. We see that this solution coincides with subsonic Davydov solitons [26]. However, it exists both at subsonic ($c < 0$) and at supersonic ($c > 0$) velocities. As in the subsonic case the excitation digs a well (3.10) and moves through the crystal together with it. We shall denote this solution a soliton of first kind.

In contrast to the first kind of solitons, a soliton of the second kind exists at supersonic velocities $c > 0$ ($v > v_0$). Its explicit shape can be obtained after a straightforward but tedious integration of eqs (3.7). As a result we get

$$\phi = 2\sqrt{A}(A - c)S^{-1}(\theta)\cosh\sqrt{c}(\theta - \theta_1), \tag{3.11}$$

$$u = \frac{d^2}{d\theta^2}\ln S(\theta), \tag{3.12}$$

where

$$S(\theta) = \sqrt{A}\cosh(\sqrt{c}(\theta - \theta_1))\cosh(\sqrt{A}(\theta - \theta_2)) - \sqrt{c}\sinh(\sqrt{c}(\theta - \theta_1))\sinh(\sqrt{A}(\theta - \theta_2)), \tag{3.13}$$

θ_1 and θ_2 being integration constants.

To obtain the parameter A that characterizes the soliton carrier frequency Ω, we use the normalization condition (2.6). Inserting the wave functions (3.9) and (3.11) into eq. (2.6) we get that for both types of solitons and for all integration constants θ_1 and θ_2, the condition

$$\sqrt{A}(A - c) = \Delta, \tag{3.14}$$

where $\Delta = 3\chi^2/J(K)w$.

So, we see from eq. (3.14) that

$$A \simeq 3\left(\frac{v_0^2}{v^2} - 1\right) + \frac{\Delta}{\sqrt{3}}\frac{v_0}{v} \quad \text{at } v \gg v_0, \tag{3.15}$$

and at subsonic velocities $v \ll v_0$, where only the first kind soliton exists,

$$A \simeq \left(1 + 2\frac{v^2}{v_0^2}\right)\frac{\Delta^2}{9} \quad \text{at } \Delta < 1 \tag{3.16}$$

and

$$A \simeq \Delta^{2/3} - 2\left(1 - \frac{v^2}{v_0^2}\right) \quad \text{at } \Delta > 1. \tag{3.17}$$

It is interesting to note that the deformation function, (3.12), has the form of the two-soliton solution of the KdV-equation [27] and can be approximately represented as

$$u(\theta) = c\ \mathrm{sech}^2\,[\sqrt{c}(\theta - \theta_1) - \delta] + A\ \mathrm{sech}^2\,[\sqrt{A}(\theta - \theta_2) + \delta] \tag{3.18}$$

where $\delta = \tanh^{-1}(\sqrt{c/A})$. So we can conclude that the excitation, $\phi(\theta)$, is similar to that of a quantum particle moving in two-well potential $-2u(\theta)$ (see eq. (2.8) and Fig. 1). One of the wells (first term in the r.h.s. of eq. (3.18)) is created by the lattice soliton (3.8). The second is caused by the interaction of the excitation with the lattice (second term in the r.h.s. of (3.18)). Part of the time the particle lives in the well that was dug by itself then it tunnels to the well that was created by the lattice soliton and so on. As a result of such a complicated behavior we obtain a solitonic wave function $\phi(\theta)$ in the form of eq. (3.11) (see Fig. 1). It is interesting to remark that at subsonic velocities $v^2 > v_0^2[1 + (0.5\Delta)^2]$, the soliton has a two-bell shape at any distance $|\theta_1 - \theta_2|$ between wells in the potential $-2u(\theta)$. However, the ratio between the maximal values

$$\Phi_1/\Phi_2 \sim \mathrm{sech}\,\sqrt{A}(\theta_1 - \theta_2) \quad \text{at } \sqrt{A}(\theta_1 - \theta_2) > 1.$$

Thus we may conclude that the major part of time the excitation (or electron) in this case spends in the well that was dug by itself. With an exponentially small rate it tunnels to the other well.

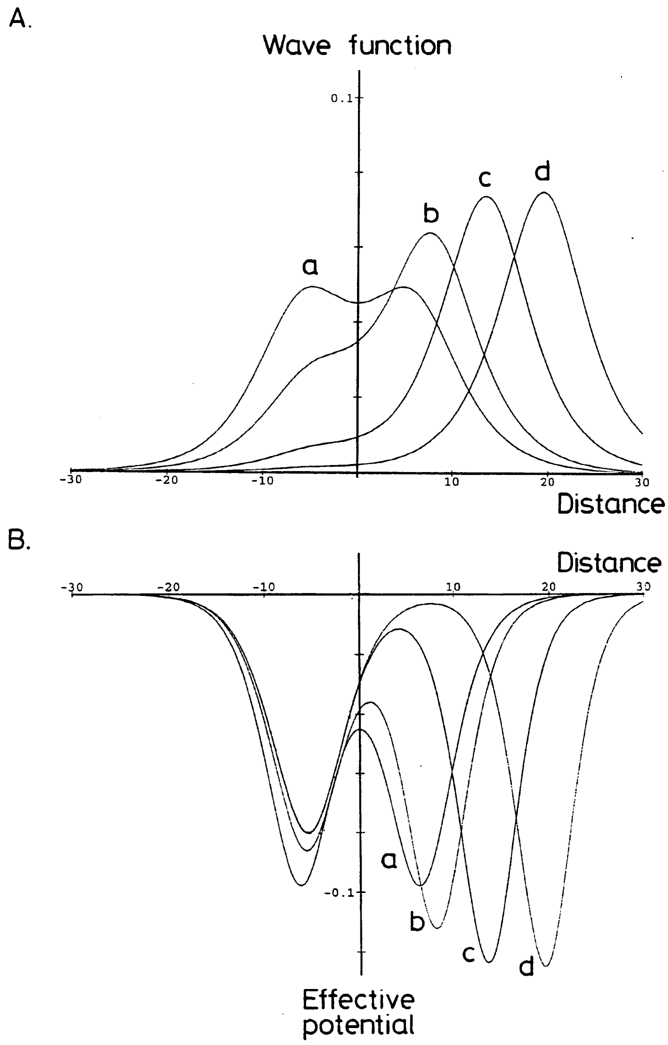


Fig. 1. A: Wave function $\phi(x)$ of the second kind of soliton and B: the effective potential function $-2u(x)$ for $A = 1/16$, $C = 1/25$ for different distances between Davydov and Boussinesq components of solition. a: $\theta_1 = \theta_2 = 0$; b: $\theta_1 = 3, \theta_2 = 0$; c: $\theta_1 = 9, \theta_2 = 0$; d: $\theta_1 = 15, \theta_2 = 0$.

