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Proton Transport in Hydrogen-Bonded Chains in the Presence of an External Field

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The motion of a kink pair consisting of kink soliton in different sublattices in hydrogen-bonded chains in the presence of an external force and damping is discussed based on a new soliton model. The scattering cross-section of a kink pair for an electromagnetic wave and the mobility of a kink pair are found.

The soliton phenomena were first observed by Scott Russell (1838). The dynamics of proton transfer along hydrogen-bonded molecular chains is an extremely interesting and important scientific problem. The one-component soliton model for proton transport in hydrogen-bonded molecular chains has been investigated by a number of authors (Kashimori *et al.*, 1982; Xu, 1990). Considering the influence of motion of the heavy ions sublattice on the proton sublattice, the two-component soliton model (ADZ model) was suggested by Antonchenko *et al.* (1983). In their model, they consider the kink excitation in the proton sublattice and the bell-shape excitation in the heavy ions sublattice. Both of these nonlinear excitations propagate along the lines of chain with the same velocity as the characteristic speed of sound of the heavy ions sublattice. Recently Pang proposed a new two-component soliton model for proton transport in hydrogen-bonded chains (Pang and Müller-Kirsten, 2000). In this model, the nonlinear excitation in the proton sublattice and in the heavy ions sublattice are kink excitations. But it is not necessary that the velocity of kinks be equal to the characteristic speed of sound of the heavy ions sublattice. In the present paper, we discuss the motion of the kink pair in the presence of an external force and damping basing on the Pang model (Pang and Müller-Kirsten, 2000). We investigate the scattering of an electromagnetic wave by a kink pair and show that scattering by a kink pair of an electromagnetic wave of high frequency is similar to Thomson scattering of a free electron. Furthermore, the expression for the mobility of the kink pair is found. Good agreement is obtained with the experimental data (Gordon, 1987, 1988, 1989).

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We consider here a new model Hamiltonian of the hydrogen-bonded molecular systems (Pang and Müller-Kirsten, 2000)

$$H = H_{\text{p}} + H_{\text{h}} + H_{\text{int}} \tag{1}$$

where

$$H_{\text{p}} = \sum_i \left\{ \frac{1}{2m} P_i^2 + \frac{1}{2} m\omega_0^2 u_i^2 - \frac{1}{2} m\omega_1^2 u_i u_{i+1} + U(u_i) \right\} \tag{2}$$

and

$$U(u_i) = \frac{1}{4} U_0 \left(1 - \left(\frac{u_i}{u_0} \right)^2 \right)^2 \tag{3}$$

$$H_{\text{h}} = \sum_i \left\{ \frac{1}{2M} P_i^2 + \frac{1}{2} \beta (\rho_i - \rho_{i-1})^2 \right\} \tag{4}$$

$$H_{\text{int}} = \sum_i \left\{ \frac{1}{2} m x_1 (\rho_{i+1} - \rho_{i-1}) u_i^2 + m x_2 (\rho_{i+1} - \rho_i) u_i u_{i+1} \right\} \tag{5}$$

where H_{p} is the Hamiltonian of the proton sublattice. Here u_i and $p_i = m\dot{u}_i$ are the proton displacements and momenta, respectively, m is the mass of the proton, $U(u_i)$ is the proton potential energy in each hydrogen bond, u_0 is the distance along the chain from the top of the barrier to one of the minima in the double-well potential. $\triangle = 2u_0$ is the distance between the two minima. 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 nondiagonal elements of the dynamical matrix of the proton, respectively. H_{h} is the Hamiltonian of the heavy ionic sublattice with low-frequency harmonic vibration, ρ_i and $P_i = M\dot{\rho}_i$ are the displacement of the heavy ion from its equilibrium position and its conjugate momentum, respectively, M is the mass of the heavy ion, $c_0 = l(\beta/M)^{1/2}$ is the velocity of sound in the heavy ionic sublattice, and l is the lattice constant. H_{int} is the interaction Hamiltonian between the protonic and the heavy ionic sublattices, x_1 and x_2 are coupling constants between the proton and the heavy ion sublattices. In the continuum approximation with the long-wavelength limit (Pang and Müller-Kirsten, 2000), this Hamiltonian can be replaced by a continuum representation

