PROPAGATION OF THE SOLITON IN A NON-PERIODIC PROTEIN CHAIN

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Abstract. The propagation of Davydov's soliton in the polymer chain with impurities has been investigated. The method is proposed and numerically verified in which the disturbance of the chain caused by the presence of the impurities is included in the system Hamiltonian through a particular term added to the Hamiltonian of the ideal polymer chain. The obtained numerical results show that the impurities must be considered as relevant obstacles, which strongly affect the soliton propagation. A single impurity could be considered as an unpermeable or partially permeable potential barrier. The increase of the number of impurities is equivalent to the increase of the barrier height.

INTRODUCTION

The fact that the Davydov soliton model [1] was a subject of intensive theoretical investigations during the last three decades [2] confirms its importance in the attempts to understand and describe the energy transport processes in α–helix proteins. In this relatively simple model the analysis of these processes has been reduced to the analysis of Frenkel's excitons [3] in the soft one-dimensional polymer chain, which are identified as amide-1 vibrational quantum exciton in proteins [4]. Due to the nonlinear and strong exciton - lattice interaction, autolocalized excitations - solitons appear in this system. Thus, these are in fact the excitonic polarons. In other words, the propagation of the exciton (amide-I quanta) along the chain is followed by local chain deformation, which means that the real excitation is the "dressed" exciton, i.e. the autolocalized solitary wave.

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However, one should bear in mind that Davydov's soliton model is mainly of the methodological importance, since it could not be accepted as a realistic one [5]. Namely, the proteins are macromolecules composed of 19 different amino acids and one imino acid (proline). Although, as it was done above, Davydov's model is described as a model which considers the excitations in the α–helix proteins, it is not entirely true. Namely, Davidov's model is using the α-helix protein made of identical monomer units, which is not true in reality. Real α-helix protein is composed of different monomer units. In this paper a nonideal polymer chain is considered (that is a chain with implanted several different monomer units, which are treated as "impurities").

As far as we know, in previous papers on Davydov model, only an ideal infinite translationally invariant chain without impurities has been considered. Taking into account the above mentioned complexity of the protein structure, having the impurities which disturb its translational invariance, in this paper we propose an approach which allows analyzing a nonideal chain with small number of impurities. The disturbance of the structure caused by the impurities, is considered as a particular perturbation of the Hamiltonian of the ideal chain. This approach, which is also numerically verified, allows adjusting the theoretical method used for analysis of the ideal chain and applying it easily to a nonideal chain with impurities.

SYSTEM HAMILTONIAN

In order to obtain the Hamiltonian of the disturbed polymer chain, i.e. the chain consisting of weakly interacting monomers, we start from standard Davydov's Hamiltonian of the ideal polymer chain, designated below as H_d, to which the term H_a describing supposed disturbance due to the existence of the impurities in the chain, shall be added and explained in detail later. Hamiltonian H_d consists of three parts: Hamiltonian H_e, which describes the monomer amide-I quantum excitations, which will be considered, in accordance with Davydov's approach, as Frenkel's excitons in so called two level approximation, which means that only the ground and the first excited levels are taken into account, because the higher excited levels are supposed to be sufficiently far away from the first excited level [3]; Hamiltonian H_p, which describes vibrations of monomer units, and Hamiltonian H_i, which

describes exciton–phonon interaction. Thus, the Hamiltonian of the disturbed nonideal polymer chain is given as

$$H_x = H_d + H_a = H_c + H_p + H_t + H_a \tag{1}$$

Hamiltonian H_c, in the usual nearest neighbours approximation, is of the following form:

$$H_c = \sum_n (\Delta + D_n) B_n^* B_n + \sum_{n,m} J_{n,m+1} B_n^* (B_{n+1} + B_{n-1}) \tag{2}$$

where B_n^* and B_n are the Bose operators which create and annihilate the excitation on the n–th chain site having the on site energy $\Delta + D_n$ where Δ is the excitation energy of the isolated monomer and D_n is the contribution to the on site energy arising due to resonant dipole–dipole interaction of the considered monomer unit with other monomer units. Matrix elements $J_{n,m}$ characterize the exciton–exciton interaction which enables the exciton propagation along the chain.

H_p is taken in the harmonic approximation, which means that

$$H_p = \frac{1}{2} \sum_n \left[\frac{1}{M} p_n^2 + k(u_n - u_{n+1})^2 \right], \tag{3}$$

where M is the mass of the monomer unit; u_n is the n–th monomer unit displacement and p_n is the corresponding conjugate momentum; k is the lattice elasticity coefficient.