4. Energy of solitons

To calculate the energies of solitons we introduce the travelling wave functions (2.7) into the Hamiltonian (2.1). For $g = 6$ we get

$$\varepsilon \equiv \frac{E}{J(K)} = \frac{1}{8\Delta}\left\{\varepsilon_{\mathrm{ex}}(v)\overline{\phi^2} - \frac{3}{10}A\overline{\phi^2} + 2(1 + 4c/15)(\overline{\phi^2} + 4c\bar{u})\right\} \tag{4.1}$$

where

$$\varepsilon_{\mathrm{ex}}(v) = \frac{1}{8J^2(K)}\left(\hbar^2\frac{v^2}{l^2} - E^2(K)\right).$$

is the exciton energy,

$$\overline{\phi^2} = \int_{-\infty}^{\infty} \mathrm{d}\theta\phi^2(\theta), \quad \bar{u} = \int_{-\infty}^{\infty} \mathrm{d}\theta u(\theta).$$

For the lattice soliton (3.8) we have

$$\overline{\phi^2} = 0, \quad \bar{u} \equiv u_{\mathrm{latt}} = 2\sqrt{c} \tag{4.2}$$

and

$$\varepsilon_{\mathrm{latt}} = \frac{2}{\Delta}\left(1 + \frac{4}{15}c\right)c^{3/2}. \tag{4.3}$$

This is the energy of the Boussinesq soliton.

In the case of the first kind of soliton, which is given by eqs (3.9) and (3.10), we obtain

$$\overline{\phi_I^2} = 8\Delta \quad \text{(normalization condition)},$$

$$\bar{u} \equiv u_I = 2\sqrt{A} \tag{4.4}$$

and its energy is given by the expression

$$\varepsilon_I = \varepsilon_{\mathrm{ex}}(v) + \frac{2}{5\Delta}\left(1 + 4\frac{v^2}{v_0^2}\right)A^{3/2} - \frac{3}{10}A. \tag{4.5}$$

Substitution of the expressions (3.15)–(3.17) for the dimensionless carrier frequency, A, into eq. (4.5) yields

$$\varepsilon_I = \varepsilon_{\mathrm{ex}}(v) - \left(1 - 1.2\frac{v^2}{v_0^2}\right)\frac{\Delta^2}{54} \quad \text{for } v \ll v_0 \tag{4.6}$$

and $\Delta < 1$,

$$\varepsilon_I = \varepsilon_{\mathrm{ex}}(v) + 4.8\frac{\sqrt{3}}{\Delta}\left(\frac{v}{v_0}\right)^5 \quad \text{for } v \gg v_0. \tag{4.7}$$

We see from these expressions that at small velocities, the soliton energy is less than the exciton energy. At high velocities the situation changes: for $v \gg v_0$ the exciton becomes more stable than the soliton. At sound velocity

$$\varepsilon_I - \varepsilon_{ex}\Big|_{v=v_0} = 2 - \frac{3}{10}\Delta^{2/3}.$$

In Fig. 2(a)–(d) the energy difference $\varepsilon_I - \varepsilon_{ex}$ is plotted as a function of the relative velocity u/v_0. It is seen that the supersonic soliton becomes energetically more favorable only when the coupling constant Δ exceeds the critical value $\Delta_c = (20/3)^{3/2}$.

For the soliton of the second kind we obtain from the expressions (3.11)–(3.13) that

$$\bar{u} \equiv u_{II} = u_I + u_{\text{latt}}, \quad \overline{\phi_{II}^2} = 8\Delta \tag{4.8}$$

$$\varepsilon_{II} = \varepsilon_I + \varepsilon_{\text{latt}}. \tag{4.9}$$

Thus the energy of the second kind soliton is a sum of the energy of the first kind soliton (the Davydov component of the second kind soliton) and the energy of the lattice soliton (the Boussinesq component). In the case under consideration, $g = 6$, the energy of the second kind soliton, ε_{II}, does not depend on the distance $|\theta_1 - \theta_2|$ between the components. However, as it will be shown below, this degeneration is not present for $g \neq 6$.

5. Variational approach

Assuming boundary conditions (3.5) the eigenvalue problem (2.12) is equivalent to the following variational problem. The functions $\phi(\theta)$ and $u(\theta)$ provide an extremum of the action