$$H = \int_{-\infty}^{\infty} \frac{dx}{l} \left\{ \left[\frac{1}{2} m u_t^2 + \frac{1}{2} m\omega_0^2 u^2 - \frac{1}{2} m\omega_1^2 u \left(u + l u_x + \frac{1}{2} l^2 u_{xx} \right) \right.\right.$$
$$\left.\left. + \frac{1}{4} U_0 \left(1 - \left(\frac{u}{u_0} \right)^2 \right)^2 \right] + \left(\frac{1}{2} M \rho_t^2 + \frac{1}{2} \beta l^2 \rho_x^2 \right) + m(x_1 + x_2) l \rho_x u^2 \right\} \tag{6}$$

where l is the lattice spacing and $u(x, t)$ and $\rho(x, t)$ are the displacement fields of the proton and the heavy ion, respectively. The Lagrangian density of the system corresponding to Eq. (6) can be written as

$$\begin{aligned} L &= T - U \\ &= \frac{1}{2}mu_t^2 + \frac{1}{2}M\rho_t^2 - \frac{1}{2}m\omega_0^2u^2 + \frac{1}{2}m\omega_1^2u\cdot\left(u + lu_x + \frac{1}{2}l^2u_{xx}\right) \\ &\quad - \frac{1}{4}U_0\left(1 - \left(\frac{u}{u_0}\right)^2\right)^2 - \frac{1}{2}\beta l^2\rho_x^2 - m(x_1 + x_2)l\rho_x u^2 \end{aligned} \tag{7}$$

The Euler-Lagrange equations of motion from (6) and (7) are

$$mu_{tt} = m\upsilon_1^2u_{xx} - 2m(x_1 + x_2)l\rho_x u + \frac{U_0u}{u_0^2}\left(1 + \frac{mu_0^2\left(\omega_1^2 - \omega_0^2\right)}{U_0} - \left(\frac{u}{u_0}\right)^2\right) \tag{8}$$

$$M\rho_{tt} = \beta l^2\rho_{xx} + 2m(x_1 + x_2)luu_x \tag{9}$$

where $\upsilon_1^2 = \frac{1}{4}l^2\omega_1^2$, υ_1 is the characteristic velocity of the proton.

Using the variable transformation $y = x - \upsilon t$ and integrating Eq. (9), we may reduce Eqs. (8) and (9) to the following equation (Cheng, 2000; Halding and Lomdahl, 1988)

$$u_{yy} + \alpha u - ru^3 = 0 \tag{10}$$

where

$$\begin{aligned} \alpha &= \frac{\varepsilon}{\upsilon_1^2 - \upsilon^2}, \quad r = \frac{G}{\upsilon_1^2 - \upsilon^2} \\ \varepsilon &= \omega_1^2 - \omega_0^2 + \frac{U_0}{mu_0^2} - 2g(x_1 + x_2)l \\ G &= \frac{U_0}{mu_0^4} - \frac{2(x_1 + x_2)^2ml^2}{Mc_0^2(1 - s^2)} \end{aligned} \tag{11}$$

here g is an, as yet, undetermined integration constant and $s = \upsilon/c_0$. When $\varepsilon > 0$, $G > 0$, and $0 < \upsilon < \upsilon_1$, $0 < \upsilon < c_0$, Eq. (10) have kink soliton solution (Cheng, 2000),

$$u = \pm\left(\frac{\varepsilon}{G}\right)^{1/2}\tanh\left[\left(\frac{\varepsilon}{2\left(\upsilon_1^2 - \upsilon^2\right)}\right)^{1/2}(x - \upsilon t)\right] \tag{12}$$

From (9) and (12) we obtain

$$\rho = \mp\frac{\sqrt{2}(x_1 + x_2)ml}{Mc_0^2(1 - s^2)G}\left[\varepsilon\left(\upsilon_1^2 - \upsilon^2\right)\right]^{1/2} \times \tanh\left[\left(\frac{\varepsilon}{2\left(\upsilon_1^2 - \upsilon^2\right)}\right)^{1/2}(x - \upsilon t)\right] \tag{13}$$

Here we choose $g = \frac{ml(x_1+x_2)u_0^2}{Mc_0^2(1-s^2)}$, if we further set

$$b = -\frac{\sqrt{2}(x_1 + x_2)ml}{Mc_0^2(1 - s^2)}\left(\frac{\upsilon_1^2 - \upsilon^2}{G}\right)^{1/2} \tag{14}$$

(13) becomes

$$\rho = bu \tag{15}$$

We see from (12)–(15) that, in the case $\upsilon < \upsilon_1$ and $\upsilon < c_0$, if the nonlinear excitation in the proton sublattice is the kink (antikink), then the nonlinear excitation in the heavy ion sublattice is the antikink (kink) soliton. They propagate along the hydrogen-bonded chains in pairs with the same velocity.

