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Nonlinear Transport in Hydrogen-Bonded Systems with Asymmetric Double-Well Potential

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We study the nonlinear transport and the motion of the bell-shape soliton in hydrogen-bonded chains with asymmetric double-well potential, based on the new two-component soliton model. Solution, momentum, effective mass, width and energy of bell-shape soliton are found. The theoretical reasults are estimated and compared with experimental ones. The agreement between them is good.

KEY WORDS: two-component model; hydrogen-bonded chains; asymmetric double-well potential; energy.

1. INTRODUCTION

The hydrogen bridge exists in a variety of solid state systems and many biological molecular chains. The proton motion is known to be responsible for the charge and energy in many hydrogen-bonded solids. Two-component soliton model for proton transport have been investigated by a number of author in hydrogen-bonded chains with symmetric double-well potential (Cheng, 2000; Pang and Muller-kirsten, 2000; Xu, 1992). However there are many cases in which protons move in asymmetric double minima potential (Kashimori *et al.*, 1982; Pnevmatikos *et al.*, 1987; Schmidt *et al.*, 1971), for example, in some ferroelectric and ferroelastic hydrogen-bonded crystals (Gordon, 1995), surperionic conductivity was discovered: $MHAO_4$ and $M_3H(AO_4)_2$ (M=K, Rb, Cs, NH_4; A=S, Se) exhibit high proton conductivity (Gordon, 1995). In the present paper, we investigate the nonlinear transport in a hydrogen-bonded chain with asymmetric double-well potential, based on a new two-component soliton model. The expressions of solution, the momentum, the effective mass, the energy of the bell-shape soliton have been obtained. Good agreement is obtained with the experimental data.

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2. MODEL AND EQUATION OF MOTION

We consider here a new two-component model Hamiltonian of the hydrogen-bonded molecular systems with asymmetric double-well potential, and assume that the compling between the proton sublattice and the heave-ion sublattice is nonlinear interaction (Cheng, 2003). The Hamiltonian of the systems may be written as a sum of three terms.

$$H = H_p + H_h + H_{\text{int}} \tag{1}$$

where

$$H_p = \sum_i \left\{ \frac{1}{2m_1} p_i^2 + \frac{1}{2} m_1 \omega_0^2 u_i^2 - \frac{1}{2} m_1 \omega_1^2 u_i u_{i+1} + V(u_i) \right\} \tag{2}$$

$$V(u_i) = \frac{1}{2} A u_i^2 - \frac{1}{3} B u_i^3 + \frac{1}{4} c u_i^4 \tag{3}$$

$$H_h = \sum_i \left\{ \frac{1}{2m_2} p_i^2 + \frac{1}{2} \beta (\eta_i - \eta_{i-1})^2 + \frac{1}{2} m_2 \Omega_0^2 \eta_i^2 \right\} \tag{4}$$

$$H_{\text{int}} = \sum_i \frac{\chi}{u_0^2} \eta_i \left(u_i^2 - u_0^2 \right) \tag{5}$$

Here H_p is the Hamiltonian of the proton sublattice, m_1 is the mass of the proton, u_i and $p_i = m\dot{u}_i$ are the proton displacements and momenta respectively, the quantity $\frac{1}{2} m \omega_1^2 u_i u_{i+1}$ shows the correlation interaction between neighbouring protons caused by the dipole-dipole interactions, ω_0 and ω_1 are diagonal and non-diagonal elements of dynamical matrix of the proton respectively (Pang and Muller-kirsten, 2000), $V(u_i)$ is an asymmetric potential with double minina, A, B and C are positive (Gordon, 1995). H_h is the Hamiltonian of the heavy ionic sublattice with low-frequency harmonic vibration, m_2 is the mass of the heavy ion, η_i and $p_i = m_2 \dot{\eta}_i$ are the displacement of the heavy ion from its equilibrium position and its conjugate momentum respectively, $c_o = l(\beta/m_2)^{1/2}$ is the velocity of sound in the heavy ionic sublattice, l is the lattice constant, and Ω_0 is the frequency of the optical mode of the heavy-ion sublattice (Cheng, 2003). H_{int} is the interaction Hamiltonian between the protonic and heavy ionic sublattice, χ is the coupling constant between the two sublattice. In the continuum approximation with the long-wavelength limit (Cheng, 2004), this Hamiltonian can be replaced by a continuum representation