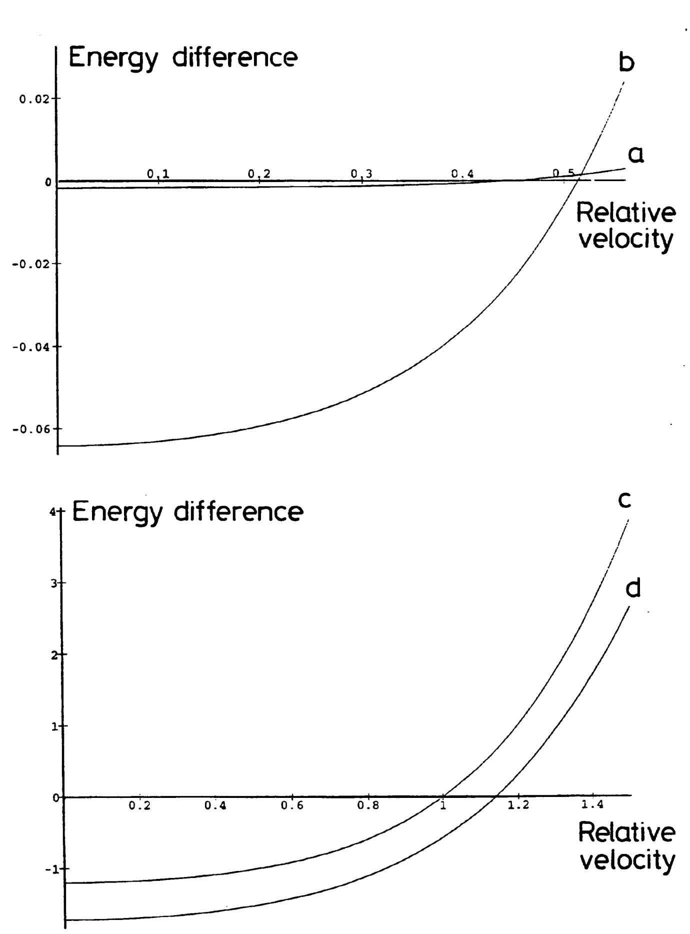


Fig. 2. Energy difference between soliton and exciton for different values of the coupling parameter Δ. a: $\Delta = 0.3$, b: $\Delta = 2$; c: $\Delta = (20/3)^{3/2}$; d: $\Delta = 25$.

functional

$$F = \int_{-\infty}^{\infty} d\theta L(\phi, u; \dot{\phi}, \dot{u}) \tag{5.1}$$

where the Lagrange function $L(\phi, u; \dot{\phi}, \dot{u})$ is defined by the eqs (2.13)–(2.15). The eqs (2.12) are in this way, the Euler–Lagrange equations for the functional (5.1).

In applying of this approach to our problem we are assuming that the shape of solitons in the case of arbitrary g is described by functions which are similar to the solutions of eq. (2.12) obtained in the completely integrable case $g = 6$. Therefore to investigate the first kind of solutions we employ the trial functions

$$\phi_I = 2\sqrt{\gamma z \Delta}\,\operatorname{sech}(\gamma z\theta), \quad u = \gamma^2 \operatorname{sech}^2(\gamma\theta) \tag{5.2}$$

where z and γ are variational parameters and the normalization condition (2.6) was taken into account. Introducing the trial functions (5.2) into the functional (5.1) we get

$$F_I = \frac{8}{3}\left\{\left(\frac{2}{3}g - 1\right)\frac{1}{5}\gamma^5 - c\gamma^3 + \frac{1}{2}\Delta\gamma^2 z^2 - 3\,\Delta\gamma^2 z \times \int_0^{\infty} d\theta \operatorname{sech}^2(z\theta)\operatorname{sech}^2\theta\right\} + 4\,\Delta A. \tag{5.3}$$

The extrema of the function (5.3) are determined by the equations

$$z = 6\int_0^{\infty} d\theta\theta \operatorname{sech}^2(z\theta)\tanh\theta \operatorname{sech}^2\theta, \tag{5.4}$$

$$\left(\frac{2}{3}g - 1\right)\gamma^4 - 3\gamma^2 c + \Delta\gamma z^2 = 6\,\Delta\gamma z\int_0^{\infty} d\theta \operatorname{sech}^2\theta \operatorname{sech}^2(z\theta). \tag{5.5}$$

The unique positive root of eq. (5.4) is $z = 1$ and eq. (5.5), as well as the expression (5.3) for the action function, take the form

$$\left(\frac{2}{3}g - 1\right)\gamma^3 - 3c\gamma = 3\,\Delta, \tag{5.6}$$

$$F_I = \frac{8}{3}\left[\left(\frac{2}{3}g - 1\right)\frac{1}{5}\gamma^5 - c\gamma^3 - \frac{3}{2}\Delta\gamma^2\right] + 4\,\Delta A. \tag{5.7}$$

It is seen that the subsonic velocities ($c < 0$) the positive root of the eq. (5.6) exists at any g. However, it exists at supersonic ($c > 0$) velocities only if $g > \frac{3}{2}$. Using the renormalization

$$\bar{c} = \frac{9}{2g - 3}c, \quad \bar{\Delta} = \frac{g}{2g - 3}\Delta \tag{5.8}$$

we obtain that $\gamma = \bar{A}$ where $\bar{A}$ is a root of eq. (3.14) in which $\Delta \to \bar{\Delta}$, $c \to \bar{c}$. Thus we may conclude that in the framework of our approach the shape of the first kind of solitons changes drastically only at $g \simeq \frac{3}{2}$. At $g > \frac{3}{2}$ the shape is described by the functions (3.9) and (3.10) with parameters renormalized according to the eq. (5.8).

It seems interesting to remark here that the parameter $\frac{2}{3}g - 1$ has a clear physical meaning. Indeed, taking into account the expressions (4.4) and (4.6) for the lattice distortion u_I and soliton energy ε_I one can obtain that

$$\frac{2}{3}g - 1 = \frac{E_{\text{anh}}}{E_{\text{b}}} - 1 \tag{5.9}$$

where $E_{\text{b}} = J(K)(\Delta^2/27)$ is the bound energy for an immobile soliton (this energy was obtained by assuming that the anharmonic term in the Hamiltonian (2.1) is absent), $E_{\text{anh}} = \frac{1}{3}\alpha w(Ju_I/\chi)^3$ is the anharmonic part of energy caused by creation of soliton. Thus the eq. (5.6) shows that one can expect the existence of supersonic solitons only in such systems where the soliton bound energy E_{b} is small as compared with the anharmonic energy E_{anh}.

