Peculiarities of soliton motion in molecular systems with high dispersion

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In this work, features of propagating protons along molecular chain of hydrogen bonds are described from position of soliton dynamics with taking into account interaction of first and second neighbors of a proton sublattice. It is proposed extension of the model that is an endless chain of water molecules in which formation of hydrogen bonds is due to participating one proton of every water molecule, a second proton no participating in hydrogen bond and being confined by covalent bond of an oxygen atom. Nonlinearity is due to peculiar properties of proton sublattice potential. The model used to obtain continual equations which contain the spatial derivatives of the fourth order that is related with dispersion of longwave oscillations. The availability of such a dispersion changes essentially dynamics of the molecular chain, which allows of manifesting new peculiarities of propagating nonlinear excitations. It is shown there are two new sorts of charge density excitations transferred by solitons determined as exact analytic dependences in such a system.

1 Introduction Recently, the activities of theoretical describing different physical and chemical processes have been increased with the point of the nonlinear dynamics view. Applying nonlinear differential equations with spatial gradients of the orders exceeding the second one is of a special interest [1–4]. Such equations can occur in describing long wave oscillations of discrete crystal lattices taking the nearest neighbors into account [5, 6]. In this work, it is represented considering peculiarities of propagating nonlinear excitations in a hydrogen bond molecular chain with interaction between the nearest and second neighbor particles. Due to this interaction, the derivatives of higher order are in the continual equations of motion. The presence of such derivatives of the order exceeding the second one causes higher dispersion effects having new peculiarities of propagating the longwave excitations in the chain.

It is well known a proton conductivity is higher along hydrogen bond one-dimensional chains in certain crystal phase compounds (hard spirits, carbohydrates) by several orders than in a cross direction [7]. Besides it is known proton mobility in ice crystals is lower by only the one order than electron mobility in metals [8–11]. The basic proposition of the ice proton conductivity theory is a proton can be transferred along the chain as two ion defects: hydroxonium ion H_3O^+ and hydroxyl ion OH^- created by water molecule dissociation due to transferring one of its protons to a neighbor molecule according to the reaction scheme: $2H_2O \Delta OH^- + H_3O^+$.

2 Model Following [12] we consider a water molecule endless chain where hydrogen bonds are formed by one of protons of every water molecule and other proton of the water molecule does not participate in a hydrogen bond and is held with an oxygen atom by covalent bond. The oxygen atom and this proton are a hydroxyl ion. As result, the water molecule chain splits up by two subsystems: the basic subsystem formed by hydroxyl groups and the proton subsystem.

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In a strain-free state of the chain, every proton participating in hydrogen bond is linked with an oxygen atom by covalent bond in one side and by hydrogen bond in other side. Covalent and hydrogen bonds change places after passing proton through a potential barrier. The potential energy of a proton participating in hydrogen bond can be written [7, 11, 12] as:

$$U(u_n) = U_0 \left(1 - \frac{u_n^2}{u_0^2}\right)^2 \tag{1}$$

where U_0 is a potential barrier height, u_n is a proton displacement from a barrier top, u_0 is minima positions of potential energy (see Fig. 1).

Hamiltonian of the system considered can be written as

$$H = H_p + H_g + H_{int} \tag{2}$$

where H_p is proton sublattice Hamiltonian involving Eq. (1) and interaction of neighbor protons and next (second) neighbor protons with interaction lattice constants ω_1^2 and ω_2^2, respectively,

$$H_p = \sum_n \{\frac{m}{2}[(\frac{du_n}{dt})^2 + \omega_1^2 (u_{n+1} - u_n)^2 + \omega_2^2 (u_{n+2} - u_n)^2] + U(u_n)\}. \tag{3}$$

where m is proton mass. The second term of Eq. (2) is Hamiltonian of the basic sublattice of hydroxyl ions. Here, we limit ourselves by interaction of only the nearest neighbors with the lattice constant Ω_1^2 [7, 12]:

$$H_g = \sum_n \frac{M}{2}\{(\frac{d\rho_n}{dt})^2 + \Omega_1^2 (\rho_{n+1} - \rho_n)^2 + \Omega_0^2 u_n^2\} \tag{4}$$

where ρ_n is the relative displacement of hydroxyl ions, M is hydroxyl mass, Ω_0^2 is the characteristic constant of the basic lattice. The third term of Eq. (2) is Hamiltonian of interaction of hydroxyl ion and proton displacements:

$$H_{int} = \lambda \sum_n \rho_n (u_n^2 - u_0^2) \tag{5}$$

where λ is a sublattice interaction parameter.