Hamiltonian H_t of the exciton–lattice interaction could be easily derived starting from exciton Hamiltonian H_c. It is necessary to expand quantities D_n and $J_{n,m+1}$ in terms of monomer unit displacements u_n up to the first order terms. In this way one could obtain that

$$
\begin{aligned}
D_n &= -D + \chi_1 (u_{n+1} - u_{n-1}), \\
J_{n,m+1} &= -J + \chi_2 (u_n - u_{n-1})
\end{aligned}
\tag{4}
$$

where χ_1 and χ_2 are the exciton–phonon coupling parameters. It should be noticed that in original Davydov's theory only constant χ_1 is included, while χ_2 is omitted. However, more detailed analysis shows that χ_2 should not be neglected [6].

After the substitution of the expansions (4) in (2), the obtained Hamiltonian could be divided into two parts. The first one, which does not include monomer unit displacements u_n corresponds to the exciton Hamiltonian, while the second one, with the terms containing the monomer unit displacements, corresponds to exciton-lattice interaction Hamiltonian H_i which is given as

$$H_i = \chi_1 \sum_n B_n^* B_n (u_{n+1} - u_{n-1}) + \chi_2 \sum_n B_n^* (B_{n+1} + B_{n-1})(u_n - u_{n-1}) \tag{5}$$

Now, it is obvious that Hamiltonian H_{int} consists of two parts with two coupling parameters χ_1 and χ_2. The first part determines the change of on–site exciton energy caused by the lattice vibrations, while the second term reflects the influence of these vibrations on exciton propagation along the chain.

The particular manner in which we include the disturbance caused by the impurities has affected some of the previously considered Hamiltonian terms. Namely, although the chain has impurities, the Hamiltonian H_d, which is in fact the Hamiltonian of ideal Davydov's model, describes an ideal polymer chain with no impurities. As we have the chain with impurities on some chain places, this means that to H_d some nonexisting terms have been added and therefore these terms must be extracted and the terms corresponding to the impurities included too. In order to solve this problem we follow the usual theory of single impurity in the crystal lattice, where it is taken that the presence of impurity on some lattice site is equivalent to presence of a local potential on that site. In other words, this means that impurity affects the coupling constants and the other relevant parameters mainly near the impurity position and consequently H_a could be extracted from the Hamiltonian H_d in which the constants Δ, J, k, χ have been renormalized in an appropriate way. However, the corrections of all these constants need not be considered because some of them are negligible quantities. We have found out that the corrections of the exciton energy Δ and the constant of exciton-exciton interaction J, are the only ones that, in somewhat different manner, should be included. These quantities should be substituted by the new ones $\Delta + \tilde{\Delta} Y(na)$, and $J + \tilde{J} Y(na)$, where $Y(na) \equiv Y_n$ is the function of the lattice position "vector" na which has following form

$$Y_n = \sum_{n_i} e^{-\beta a(n-n_i)^2} , \tag{6}$$

that has maxima at n_i, the lattice site where the impurity is placed. As it can be seen Y_n is chosen to be sufficiently fast decreasing (exponentially). Constant β depends on the potential induced by the impurity effects and will be obtained from the physical condition that the impurity affects only several nearest neighbors.

Taking into account the previous facts, which indicate that only the exciton parameters are corrected, it is easy to show that the exciton Hamiltonian of the nonideal chain could be expressed as a sum of aforementioned exciton Hamiltonian of the ideal chain H_c and Hamiltonian of the residue, H_a which is of the form

$$H_a = \sum_n \tilde{\Delta} Y_n B_n^* B_n - \sum_n \tilde{J} Y_n B_n^* (B_{n+1} + B_{n-1}) \tag{7}$$

The non–zero terms in the above sums are only due to lattice points in which the impurities are present.