Let us consider now the second kind of solitons. To do it we introduce the trial functions

$$\Phi_{II} = 2\sqrt{\gamma(\gamma^2 - \beta^2)\,\Delta}\cosh\beta(\theta - R)/S(\beta, \gamma, R; \theta)$$

$$u_{II} = \frac{\mathrm{d}^2}{\mathrm{d}\theta^2}\ln S(\beta, \gamma, R; \theta), \tag{5.10}$$

$$S(\beta, \gamma, R; \theta) = \gamma\cosh(\gamma\theta)\cosh\beta(\theta - R) - \beta\sinh(\gamma\theta)\sinh\beta(\theta - R)$$

where γ, $\beta(\gamma > \beta)$ and R are variational parameters. Inserting the functions (5.10) into eq. (5.1) we get that the functional F can be represented as a sum

$$F = F_I + F_{\text{latt}} + F_{\text{int}}. \tag{5.11}$$

Here, F_I is the action for the first kind of soliton;

$$F_{\text{latt}} = \frac{8}{3}\left[\left(\frac{2}{3}g - 1\right)\frac{1}{5}\beta^5 - c\beta^3\right] \tag{5.12}$$

is the action for the lattice Boussinesq-soliton:

$\phi = 0, \quad u_{\text{latt}} = \beta^2\,\text{sech}^2(\beta\theta);$

and

$$F_{\text{int}} = \frac{4}{9}(g - 6)\left\{(\gamma^2 - \beta^2)\times\int_{-\infty}^{\infty}\frac{\text{sech}^2(\gamma x)\,\mathrm{d}x}{[\gamma - \beta\tanh(\gamma x)\tanh\beta(x - R)]^3} - 2\right\}\times\gamma^3(\gamma^2 - \beta^2) \tag{5.13}$$

is the part of the total action which corresponds to the interaction between the Davydov and Boussinesq component of the soliton. Note that the parameter R denotes the distance between the components. At small tanh (βR) eq. (5.13) takes the form

$$F_{\text{int}}(R) = F_{\text{int}}(0) + \frac{4}{9}(g - 6)\gamma^5 B\left(\frac{\beta}{\gamma}\right)\tanh^2(\beta R) \tag{5.14}$$

where the positive coefficient $B(\eta)$ is defined by the expressions

$$B(\eta) = \begin{cases} 12(1 - \eta) & \text{at } 1 - \eta \ll 1, \\ 7\eta^2 & \text{at } \eta \ll 1. \end{cases}$$

At large βR and $\beta \ll \gamma$

$$F_{\text{int}} = -\frac{4}{9}(g - 6)\gamma^3\beta^2\,\text{sech}^2(\beta R). \tag{5.15}$$

Introducing the functions (5.13) into the Hamiltonian H one can obtain that the energy of the second kind of soliton can be represented at arbitrary g as follows

$$\varepsilon_{II} = \varepsilon_I + \varepsilon_{\text{latt}} + \frac{1}{8\Delta}F_{\text{int}} \tag{5.16}$$

where

$$\varepsilon_I = \frac{1}{8\Delta}\left(F_I + 16\left(1 + \frac{c}{3}\right)\gamma^3\right) \tag{5.17}$$

is the energy of the Davydov component (the first kind of soliton)

$$\varepsilon_{\text{latt}} = \frac{1}{8\Delta}\left(F_{\text{latt}} + 16\left(1 + \frac{c}{3}\right)\beta^3\right) \tag{5.18}$$

is the energy of the Boussinesq soliton.

As it is seen from the eqs (5.13)–(5.16) the Davydov and Boussinesq solitons repel each other at $g < 6$ and the energy (5.16) reduces to the sum $\varepsilon_I + \varepsilon_{\text{latt}}$. In the case $g > 6$ the action (5.11) as well as the energy (5.16) is a function of R and has a minimum at $R = 0$. We can therefore reach a conclusion that the second kind of soliton at $g > 6$ is a bound state of the Davydov and Boussinesq soliton. The action (5.11) in this case takes the form

$$F_{II} = F_I + F_{\text{latt}} - \frac{4}{9}(g - 6)\gamma^3\beta^2 \tag{5.19}$$

for $\beta \ll \gamma$. The extrema of the function (5.19) are determined by the equations

$$\left(\frac{2}{3}g - 1\right)\gamma^3 - 3c\gamma = \frac{1}{2}(g - 6)\beta^2\gamma + 3\Delta, \tag{5.20}$$

$$\left(\frac{2}{3}g - 1\right)\beta^3 - 3\beta c = \frac{1}{3}(g - 6)\gamma^3. \tag{5.21}$$

For $c \to 0$

$$\beta \simeq \left(\frac{g - 6}{2g - 3}\right)^{1/3}\gamma, \quad \gamma \simeq \left[1 - \frac{3}{2}\left(\frac{g - 6}{2g - 3}\right)^{5/3}\right]^{-1}\Delta.$$

So the Boussinesq component does not disappear now at the sound velocity. Moreover, in contrast with the case $g = 6$, for $g > 6$ the second kind of soliton may exist both at supersonic and subsonic velocities and for slow solitons e.g. $(v < v_0)$ and $\Delta \ll 1$ we obtain from the eqs (5.20)–(5.21) that

$$\gamma \simeq \frac{\Delta}{|c|}, \quad \beta \simeq \frac{g - 6}{9c^4}\Delta^3.$$

Thus in the framework of our variational approach we may conclude that in highly anharmonic systems where $g > 6$ (or in other words, $E_{\text{anh}} > 4E_{\text{b}}$ (see eq. (5.9)) two kinds of envelope solitons can exist: a Davydov soliton and a bound state of Davydov and Boussinesq solitons.

6. Numerical results

The dynamical stability of states of the Davydov and Boussinesq solitons was studied numerically. In our numerical simulations we used periodic boundary conditions. For integrating the eqs (2.2) and (2.3) we used an eight order deterministic Runge–Kutta Scheme (due to Dormand and Prince [28] with a step size control). In terms of the dimensionless time $\tau = \sqrt{(w/M)}\,t$ our timestep was fixed at $\Delta\tau = 0.9$–1.0 and the size of the system was 70 or 100 sites. The conservation of the total energy of the system (up to 0.2%) and the normalization condition (2.6) (up to 0.5%) kept control over the accuracy of the numerical simulations. The imaginary part of the energy, which can occur due to numerical inaccuracies, was zero within an accuracy of 10^{-19}. The solitary excitations for simulations were created by placing the solution (3.11)–(3.13) in the chain and letting the system evolve.

