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Electrosoliton and lattice defects in hydrogen-bonded chains

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Abstract. In this paper, we investigate the behaviour of electrons in hydrogen-bonded chains and show that an electron can be bound in the compression area of the proton sublattice and becomes an electrosoliton state described by a bell-shaped electronic wave function. The influence of motion of the heavy-ion sublattice on the velocity of soliton defects and the cooperative transport of electrons and protons in hydrogen-bonded chains are discussed, respectively. The stability of the solution is discussed.

1. Introduction

The charge transfer in hydrogen-bonded condensed matter, organic and biological systems is an important and interesting problem. The proton transfer along hydrogen-bonded chains has been recognized to be responsible for the energy and charge conduction by means of the Grotthaus mechanism [1]. Solitonic defects are excited in the process of proton transfer, i.e. ionic and bonding defects are formed. The former involve an intraband motion of the (unique) binding proton, while the latter result from interbond or intermolecular motion of the protons due to rotations of the molecules (e.g. the water molecules in ice). It has shown that the ionic (I^-) and bonding (B^-) kink defects are carriers of a fractional negative charge so that their combined dynamics generates a 'proton hole' transfer $e_{I^-} + e_{B^-} = -e$, where $e > 0$ is the unit charge of one proton, to the next bond. On the other hand, the ionic (I^+) and bonding (B^+) antikink defects are carriers of a fractional positive charge, so that their combined dynamics generates a proton transfer ($e_{I^+} + e_{B^+} = e$) to the next bond. Antikinks excited in the proton sublattice possess excess fractional positive charge, corresponding to localized compression in the proton sublattice (for example, the hydroxonium ion H_3O^+ in an ice lattice), and kinks excited in the proton sublattice possess excess fractional negative charge, corresponding to localized rarefaction in the proton sublattice (for example, the hydroxyl ion OH^- in an ice lattice). In fact, the hydrogen-bonded chain can be considered to be composed of a proton sublattice and a heavy-ion sublattice. For example, the ice lattice is composed of a proton sublattice $(H^+)_x$ and a heavy-ion sublattice $(HO^-)_x$. Considering the influence of the motion of the heavy-ion sublattice on the proton sublattice, the two-component soliton model was suggested by some authors [2–6]. Because of the interaction between two sublattices, soliton defects corresponding to the heavy-ion sublattice localized deformation are excited [6]. On the other hand, there is a class of systems where the protonic and the electronic nature of the conductivity coexist at least for certain ranges of temperature [7, 8]. In biological systems, the coupling between proton and electron transfer is responsible for some reaction processes, for instance, there is coupling between proton and electron transfer in the charge relay system of α-chymotrypsin [9]. Thus, it is necessary to research the behaviour of electrons, i.e. investigate the influence of the deformation of proton and heavy-ion sublattices upon the motion of electrons. (Abdullaev *et al* had investigated only the system of protons and electrons [10].) For the sake of simplicity, we do not alone consider the interaction between electron and heavy-ion sublattices but incorporate it into the coupling between protons and electrons because interaction between proton and heavy-ion sublattices is considered. The results in this paper show that one electron can be trapped by the lattice defects (slow antikink–kink pair or fast antikink–antikink pair) in the hydrogen-bonded chain. The bell-shaped electronic wave function (electrosoliton state) is localized in the compression area of the proton sublattice. The lattice defects and electrosoliton state propagate along the hydrogen-bonded chain with the same velocity in pairs, representing a bound state called the electrosoliton–soliton pair, which possesses a fractional negative charge [11]. Moreover, the influence of motion of the heavy-ion sublattice on the velocity of soliton defects is discussed. The stability of the solution is proved. Finally for the concept of the electrosoliton–soliton pair, the conduction mechanism of the solitonic defect in a finite-length hydrogen-bonded chain is given qualitatively.

2. Electrosoliton–soliton pair

Here we consider the interaction between electron and lattice defects in the hydrogen-bonded chain. The total Hamiltonian of system is

$$H = H_{pe} + H_{pi} + H_i \tag{1}$$

where

$$H_{pe} = \sum_n \left[\frac{1}{2} m_1 \left(\frac{\mathrm{d}u_n}{\mathrm{d}t} \right)^2 + \frac{1}{2} m_1 \left(\frac{c_0}{a} \right)^2 \left(u_{n+1} - u_n \right)^2 + \varepsilon_0 \left(1 - \frac{u_n^2}{u_0^2} \right)^2 + E_0 C_n^+ C_n - J \left(C_{n+1}^+ C_n + C_n^+ C_{n+1} \right) + \chi \left(u_n - u_{n-1} \right) C_n^+ C_n \right] \tag{2}$$

is the Hamiltonian of the proton–electron system [11],

$$H_{pi} = -g \sum_n \left(u_n^2 - u_0^2 \right) \left(\rho_n - \rho_{n-1} \right) \tag{3}$$

is the Hamiltonian for interaction between proton and heavy-ion sublattices [6], and

$$H_i = \sum_n \left[\frac{1}{2} m_2 \left(\frac{\mathrm{d}\rho_n}{\mathrm{d}t} \right)^2 + \frac{1}{2} m_2 \left(\frac{v_0}{a} \right)^2 \left(\rho_{n+1} - \rho_n \right)^2 \right] \tag{4}$$