In the presence of an external force and damping, the equations of motion (8) and (9) are replaced by the following equations (Peyrared *et al.*, 1987):

$$u_{tt} - \upsilon_1^2 u_{xx} + 2(x_1 + x_2)lu\rho_x - \frac{U_0 u}{mu_0^2}\left[1 + \frac{mu_0^2(\omega_1^2 - \omega_0^2)}{U_0} - \frac{u^2}{u_0^2}\right]$$
$$= -\Gamma_1 u_t - \frac{F_1}{m} \tag{16}$$

$$\rho_{tt} - c_0^2\rho_{xx} - \frac{2(x_1 + x_2)ml}{M}uu_x = -\Gamma_2\rho_t - \frac{F_2}{M} \tag{17}$$

where F_1 and F_2 are the external forces on the proton and the heavy ion, respectively. Γ_1 and Γ_2 are the damping coefficients for the proton and heavy-ion motion, respectively.

It is usually considered that the effect of an external force and damping on a kink will only lead to a little variation of the velocity of the kink but the waveform of the kink will not be changed. From (12)–(15) and the appropriate boundary conditions we find the momentum of the kink pair to be

$$P = -\frac{1}{l}\int_{-\infty}^{\infty}(mu_t u_x + M\rho_t\rho_x)\ dx \tag{18}$$

From Eqs. (18), (16), and (17) and considering the boundary conditions, as,

$$\frac{dP}{dt} = -\Gamma_1 P_{\mathrm{k}} - \Gamma_2 P_{\mathrm{ak}} + \frac{2F}{l}\left(\frac{\varepsilon}{G}\right)^{1/2} \tag{19}$$

where

$$F = F_1 + bF_2 \tag{20}$$

P_{k} is the momentum of the protonic kink soliton,

$$P_{\mathrm{k}} = -\frac{m}{l}\int_{-\infty}^{\infty} u_x u_t\ dx = m^*\upsilon \tag{21}$$

$$m^* = \frac{2\sqrt{2}m\varepsilon^{3/2}}{3\left(\upsilon_1^2 - \upsilon^2\right)^{1/2} Gl} \tag{22}$$

m^* is the effective mass of the kink in the proton sublattice. P_{ak} is the momentum of the antikink in the heavy-ion sublattice,

$$P_{\text{ak}} = -\frac{M}{l}\int_{-\infty}^{\infty} \rho_x \rho_t \; dx = M^* \upsilon \tag{23}$$

$$M^* = \frac{2\sqrt{2}Mb^2\varepsilon^{3/2}}{3\left(\upsilon_1^2 - \upsilon^2\right)^{1/2} Gl} \tag{24}$$

M^* is the effective mass of the antikink soliton. P is the momentum of the kink pair,

$$P = P_{\text{k}} + P_{\text{ak}} = (m^* + M^*) = M_{\text{sol}}^* \upsilon \tag{25}$$

$$M_{\text{sol}}^* = m^* + M^* \tag{26}$$

M_{sol}^* is the effective mass of the kink pair.

Substituting Eqs. (21)–(26) into (19), we obtain the equation of motion of the kink pair in the presence of an external force and damping.

$$\frac{d\upsilon}{dt} + \wedge \upsilon = \frac{2F}{M_{\text{sol}}^* l}\left(\frac{\varepsilon}{G}\right)^{1/2} \tag{27}$$

where

$$\wedge = \frac{1}{M_{\text{sol}}^*}\left(\Gamma_1 m^* + \Gamma_2 M^* + \frac{dM_{\text{sol}}^*}{dt}\right) \tag{28}$$

It is difficult to solve Eq. (27), we discuss only the case where $\upsilon \ll \upsilon_1$ and $\upsilon \ll \text{c}_0$. Under this approximation, b, G, ε, M_{sol}^* and $\wedge$ can be regarded as constants and be written by b_0, G_0, ε_0, M_{sol}^{0*}, and $\wedge_0$, for example

$$b_0 = -\frac{\sqrt{2}(x_1 + x_2)ml\upsilon_1}{Mc_0^2\sqrt{G_0}} \tag{29}$$

$$G_0 = \frac{U_0}{mu_0^4} - \frac{2(x_1 + x_2)^2 ml^2}{Mc_0^2} \tag{30}$$

$$\wedge_0 = \frac{1}{M_{\text{sol}}^{0*}}(\Gamma_1 m^* + \Gamma_2 M^*) \tag{31}$$

Equation (27) becomes

$$\frac{d\upsilon}{dt} + \wedge_0 \upsilon = \frac{2F}{M_{\text{sol}}^{0*} l}\left(\frac{\varepsilon_0}{G_0}\right)^{1/2} \tag{32}$$

We now discuss the scattering of the kink pair for an electromagnetic wave.