DYNAMIC EQUATIONS OF THE SOLITARY WAVES IN THE CHAIN WITH IMPURITIES

As it is known from the theory of Davydov's model, described here by Hamiltonian H_d, in the case of strong exciton-lattice coupling and small longitudinal elasticity coefficient ("soft" polymer chain), the solitonic excitations could arise in the system. The following calculation, which treats the nonideal chain with impurities, is completely based on the presumptions of Davidov's soliton theory, and therefore it will be given in short. The only differences in our case, which do not change the calcualtion procedure, are following: the presence of H_a in the system Hamiltonian and, as mentioned above, we included the parameter χ_2 also, contrary to the usual approach, in which only coupling parameter χ_1 was taken into account. The calculation procedure given here is the derivation of basic dynamical equations of the theory of Davydov's model. The first step is to write down the averaged equation of motion of the lattice and the time dependent Schrödinger equation of the whole system, using system Hamiltonian H_s and following one–quasi-particle wave function

$$\left|\Psi\right\rangle = e^{-\frac{i}{\hbar}S(t)} \sum_n \left[A_n(t) B_n^* \left|0\right\rangle \right], \quad S(t) = \sum_n \left[\pi(t) p_n - \alpha_n(t) u_n \right]$$

$$\alpha(t) = \left\langle \Psi | p_n | \Psi \right\rangle; \quad \pi(t) = \left\langle \Psi | u_n | \Psi \right\rangle \tag{8}$$

where $\left|0\right\rangle$ is the vacuum state function, $\exp[S(t)]$ is the unitary operator usually used in the theory of lattice vibrations in the presence of external forces, while $A_n(t)$ determines the probability of creating the exciton on the lattice site n, which means that

$$\sum_n \left| A_n(t) \right|^2 = 1. \tag{9}$$

The averaged equation of motion of the lattice, i.e. of the quantity α_n is of the form

$$M \frac{d^2 \alpha_n}{dt^2} = -k[2\alpha_n - \alpha_{n+1} - \alpha_{n-1}] - \chi_1 [|A_{n+1}|^2 - |A_{n-1}|^2]$$
$$+ \chi_2 [A_n^*(A_{n+1} - A_{n-1}) + (A_{n+1}^* - A_{n-1}^*)A_n] \tag{10}$$

On the other hand, by substituting $\left|\Psi\right\rangle$ (Eq. 8) into the time dependent Schrödinger equation, where total system Hamiltonian H_x has been used, we have derived that:

$$i\hbar \frac{\partial A_n}{\partial t} = [\Lambda + \varepsilon Y_n + \chi_1 (\alpha_{n+1} - \alpha_{n-1})] A_n - (J + \tilde{J} Y_n)(A_{n+1} + A_{n-1} - 2A_n)$$
$$+ \chi_2 [(\alpha_{n+1} - \alpha_{n-1}) + (\alpha_n - \alpha_{n-1}) A_{n-1}], \tag{11}$$
$$\Lambda = \Delta - D + \frac{1}{2} \sum_n \left[\frac{1}{M} \pi_n^2 + k(\alpha_n - \alpha_{n+1})^2 \right] - 2J, \quad \varepsilon = \tilde{\Delta} - 2\tilde{J}$$

Since our main aim is to carry out the numerical analysis of the last two equations, it is useful to write down these equations in the continual approximation ($na \to x$; $(n \pm 1)a \to x \pm a$; $A(na,t) \to A(x,t)...$) in which we have

$$A_{n\pm 1} \cong A(x,t) \pm a \frac{\partial A(x,t)}{\partial x} + \frac{1}{2} a^2 \frac{\partial^2 A(x,t)}{\partial x^2}$$
$$\alpha_{n\pm 1} \cong \alpha(x,t) \pm a \frac{\partial \alpha(x,t)}{\partial x} + \frac{1}{2} a^2 \frac{\partial^2 \alpha(x,t)}{\partial x^2} \tag{12}$$

After substituting expansions (12) into (11) we obtain the following equations

$$\left(\frac{\partial^2}{\partial t^2} - v_0^2 \frac{\partial^2}{\partial x^2}\right)\rho(x,t) + v_0^2 \frac{2k}{\chi} \frac{\partial |B(x,t)|^2}{\partial x} = 0$$

$$\left[ih\frac{\partial}{\partial t} - \Lambda + \frac{h^2}{2m_{ex}}\frac{\partial^2}{\partial x^2} + 2ak\,\rho(x,t)\right]B(x,t) = \varepsilon\,Y(x)\,B(x,t)$$

(13)

where a is the lattice constant and

$$\rho = \frac{\partial\alpha}{\partial x}, \quad B(x,t) = \frac{1}{\sqrt{a}}A(x,t)\,e^{\frac{t}{h}\Lambda t}, \quad v_0^2 = \frac{ka^2}{M},$$

$$\chi = \chi_1 + \chi_2, \quad m_{ex} = \frac{\hbar^2}{2a^2[J + \tilde{J}Y(x)]},$$

(14)

v_0 is the sound velocity in the unperturbed phonon system; E_{ph} is the lattice phonon energy; m_{ex} is the exciton mass. As it can be seen, the expression for the exciton mass in the disturbed chain with impurities contains the additional term $2a^2\tilde{J}Y(x)$, which means that the exciton is, in some sense, dressed in the additional local potential, due to the presence of the impurities.