Further we limit ourselves studying a longwave approximation. For this, we suppose $na \to x$, $u_n \to u(x)$, $\rho_n \to \rho(x)$, $\sum_n \to \frac{1}{a} \int dx$ in Eqs. (3)-(5). Here a is an equilibrium distance between two neighbor hydroxyl ions. It corresponds to the Taylor series expansion of discrete equations (3)–(5). It was shown in the Ref. [5] that taking into account interaction with the second neighbors in the one-dimension chain at transition to the longwave approximation leads to appearing the spatial derivatives of the fourth order in the equations of motion and to redefining a velocity (and frequency) of proper sound waves. As a result of such a correct transition to the longwave approximation, we receive from Eqs. (3)–(5) general continual Hamiltonian of the considered system:

$$H = \frac{1}{a} \int \{\frac{m}{2}(u_t^2 + s_0^2 u_x^2 + b u_{xx}^2) + U_0(1 - \frac{u^2}{u_0^2})^2 + \frac{M}{2}(\rho_t^2 + V_0^2 \rho_x^2 + \Omega_0^2 \rho^2) + \lambda\rho(u^2 - u_0^2)\} dx \tag{6}$$

where u_t, u, u , ρ_t , ρ are the derivatives over t, x and the second derivative over x, respectively, of the functions $u(x)$ and $\rho(x)$. We explain the parameters of the considered system (see the Ref. [5]): $s_0^2 = a^2(\omega_1^2 - 4\omega_2^2) > 0$ is the squared velocity of linear waves in the proton sublattice ("proton sound"); $b = a^4(16\omega_2^2 - \omega_1^2)/12$ is the dispersion parameter in the proton sublattice; $V_0 = a \Omega_1$ is the velocity of

the linear waves in the basic sublattice. Conditions of expansion validity with such a precision were discussed in the Ref. [5].
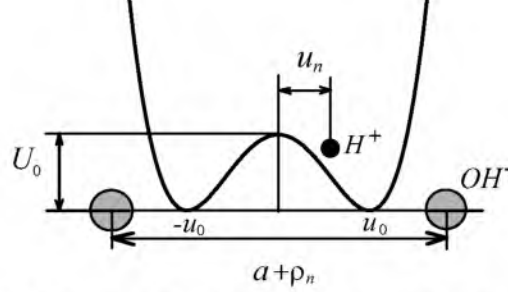

Fig. 1 Potential well of proton participating in hydrogen bond [7].

The equation system of motion corresponding to Hamiltonian (6) takes the form:

$$\begin{cases} u_{tt} - s_0^2 u_{xx} + b u_{xxxx} - \omega_0^2 u\left(1 - \dfrac{u^2}{u_0^2}\right) + 2\dfrac{\lambda}{m} u\rho = 0, \\ \rho_{tt} - V_0^2 \rho_{xx} + \Omega_0^2 \rho + \dfrac{\lambda}{M}(u^2 - u_0^2) = 0, \end{cases} \qquad (7)$$

where $\omega_0^2 = 4U_0 / mu_0^2 > 0$. For convenience, we introduce the following parameters: the parameter of nonlinearity $\alpha = a^2\omega_0^2 / s_0^2 > 0$, the dispersion parameter $\beta = b / a^2 s_0^2$ and the parameter of sublattice interaction $\gamma = 2\lambda\rho_0 a^2 / ms_0^2$