$$\begin{aligned} H = \int_{-\infty}^{\infty} \frac{dx}{l} \Bigg[& \frac{1}{2} m_1 u_t^2 + \frac{1}{2} m_1 \omega_0^2 u^2 - \frac{1}{2} m_1 \omega_1^2 u \left(u + l u_x + \frac{1}{2} l^2 u_{xx} \right) \\ & + \left(\frac{1}{2} m_2 \eta_t^2 + \frac{1}{2} \beta l^2 \eta_x^2 + \frac{1}{2} m_2 \Omega_0^2 \eta^2 \right) + V(u) + \frac{k}{u_0^2} \eta \left(u^2 - u_0^2 \right) dx \Bigg] \end{aligned} \tag{6}$$

$$V(u) = \frac{1}{2}Au^2 - \frac{1}{3}Bu^3 + \frac{1}{4}cu^4 \tag{7}$$

Here $u(x, t)$ and $\eta\ (x, t)$ are the displacement fields of proton (mass m_1) and heavy ion (mass m_2), respectively. $k = \chi l^2$ is the coupling constant between the two sublatlices. The Lagrange density of system corresponding to Eq. (6) can be written as

$$L = T - U = \frac{1}{2}m_1 u_t^2 + \frac{1}{2}m_2 \eta_t^2 - \frac{1}{2}m_1\omega_0^2 u^2 + \frac{1}{2}m_1\omega_1^2 u\left(u + lu_x + \frac{1}{2}l^2 u_{xx}\right)$$
$$-\frac{1}{2}\beta l^2 \eta_x^2 - \frac{1}{2}m_2\Omega_0^2\eta^2 - V(u) - \frac{k}{u_0^2}\eta(u^2 - u_0^2) \tag{8}$$

The Euler-Lagrange equations of motion from (6) and (8) are

$$m_1 u_{tt} - m_1 \upsilon_1^2 u_{xx} + \frac{2k}{u_0^2}\eta u + \alpha u - Bu^2 + cu^3 = 0 \tag{9}$$

$$m_2\eta_{tt} - m_2 c_0^2 \eta_{xx} + \frac{k}{u_0^2}\left(u^2 - u_0^2\right) + m_2\Omega_0^2\eta = 0 \tag{10}$$

where $\alpha = A + m_1(\omega_0^2 - \omega_1^2)$, $\upsilon_1^2 = \frac{1}{4}l^2\omega_1^2$, υ_1 is the characteristic velocity of the proton.

3. BELL SHAPE SOLITON SOLUTION

By means of the transformation $\xi = x - \upsilon t$, Eqs. (9) and (10) become

$$m_1\left(\upsilon^2 - \upsilon_1^2\right)u_{\xi\xi} + \frac{2k}{u_0^2}\eta u + \alpha u - Bu^2 + cu^3 = 0 \tag{11}$$

$$m_2\left(\upsilon^2 - c_0^2\right)\eta_{\xi\xi} + \frac{k}{u_0^2}\left(u^2 - u_0^2\right) + m_2\Omega_0^2\eta = 0 \tag{12}$$

when $\upsilon = c_0$ i.e. the velocity of the soliton is just equal to the characteristic speed of sound of the heavy-ion sublattice (Peyrard *et al.*, 1987). From Eq. (12), we get

$$\eta = -\frac{k}{m_2 u_0^2 \Omega_0^2}\left(u^2 - u_0^2\right) \tag{13}$$

so that Eq. (11) can be written as

$$m_1\left(\upsilon_1^2 - \upsilon^2\right)u_{\xi\xi} = \wedge u - Bu^2 + Gu^3 \tag{14}$$