The velocity v was chosen equal to the group velocity $v_g(K)$: $v = v_g(K)$. We investigate supersonic solitons and let $v_g(K) = 1.05v_0$. We choose $J = \hbar\sqrt{(w/M)}$ (it means that the bandwidth of the excitation is in two times more than the maximal value of the phonon energy) and $\Delta = 0.009$.

In Figs 3(a)–(c) we plot the results of numerical simulations for a subcritical value of the parameter $g = 4.25$. As an initial state we choose a symmetric two-bell soliton. As time increases, the distance between the bells increases and the height of one of the bells decreases. A similar behavior is observed for the depths of the wells in the $-u_n$ distribution. So, in accordance with our analytical analysis, Davydov and Boussinesq solitons repel each other and the bound state is not formed.

In Figs 4(a)–(e) we present results for $g = 8.5$. As an initial state we choose an asymmetric two-bell soliton. As time increases the bells approach each other and their heights (as well as the depths of wells) equalize. Afterwards the distance between the bells increases and a mirror reflected asymmetric two-bell soliton is created. Thus, in this case Davydov and Boussinesq solitons form a bound state and they behave more like a breather.

We see that the excitation (electron) really tunnels from one well to another and this motion provides a stability of the two soliton bound states.

It is worth to note also that the new bound state may be influenced by an electromagnetic field in the frequency region corresponding to the vibrations of the solitons near their equilibrium position. In a later paper we shall discuss this process in more detail.

7. Summary and conclusions

We have investigated a soliton energy (or charge) transport in anharmonic molecular systems and found that when the anharmonicity parameter g exceeds the critical value $g_c = 6$ there are two kinds of envelope solitons: One is the usual Davydov soliton. It has one-bell shape and may exist at any g. A second kind has a two-bell shape. It is a bound state of Davydov and Boussinesq solitons. We have demonstrated that the latter kind is caused by the excitation (electron) tunnelling in the effective two-well potential which is created by the exciton (electon)-phonon interaction and anharmonic terms in the lattice potential. The stability of the new soliton state was proved numerically. We have showed that there is a breather-like motion in the second kind soliton state.

The parameter g is defined as the ratio of a characteristic anharmonic energy E_{anh} and a bound energy of the Davydov soliton E_b:

$$g = \frac{2}{3}\frac{E_{\mathrm{anh}}}{E_b} = \frac{12\alpha J}{\chi}.$$

To estimate this parameter for the case of Davydov vibrational soliton motion in the alpha-helix molecule we have chosen an interatomic potential in the Lennard–Jones form

$$V = 4\varepsilon\left[\left(\frac{\sigma}{l + u_{n+a} - u_n}\right)^{12} - \left(\frac{\sigma}{l + u_{n+a} - u_n}\right)^{6}\right] \tag{7.1}$$

with parameters $\varepsilon = 0.23N$ and $\sigma = 4.01$ Å, $l = 4.5$ Å which are fitted to bound energy and equilibrium distance in the alpha-helix. From eq. (7.1) we get that the anharmonicity parameter $\alpha = 2.3\,\text{Å}^{-1}$. For parameter values very often used in alpha-helix motion: $J = 9.7 \cdot 10^{-4}$ eV, $\chi = 5.25 \cdot 10^{-11}$ N, $M = 1.9 \cdot 10^{-25}$ kg [29] we find that the sound velocity is $v_0 = 3.7 \cdot 10^3\,\mathrm{m\,s^{-1}}$, the maximum group velocity of the vibron excitation is $v_g = 1.4 \cdot 10^3\,\mathrm{m\,s^{-1}}$ and $g = 0.8$. Then we can conclude that the anharmonicity parameter, α, and the group velocity of the vibron soliton, v_g, are too small to make a creation of the bound state of the supersonic Davydov soliton and Boussinesq soliton possible. Collisions between the Davydov soliton and lattice solitons in the alpha-helix were investigated in Ref. [30] and it was shown that as a result of these collisions the Davydov vibron soliton is destabilized.

Let us consider now the possibility of the coupling of Davydov electrosoliton and Boussinesq soliton in the alpha-helix. Davydov's idea of the electrosoliton as a charge carrier in polypeptide molecules is based upon the fact that the peptide group (CONH) has a comparatively large static dipole moment (about 3.46 D) and an extra electron can be bound to it. The propagation of this electron is as mentioned above in many points similar to the excitations transport but now J is the nearest neighbor electronic overlap integral and χ is a coupling electron–acoustic phonon constant. The parameter χ consists of two parts:

$$\chi = \chi_c + \chi_J \tag{7.2}$$

The first term (χ_c) in eq. (7.2) is caused by the Coulomb interaction between an extra electron and static dipole moments of the peptide groups. Estimates show [1, 31] that $\chi_c \simeq -7.5 \cdot 10^{-10}$ N. The negative sign of the parameter χ_c means that the Coulomb interaction leads to increasing distance between peptide groups. The second term in eq. (7.2) arises from the dependence of the overlap integral J on the distance l between peptide groups

$$\chi_J = \kappa \cdot J \tag{7.3}$$

where the parameter $\kappa = -(\mathrm{d}/\mathrm{d}l) \ln J(l)$ characterizes the pace of the overlap integral decrease with distance. In Ref. [32] the value $J = 0.3$ eV for a model polypeptide structure was calculated. Taking for the parameter κ values for the interval $(2, \ldots, 4)\,\text{Å}^{-1}$ we obtain from eqs (7.2) and (7.3) that

$$\frac{\chi}{J} = \kappa - 1.6\,\text{Å}^{-1} = (0.4, \ldots, 2.4)\,\text{Å}^{-1}.$$

Inserting this value together with the anharmonicity parameter α estimated above into the expression for the coupling constant g we get that $g \geqslant 12$. Thus we arrive at the conclusion that a bound state of a supersonic Davydov electrosoliton and a lattice Boussinesq soliton can exist in alpha-helix biopolymers.