We find two types of the exact solutions of the equation system (7) in the general case at $\lambda \neq 0$. At $\lambda < 2MU_0\Omega_0^2 / u_0^4$ and $\omega_1 > 4\omega_2$ the system (7) has the simple solution

$$u(\xi) = u_0 \frac{A_1 \sinh k\xi}{\cosh^2 k\xi}, \quad \rho(\xi) = \rho_0\left(\frac{A_2}{\cosh^2 k\xi} + 1\right), \quad A_1 = \pm 2k^2\sqrt{30\beta/(\gamma-\alpha)}, \quad A_1^2 = 6A_2 k^2(s_0^2 - V_0^2 V^2)/a^2\Omega_0^2, \quad (8)$$

$$k^2 = (1 - V^2 \pm ([(1-V^2)^2 + 4\beta(\alpha - 2\gamma)]^{1/2})/(2\beta), \quad V^2 = 1 \pm 10(3\alpha - 5\gamma) \times$$

$$\times (\beta(1 - \gamma/(\alpha - \gamma))/(99\alpha - 159\gamma))^{1/2}$$

where $\xi = (x - x_0 - Vt)/a$, V is the velocity of propagating excitations, $\rho_0 = \lambda u_0^2 / M\Omega_0^2$.

At $\lambda > 2MU_0\Omega_0^2 / u_0^4$ and $\omega_1 > 4\omega_2$ the system (7) has the simple solution of the another type

$$u(\xi) = u_0\left(\frac{A_1}{\cosh^2 k\xi} + 1\right), \quad \rho(\xi) = \rho_0 \frac{A_3}{\cosh^2 k\xi}, \quad A_3 = 2A_1(A_1^2/3 + 1/\sqrt{\beta}), \qquad (9)$$

$$k^2 = 0{,}025(7{,}5 - R_1)/(5\gamma - 3\alpha) - 0{,}5\sqrt{0{,}3}, \quad R_1 = (56{,}25 + 60a^2\Omega_0^2(5\gamma - 3\alpha)/s_0^2)^{1/2}$$

The solutions (8) and (9) can exist only in the certain molecular chains in which the values of the initial parameters satisfy complex enough relationships.

3 Discussion and conclusions The considered model is an extension of the Davydov water molecule chain [7] where interaction between only the nearest neighbors is taken up. The hydrogen bond of water

and spirit molecules takes a form of the proton potential energy curve with two minima corresponding to two possible proton equilibrium positions (see Fig. 1). Specific to our model is that we adopt influence of the second neighbors besides the nearest ones on soliton motion in molecular systems. It is necessary to note taking into account interaction between not only the nearest neighbors is needed for correctness of the Taylor series expansion of discrete equations in deriving the continual differential equations of motion in the longwave approximation. Due to this, the obtained continual equations contain the spatial derivatives of the fourth order that is related with dispersion of longwave oscillations. The availability of such a dispersion changes essentially dynamics of the molecular chain, which allows of manifesting new peculiarities of propagating nonlinear excitations.

Here are two types of charge density longwave excitations, which is principally different from an excitation in the chain with interaction between only the nearest neighbors in the longwave approximation. The found excitations (see Eqs. (8), (9)) transfer a proton charge by a high enough velocity exceeding the velocity of propagating wave in the linear chain. In the special case, when interaction of proton and hydroxyl displacements is negligible ($\lambda \ll 1$) the solution corresponding to the proton sublattice describes the soliton to move with velocity $V^2 = s_0^2(1 + 110\sqrt{11\alpha\beta}/121)$, amplitude $A_1 = \pm 2\sqrt{30/11}$ and wave number $k^2 = \sqrt{\alpha/11\beta}$. As seen from this: $V > s_0$. It explains the high proton mobility along the molecular chains of hydrogen bonds in crystals of ice and hard spirits. The analogous phenomenon takes place in the general case of interaction of proton and hydroxyl displacements.

Proton migration is equally determined by both proton sublattice displacements and hydroxyl sublattice ones. The excitation velocities in the sublattices are equal at interaction of these displacements. So it is enough to discuss one of two. No hydroxyl and hydroxonium but smeared areas of compression and rarefication of the average proton density propagate along the chain. An effect of the smearing is a result of collective nonlinear interactions in the system. This obeys a high stability of corresponding proton migration.

The new peculiarities considered of propagating solitons in molecular systems with the spatial dispersion can be applied to molecular biophysics. These are important, for instance, to understand mechanisms of proton transport in structured water channels of cell mitochondrions.

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