where $\wedge$ and G are constants A and C renormalized by the proton-ion interaction

$$\wedge = A + m_1\left(\omega_0^2 - \omega_1^2\right) + \frac{2k^2}{m_2 u_0^2 \Omega_0^2} \tag{15}$$

$$G = C - \frac{2k^2}{m_2 u_0^4 \Omega_0^2} \tag{16}$$

we now set $Y = \frac{du}{d\xi}$, $\rho = m_1(\upsilon_1^2 - \upsilon^2)$, $F(u) = \wedge u - Bu^2 + Gu^3$. Eq. (14) can be written as

$$Y dY = \frac{1}{\rho} F(u) du \tag{17}$$

Integrating (17) we have

$$\frac{du}{d\xi} = \frac{\sqrt{2}}{[m_1(\upsilon_1^2 - \upsilon^2)]^{1/2}} u \left[\frac{1}{2} \wedge \left(1 - \frac{2}{3}\frac{B}{\wedge} u + \frac{1}{2}\frac{G}{\wedge} u^2\right)\right]^{1/2} \tag{18}$$

Further integrating (18), we get bell-shape soliton solution.

$$u = \frac{3\wedge}{B\left\{1 + (1 - 9 \wedge G/2B^2)^{1/2} \cosh\left[\left(\frac{\wedge}{m_1(\upsilon_1^2 - \upsilon^2)}\right)^{1/2} (x - \upsilon t)\right]\right\}} \tag{19}$$

Here the width of the soliton is W_s

$$W_s = \left[\frac{m_1(\upsilon_1^2 - \upsilon^2)}{\wedge}\right]^{1/2} = \left\{\frac{m_1(\upsilon_1^2 - \upsilon^2)}{A + m_1(\omega_0^2 - \omega_1^2) + 2k^2/m_2 u_0^2 \Omega_0^2}\right\}^{1/2} \tag{20}$$

we see that the width of the bell-shape soliton decrease as interaction between the two sublattice and the influence of the optical mode of the heavy-ion sublattice, the bell-shape soliton describes the ionic nonlinear defect, because the charge density depends directly on $\delta_e = -\partial u/\partial x$ (Cheng, 2001). Equation (16) show that the motion of this soliton describes the propagation of the charge, it transports momentum and energy along hydrogen-bonded molecular chains.

4. ELEMENTARY PROPERTIES OF BELL SHAPE SOLITON

In this section we investigate the elementary properties of bell-shape soliton, but here we consider only a few physically important quantities concerning bell-shape soliton.

4.1. Momentum and Effective Mass of Bell-Shape Soliton

If we further set

$$g = \frac{B}{3}\left(\frac{2}{\wedge G}\right)^{1/2} \tag{21}$$

Equation (19) becomes

$$u = \frac{[2\wedge/G]^{1/2}}{g + (g^2 - 1)^{1/2}\cosh\frac{\xi}{W_s}} \tag{22}$$

From Eqs. (21) and (22), we find the momentum of the bell-shape soliton to be

$$\begin{aligned} p &= -\frac{m_1}{l}\int_{-\infty}^{\infty} u_x u_t dx = \int_{-\infty}^{\infty}\frac{dx}{l}\frac{m_1\left(\frac{2\wedge}{G}\right)(g^2-1)\frac{\upsilon}{W_s^2}\sinh^2\left(\frac{x-\upsilon t}{W_s}\right)}{\left[g + (g^2-1)^{1/2}\cosh\left(\frac{x-\upsilon t}{W_s}\right)\right]^4} \\ &= \frac{4\wedge(g^2-1)m_1\upsilon}{lGW_s}\int_0^{\infty}\frac{\sinh^2 u du}{[g + (g^2-1)^{1/2}\cosh u]^4} \\ &= \frac{4\wedge m_1\upsilon}{15lGW_s}\cdot\frac{g^2-1}{g^4}\cdot F\left(\frac{5}{2}, 2, \frac{7}{2}, g^{-2}\right) \\ &\approx \frac{4\wedge m_1\upsilon}{15lGW_s g^2}F\left(\frac{5}{2}, 2, \frac{7}{2}, g^{-2}\right) = \frac{6\wedge^2 m_1\upsilon}{5lW_s B^2}F\left(\frac{5}{2}, 2, \frac{7}{2}, g^{-2}\right) \end{aligned} \tag{23}$$