It is worth to remark also that very often in molecular conducting polymers only the part χ_J connected with the overlap electronic integral contributes to the electron–phonon coupling. This means that in this case the condition for the existence of the bound state of supersonic electro-

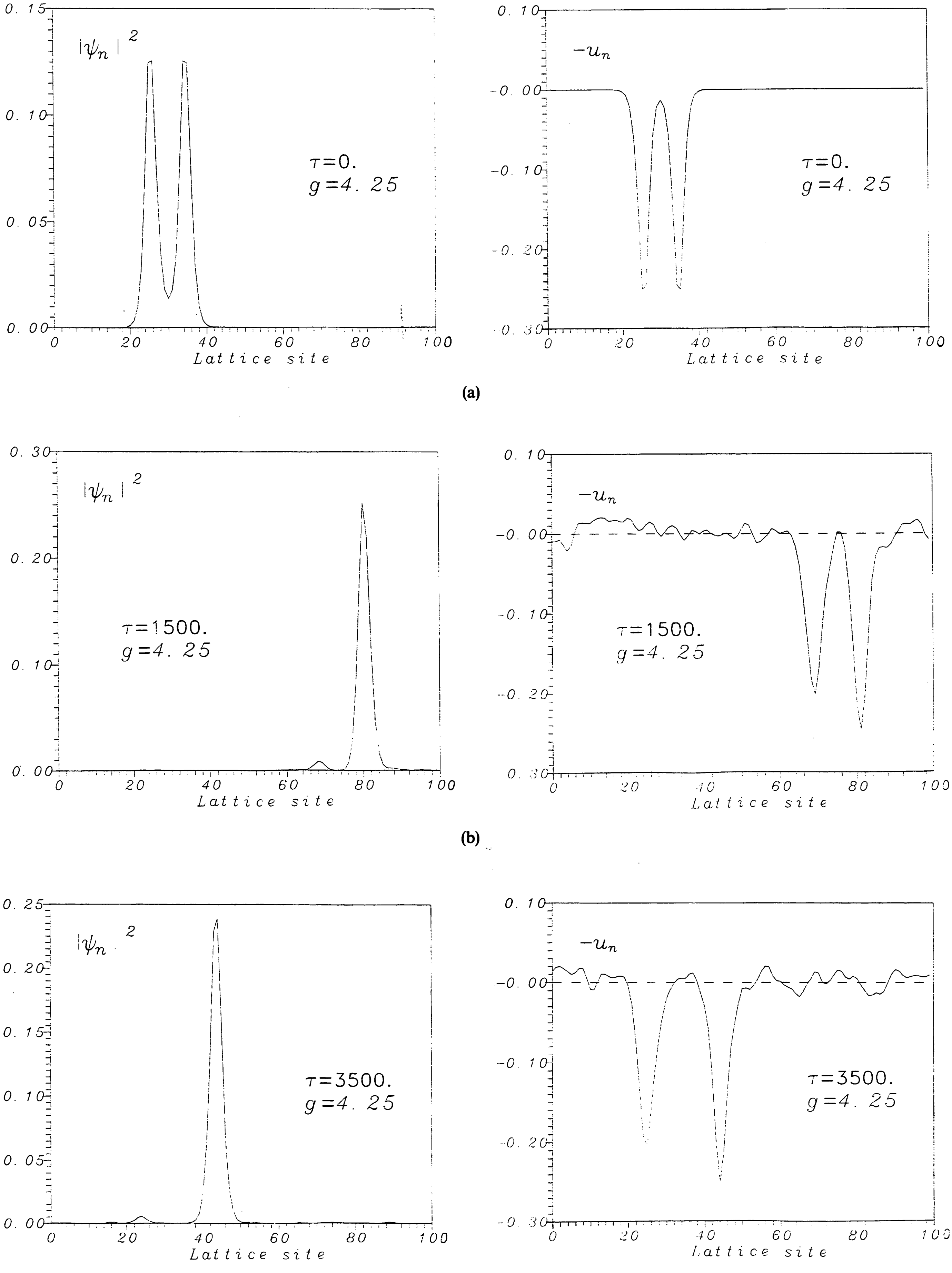
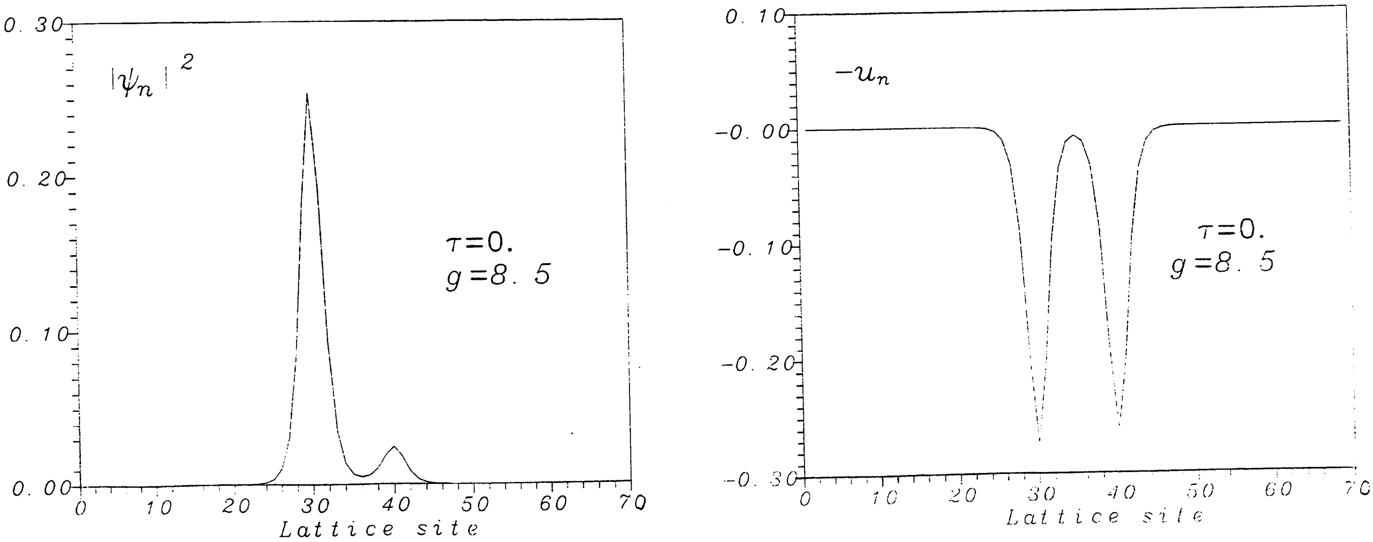
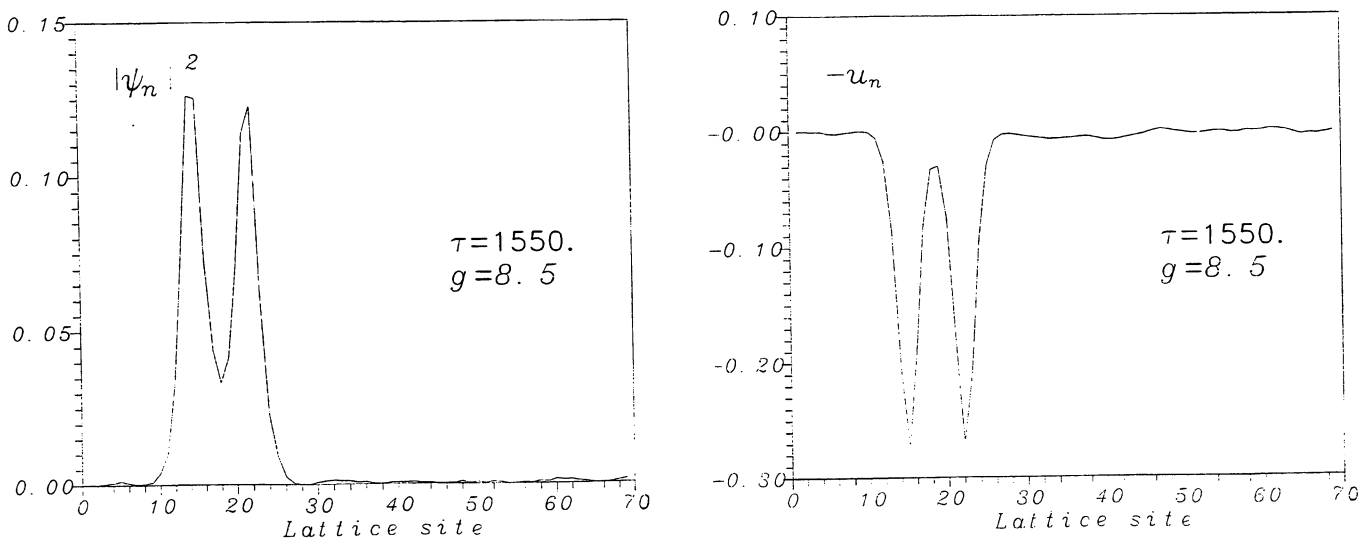