We assume that the velocity and the displacement of the kink pair are very much less than the speed of light and the wavelength of the incident electromagnetic wave, respectively, and the incident electrical field is written by $E = E_{\rm m}e^{-i\Omega t}$, where $E_{\rm m}$ and Ω are the amplitude and the frequency of the incident electrical field respectively. In this case, influence of the incident magnetic field on the kink pair can be neglected. Thus Eq. (32) becomes

$$\frac{d\upsilon}{dt} + \wedge_0 \upsilon = \frac{2e^* E_{\rm m}}{M_{\rm sol}^{0*} l}\left(\frac{\varepsilon_0}{G_0}\right)^{1/2} e^{-i\Omega t} \tag{33}$$

where $F = e^* E_{\rm m} e^{-i\Omega t} = (e_1 + b_0 e_2) E_{\rm m} e^{-i\Omega t}$, e_1 and e_2 are the effective charges of the kink in the proton and in the heavy ion sublattice, respectively.

From Eq. (33), we get the acceleration of the kink pair,

$$a = \frac{d\upsilon}{dt} = \frac{2e^* \Omega E_{\rm m}}{M_{\rm sol}^{0*} l \left(\wedge_0^2 + \Omega^2\right)^{1/2}}\left(\frac{\varepsilon_0}{G_0}\right)^{1/2} e^{-i(\Omega t - \varphi + \frac{\pi}{2})} \tag{34}$$

Here

$$\tan\varphi = \frac{\Omega}{\wedge_0}$$

The accelerated kink pair will produce electromagnetic radiation. The average power of the electromagnetic wave scattered by a kink pair, obtained from Eq. (34), is

$$W = \frac{2\Omega^2 e^{*4}}{3\pi \varepsilon^2 c^4 M_{\rm sol}^{0*2} l^2 \left(\wedge_0^2 + \Omega^2\right)}\left(\frac{\varepsilon_0}{G_0}\right) I_0 \tag{35}$$

where ε is the dielectric constant, c is the speed of light, $I_0 = \frac{1}{2}\varepsilon c E_{\rm m}^2$ is the average energy flow of the incident electromagnetic wave. Thus we obtain the scattering cross-section of the kink pair for an electromagnetic wave,

$$\sigma = \frac{W}{I_0} = \frac{2\Omega^2 e^{*4}}{3\pi \varepsilon^2 c^4 M_{\rm sol}^{0*2} l^2 \left(\wedge_0^2 + \Omega^2\right)}\left(\frac{\varepsilon_0}{G_0}\right) \tag{36}$$

In the limit of low frequency, that is, $\Omega \ll \wedge_0$, Eq. (36) is given by

$$\sigma = \frac{2\Omega^2 e^{*4}}{3\pi \varepsilon^2 c^4 M_{\rm sol}^{0*2} l^2 \wedge_0^2}\left(\frac{\varepsilon_0}{G_0}\right) \tag{37}$$

namely the scattering cross-section is directly proportional to Ω^2.

In the limit of high frequency, that is, $\Omega \gg \wedge_0$, Eq. (36) is written as

$$\begin{aligned}\sigma &= \frac{2e^{*4}}{3\pi\varepsilon^2 c^4 M_{\text{sol}}^{0*2} l^2}\left(\frac{\varepsilon_0}{G_0}\right)\\ &= \frac{8}{3}\pi r_s^2\end{aligned} \tag{38}$$

This is just the Thomson scattering cross-section,
where

$$r_s = \frac{2e^{*2}}{4\pi\varepsilon c^2 M_{\text{sol}}^{0*} l}\left(\frac{\varepsilon_0}{G_0}\right)^{1/2} \tag{39}$$

is the effective scattering radius of kink pair. Therefore, the kink pair is much like the free electron for the case of scattering of an electromagnet wave with high frequency.