RESULTS OF THE NUMERICAL ANALYSIS

Equations (10) and (11), which determine the dynamics of the considered disturbed nonideal chain, have been analysed numerically. The results are presented graphically in the figures given below, all of them representing the time dependence of the quantity $|A_n(t)|^2$, which is the density of probability to obtain the excitation on the given lattice site n in the given time t. In all presented cases it was assumed that: the cyclic boundary conditions could be applied, the chain has 200 monomer units, the first chain monomer unit was excited, the monomer unit mass is $M = 1.9 \cdot 10^{-25}$ kg, the elasticity coefficient is $k = 20\,\text{Nm}^{-1}$ and $\tilde{\Delta} = -4.4 \cdot 10^{-23}$ J, $\tilde{J} = -1.5 \cdot 10^{-23}$ J. Constant β, which appears in Y_n is taken to be equal to 1.8, while the values of quantities χ_1 and χ_2 differ from case to case and will be given in the forthcoming analysis of the figures.

In Fig. 1. and Fig. 2. the propagation of the solitary wave in the monomer chain with one impurity on the lattice site $n = 120$ is presented. Fig. 1. corresponds to the case

$\chi_1 = 6.0 \cdot 10^{-11}$ N and $\chi_2 = 0.2 \cdot 10^{-11}$ N, while in the case presented in Fig.2 it is taken that $\chi_1 = 5.5 \cdot 10^{-11}$ N and $\chi_2 = 0.2 \cdot 10^{-11}$ N. These values are in the value range which gives the numerical solutions of the dynamic equations of Davydov's model.
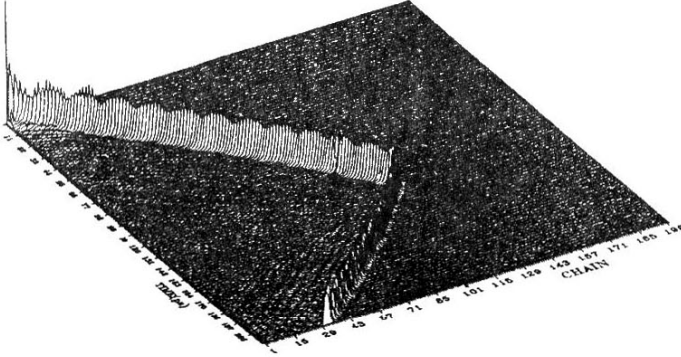

FIGURE 1. Total reflection of the soliton at one impurity (at 120th site): $\chi_1 = 6.0 \cdot 10^{-11}$ N, $\chi_2 = 0.2 \cdot 10^{-11}$ N, $\tilde{\Delta} = -0.44 \cdot 10^{-22}$ J, $\tilde{J} = -0.15 \cdot 10^{-22}$ J, $\beta=1.8$

As it can be seen, in Fig. 1. we have the total reflection of the soliton on the impurity, which means that it could be considered as a potential barrier. Before and after the reflection the soliton propagates with constant velocities, where the velocity after the reflection is increased. This velocity increasing after the total reflection, which indicates the decreasing of the exciton mass, depends on the values of the parameters ε, $\tilde{J}$, being the measure of the change of the overlap integrals (monomer unit to unit interaction) in the vicinity of the impurity. The decrease of the exciton mass, in accordance with Eq. (14), corresponds to the positive values of the quantity $\tilde{J}$. However $\tilde{J}$ can also be negative, which means that the soliton velocity may also decrease after the total reflection. The wavy area on the left side of the figure indicates the weak dispersion of the reflected solitary wave.
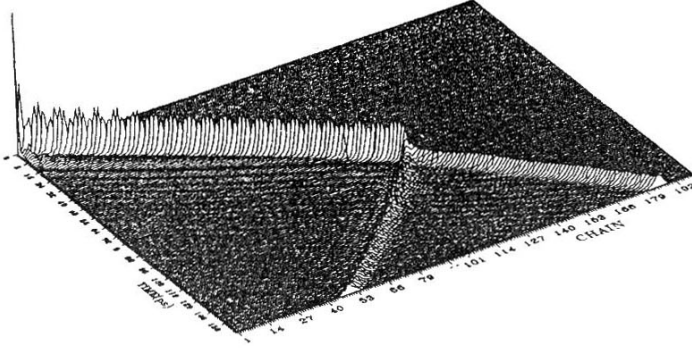
FIGURE 2. Partial passage of the soliton and partial reflection of the soliton at one impurity (at 120th site): $\chi_1 = 5.5 \cdot 10^{-11}$ N, $\chi_2 = 0.2 \cdot 10^{-11}$ N, $\tilde{\Delta} = -0.44 \cdot 10^{-22}$ J, $\tilde{J} = -0.15 \cdot 10^{-22}$ J, $\beta = 1.8$