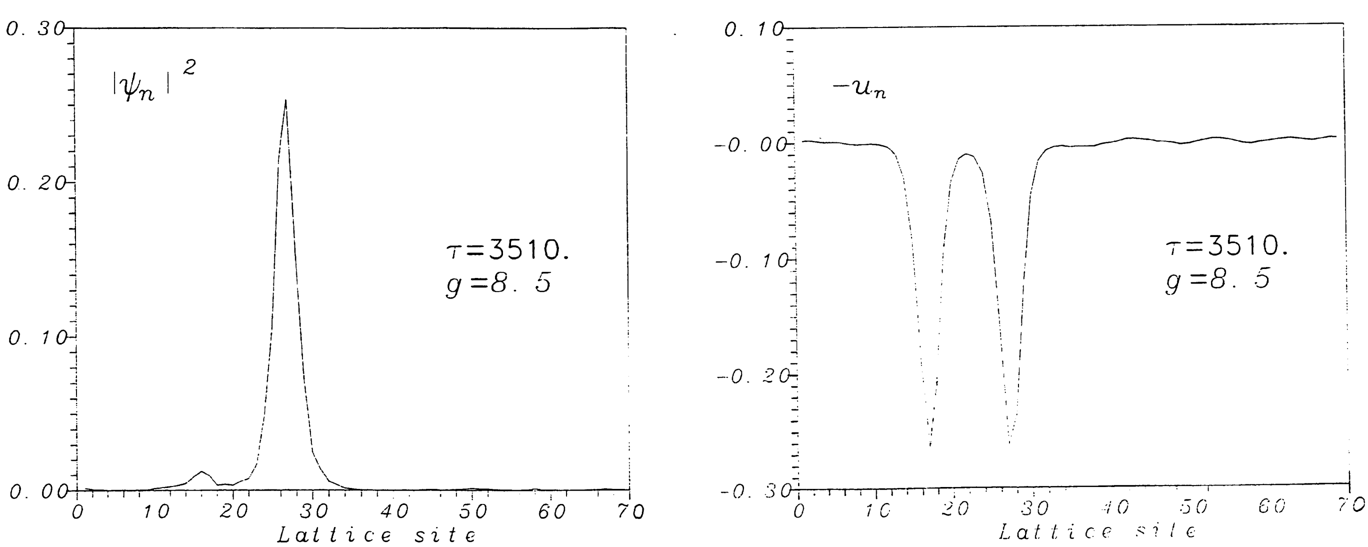
Fig. 3. (a)–(c): Numerical calculations of the excitation probability distribution, $|\Psi_n|^2$, and molecular displacements, u_n, for $g = 4.25$ at different moments of dimensionless time. (a) $\tau = 0$, (b) $\tau = 1500$, (c) 3500.