$$p = M_{sol}^{*}\upsilon \tag{24}$$

From Eqs. (23), (24)we obtain the effective mass of the bell-shape soliton

$$M_{sol}^{*} = \frac{6\wedge^2 m_1}{5lW_s B^2}F\left(\frac{5}{2}, 2, \frac{7}{2}, g^{-2}\right) \tag{25}$$

where $F(\frac{5}{2}, 2, \frac{7}{2}, g^{-2})$ is a hypergeometric function.

4.2. Energy of Bell-Shape Soliton

The kinetic energy of the bell-shape soliton (22) is given by

$$\begin{aligned} E_k &= \int_{-\infty}^{\infty}\frac{dx}{l}\left(\frac{1}{2}m_1 u_t^2\right) = \int_{-\infty}^{\infty}\frac{dx}{l}\frac{m_1}{2}\frac{\frac{2\wedge}{G}(g^2-1)\frac{\upsilon^2}{W_s^2}\sinh^2\left(\frac{x-\upsilon t}{W_s}\right)}{\left[g + (g^2-1)^{1/2}\cosh\left(\frac{x-\upsilon t}{W_s}\right)\right]^4} \\ &= \frac{2\wedge(g^2-1)m_1\upsilon^2}{lGW_s}\int_0^{\infty}\frac{\sinh^2 u du}{\left[g + (g^2-1)^{1/2}\cosh u\right]^4} \\ &= \frac{3\wedge^2 m_1\upsilon^2}{5lW_s B^2}F\left(\frac{5}{2}, 2, \frac{7}{2}, g^{-2}\right) \end{aligned} \tag{26}$$

Then the total energy of the bell-shape soliton is

$$E = M^*_{sol}\gamma \upsilon_1^2 = M^*_{sol}\left(1 - \frac{\upsilon^2}{\upsilon_1^2}\right)^{-1/2} \cdot \upsilon_1^2 \tag{27}$$

We discuss the case of the slowly moving $\upsilon << \upsilon_1$, the Eq. (27) becomes

$$E = \frac{6 \wedge^2 m_1 \upsilon_1^2}{5l W_s B^2} F\left(\frac{5}{2}, 2, \frac{7}{2}, g^{-2}\right) \tag{28}$$

we have chosen the following set of model parameters for ice (Cheng, 2004; Gordon, 1989; Pang and Muller-kirsten, 2000): $m_1 = 1.67 \times 10^{-24} g$, $\upsilon_1 = 1.1 \times 10^6$ cms^{-1}, $l = 5$Å. The continuum approximation model (6) is valid only for bell-shape soliton width $W_s >> l$, taking $W_s = 60$Å, for a weak proton-ion interaction case, $\wedge \approx$ A = 5.4(ev/Å^2), B = 0.63(ev/Å^3) (Kashimori *et al.*, 1982). Using the condition g^2>>1, we take g = 10. The calculation according to Eq. (28) give E = 0.375 eV. This vales is close to the experimental ones of the activation energy measured by the proton conductivity in ice. E = (0.34 ± 0.02)eV (Gordon, 1989), E = 0.37eV (Gordon, 1989).

5. CONCLUSIONS

In summary, we have studied proton transfer in hydrogen-bonded chains with asymmetric double-well potential, using a new two-component soliton model. We obtain the general expression of the bell-shape soliton solution in Eq. (19). The width of the bell-shape soliton decrease as interaction between the two sublattice and influence of the optical model of the heavy-ion sublattice. The momentum, the effective mass, the energy of the bell-shape soliton are calculated. The calculated energy is in satisfactory agreement with the experiment.

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