Fig. 2. shows that the result of the numerical analysis strongly depends on the values of the relevant physical quantities. Even the small change of the value of χ_1, leads to quite different results, which show that the impurity acts like partially permeable potential barrier, because two solitary waves appear there. One of them is reflected on the impurity and propagates in the opposite direction, while the other passes over it and propagates in the primary direction. Which is in fact Above Barrier Reflection, as the energy of the solitary wave is greater than the energy of the barrier - i.e. impurity. The amplitudes of these two solitons are decreased (which does not need any additional explanation), while the velocities are increased and the cause of this effect is similar to that mentioned in the previous case.

In Fig. 3. the propagation of the solitary wave in the polymer chain with five impurities on the lattice sites $n = 120 - 124$ is presented. The values of quantities χ_1 and χ_2 are the same as in the case presented in Fig. 2: $\chi_1 = 5.5 \cdot 10^{-11}$ N and $\chi_2 = 0.2 \cdot 10^{-11}$ N . Contrary to that case, where the impurity acts like partially permeable potential barrier, here five impurities act like unpermeable potential barrier and the solitary wave is totaly reflected. This means that the increase of the number of impurities is equivalent to the increase of the potential barrier height. The wavy area on the left side indicates that the dispersion of the reflected solitary wave is stronger than in the case when one impurity is present.
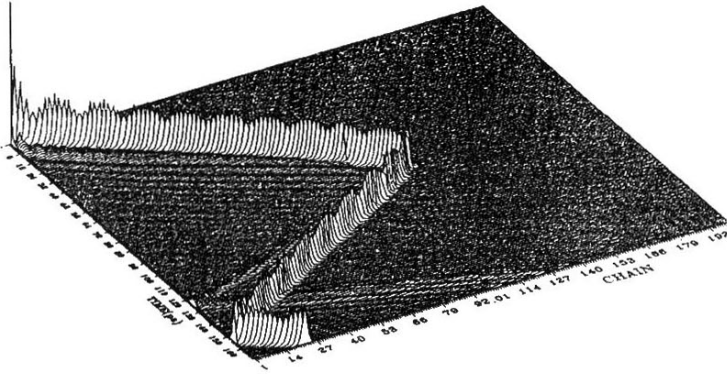
FIGURE 3. Total reflection of the soliton at five impurities (at $n = 120 - 124$ sites): $\chi_1 = 5.5 \cdot 10^{-11}$ N, $\chi_2 = 0.2 \cdot 10^{-11}$ N, $\tilde{\Delta} = -0.44 \cdot 10^{-22}$ J, $\tilde{J} = -0.15 \cdot 10^{-22}$ J, $\beta = 1.8$

CONCLUSIONS

The presented results could be emphasized as follows:

- The method is proposed which allows a simple analysis of the solitary waves in the disturbed Davydov's model, where the polymer chain contains the impurities. The disturbance of the chain caused by the presence of the impurities is included in the system Hamiltonian through a particular term, which is added to the Hamiltonian of the ideal polymer chain. The presented numerical result confirms the simplicity and the efficiency of this approach.

- The impurities must be considered as relevant obstacles, which strongly affect the soliton propagation in the polymer chain. Even the single impurity could be unpermeable potential barrier, which reflects the solitary wave. Though they have lower energy than the solitary wave, so, as already mentioned, this could be considered the case of Above Barrier Reflection. If it is not the case, then the impurity is partially permeable potential barrier, because there appear two solitary waves, and one of them is reflected on the impurity barrier and propagates in the opposite direction, while the other passes over the barrier and propagates in the primary direction.

- The increase of the number of impurities in the polymer chain is equivalent to the increase of the potential barrier height, which becomes impermeable for the solitons.

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