(a)

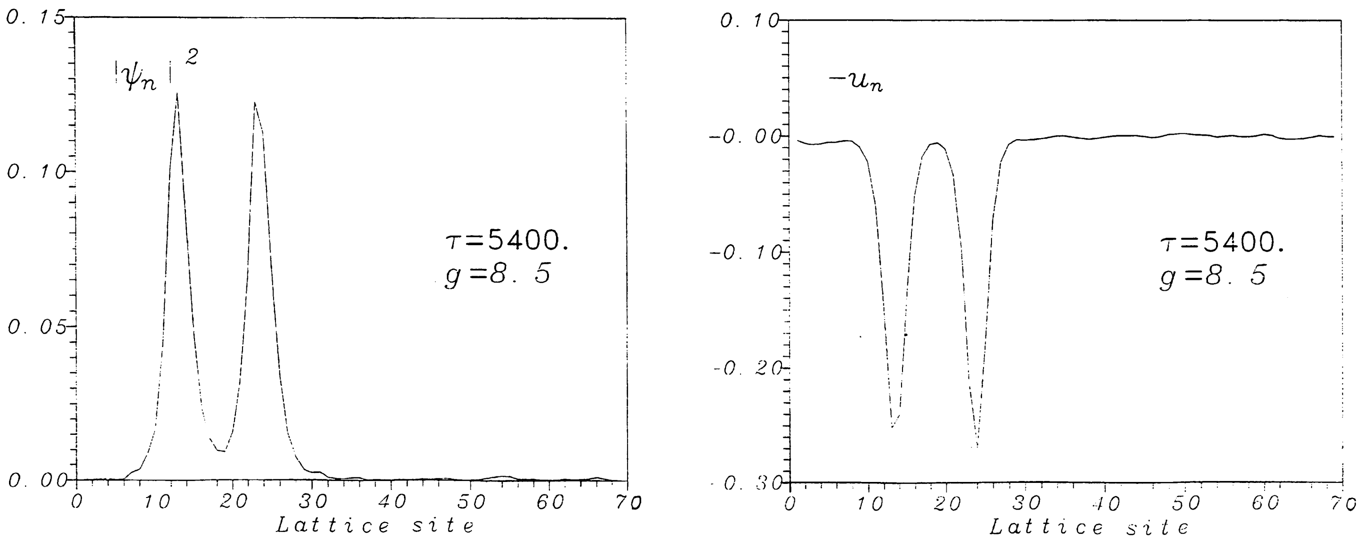


(b)

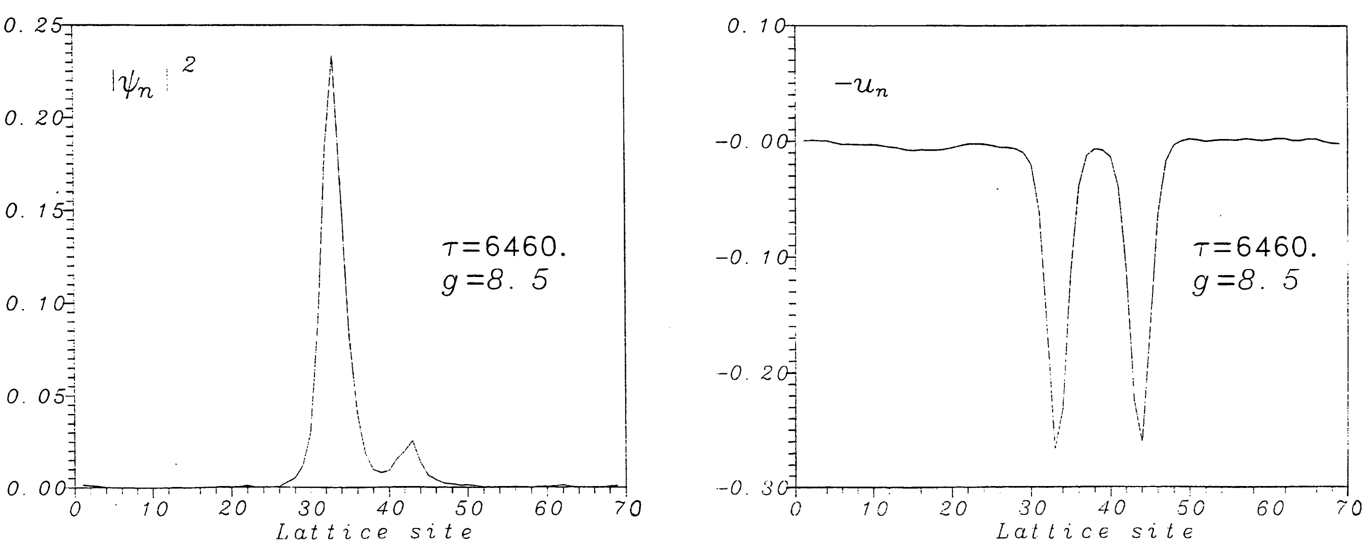


(c)

Fig. 4. (*continued*)



(d)



(e)

Fig. 4. (a)–(e): Numerical calculations of the excitation probability distribution, $|\Psi_n|^2$, and molecular displacements, u_n, for $g = 8.5$ at different moments of dimensionless time. (a) $\tau = 0$, (b) $\tau = 1500$, (c) $\tau = 3500$, (d) $\tau = 5400$, (e) $\tau = 6460$.

soliton (acoustic polaron) with a lattice solitons takes very simple form:

$$\kappa < 2\alpha.$$

In other words one can expect an existence of such a bound state in anharmonic lattices with loose on-site electronic states for which the overlap integral smoothly depends on intersite distance.

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