When the frequency of the external electrical field is equal to the zero, namely, the system is subjected to a constant electrical field with strength E. In this case, $F = e^* E = (e_1 + b_0 e_2)E$. Equation (32) becomes

$$\frac{d\upsilon}{dt} + \wedge_0 \upsilon = \frac{2e^* E}{M_{\text{sol}}^{0*} l}\left(\frac{\varepsilon_0}{G_0}\right)^{1/2} \tag{40}$$

The solution of Eq. (40) is

$$\upsilon(t) = \upsilon(0)e^{-\wedge_0 t} + \frac{2e^* E}{M_{\text{sol}}^{0*} \wedge_0 l}\left(\frac{\varepsilon_0}{G_0}\right)^{1/2}(1 - e^{-\wedge_0 t}) \tag{41}$$

Here $\upsilon(0)$ is the initial velocity. When $t \to \infty$, we get

$$\upsilon(\infty) = \frac{2e^* E}{M_{\text{sol}}^{0*} \wedge_0 l}\left(\frac{\varepsilon_0}{G_0}\right)^{1/2} = \upsilon_\infty \tag{42}$$

where υ_∞ is the power balance velocity at which the power input to the system is just balanced by the power loss due to dissipation (Mclaughlin and Scott, 1978). Thus we obtain the mobility of the kink pair,

$$\mu = \frac{2e_1\left(1 + b_0 \frac{e_2}{e_1}\right)}{(\Gamma_1 m^* + \Gamma_2 M^*)l}\left(\frac{\varepsilon_0}{G_0}\right)^{1/2} \tag{43}$$

Equation (43) can be written as

$$\mu = \mu_0 Q\left(1 + b_0 \frac{e_2}{e_1}\right) \tag{44}$$

where

$$Q = \left(1 + b_0^2 \frac{\Gamma_2 M}{\Gamma_1 m}\right)^{-1} \left(1 - \frac{m u_0^2}{U_0}(\omega_0^2 - \omega_1^2) - \frac{2g(x_1 + x_2) m u_0^2}{U_0}\right)^{-\frac{1}{2}} \quad (45)$$

$$\mu_0 = \frac{3 e_1 \upsilon_1}{\Gamma_1 m \omega_H} \left(\frac{G_0}{\varepsilon_0}\right)^{1/2} \quad (46)$$

Here μ_0 is the mobility of the kink in the one-component solition model (Xu, 1990). Computed to the first (linear) approximation of coupling constant x_1 and x_2, Eq. (44) becomes

$$\mu = \mu_0 \left[1 - \frac{\sqrt{2}(x_1 + x_2) e_2 l m \upsilon_1}{\sqrt{G_0} e_1 M c_0^2}\right] \quad (47)$$

This equation imply that the influence of motion of the heavy ions and the coupling between the two sublattices is to reduce the mobility.

We have chosen the following set of model parameters for ice (Gordon, 1987, 1988, 1989; Pang and Müller-Kirsten, 2000; Xu, 1990): $m = m_\mathrm{p}$, $M = 100\, m_\mathrm{p}$, $U_0 = 10$ ev, $\upsilon_1 = 10^4$ m s^{-1}, $c_0 = 0.1\upsilon_1$, $\Delta = 2u_0$, $\Delta = 0.367$–0.780 Å, $l = 5$ Å, $x_1 = 3 \times 10^{47}$ m s^{-2}, $x_2 = 0.2 \times 10^{44}$ m s^{-1}, $\Gamma_1 = 6 \times 10^{13}\, s^{-1}$, $\nu_\mathrm{H} = 3250$ cm^{-1} and $e_1 = 1.5e$, where e is the protonic charge. The calculations according to Eqs. (46) and (47) give $\mu = (3.0$–$6.4) \times 10^{-2}$ cm^2 s^{-1} v^{-1}. These values are close to the observed one $\mu = 7.5 \times 10^{-2}$ cm^2 s^{-1} v^{-1} (Gordon, 1987, 1988, 1989).

In summary, we have studied Dynamic properties of proton transfer in hydrogen bonded chains in presence of an external force and damping, using a new two-component soliton model. We also investigated the scattering by a kink pair of an electromagnetic wave and show that scattering by a kink pair of an electromagnetic wave of high frequency is similar to Thomson scattering of a free electron. We have found the scattering cross-section of a kink pair for an electromagnetic wave and the mobility of a kink pair. The calculated mobility is in satisfactory agreement with the experiment.

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