is the Hamiltonian of the heavy-ion sublattice [6]. a is the lattice spacing. c_0 and v_0 are the characteristic velocities of the proton and heavy-ion sublattices, respectively. ε_0 is the barrier height in the double-well potential. u_n is the displacement of the nth proton (mass m_1) along the chain from one of the two minima in the double-well potential. ρ_n is the displacement of the nth heavy ion (mass m_2) from its equilibrium position. u_0 is the equilibrium position of the proton. g is the coupling constant between the two sublattices. E_0 is the energy of the electron in the undistorted chain, J is the intersite transfer energy and $\chi > 0$ is the coupling constant of the interaction between the electronic and the protonic subsystems. Finally, C_n^+ (C_n) creates (annihilates) one electron on the nth site of the protonic chain. The same Hamiltonian can be used in order to describe the dynamics of one electron hole in the chain. In this case, $\chi < 0$, and C_n^+ (C_n) creates (annihilates) one hole on the nth site of the chain.

The one-electron state can now be written [11]

$$|\Psi(t)\rangle = \sum_n A_n(t) C_n^+ |0\rangle \tag{5}$$

where the probability amplitude is normalized to unity, i.e. $\sum_n |A_n(t)|^2 = 1$. The mean value of Hamiltonian in the system is written

$$\begin{aligned} E = \langle\Psi|H|\Psi\rangle &= \sum_n A_n^* \big[E_0 A_n - J\big(A_{n+1} + A_{n-1}\big) + \chi\big(u_n - u_{n-1}\big)A_n\big] \\ &+ \sum_n \left[\frac{1}{2}m_1\left(\frac{\mathrm{d}u_n}{\mathrm{d}t}\right)^2 + \frac{1}{2}m_1\left(\frac{c_0}{a}\right)^2\big(u_{n+1} - u_n\big)^2 + \varepsilon_0\left(1 - \frac{u_n^2}{u_0^2}\right)^2\right] \\ &+ \sum_n \left[\frac{1}{2}m_2\left(\frac{\mathrm{d}\rho_n}{\mathrm{d}t}\right)^2 + \frac{1}{2}m_2\left(\frac{v_0}{a}\right)^2\big(\rho_{n+1} - \rho_n\big)^2 - g\Big(u_n^2 - u_0^2\Big)\big(\rho_n - \rho_{n-1}\big)\right]. \end{aligned} \tag{6}$$

In the continuum approximation model, from the Lagrangian density we can derive the equations of motion

$$\mathrm{i}\hbar\frac{\partial A}{\partial t} = \big(E_0 - 2J\big)A - Ja^2\frac{\partial^2 A}{\partial x^2} + \chi a\frac{\partial u}{\partial x}A \tag{7}$$

$$m_1\frac{\partial^2 u}{\partial t^2} = m_1 c_0^2\frac{\partial^2 u}{\partial x^2} + 4\varepsilon_0\frac{u}{u_0^2}\left(1 - \frac{u^2}{u_0^2}\right) + \chi a\frac{\partial|A|^2}{\partial x} + 2gau\frac{\partial\rho}{\partial x} \tag{8}$$

$$m_2\frac{\partial^2\rho}{\partial t^2} = m_2 v_0^2\frac{\partial^2\rho}{\partial x^2} - 2gau\frac{\partial u}{\partial x}. \tag{9}$$

Obviously, (7), (8) and (9) are coupled nonlinear equations. It is very difficult to solve them. Here we use a self-consistent method, and let self-consistent solutions of (7) and (8) have the following relationship

$$|A|^2 = q_1 u_x \tag{10}$$

where q_1 is an undetermined coefficient. Substituting (10) into (8) and using the variable transformation $\xi = x - vt$, we may reduce (8) and (9) to the following equation [6]

$$\frac{\partial^2 u}{\partial\xi^2} + \alpha u - \beta u^3 = 0 \tag{11}$$

where

$$\alpha = \beta u_0^2 = \frac{1}{c_0^2 + \chi a q_1/m_1 - v^2}\left[\frac{4\varepsilon_0}{m_1 u_0^2} - \frac{2g^2 a^2 u_0^2}{m_1 m_2 (v_0^2 - v^2)}\right] \tag{12}$$

and obtain their solutions

$$u_k = \sigma u_0 \tanh\sqrt{\frac{\alpha}{2}}(x - vt) \tag{13}$$

$$\rho_k = q_2 u \tag{14}$$

where

$$q_2 = -\frac{\sqrt{2}ga}{m_2\sqrt{\beta}(v_0^2 - v^2)} \tag{15}$$

and $\sigma = \pm 1$ is the polarity of the soliton. $\sigma = 1$ corresponds to the kink solution, and $\sigma = -1$ to the antikink.

Substituting (10) into (7), we have

$$i\hbar \frac{\partial A}{\partial t} - (E_0 - 2J)A + Ja^2 \frac{\partial^2 A}{\partial x^2} - \frac{\chi a}{q_1}|A|^2 A = 0. \tag{16}$$

(16) is a nonlinear Schrödinger (NLS) equation, where $G = -\chi a/q_1$ is a coefficient of the nonlinear term of the NLS equation. If $G > 0$ (i.e. $q_1 < 0$), (16) has an envelope-soliton solution, while if $G < 0$ (i.e. $q_1 > 0$), (16) has a dark-soliton solution [13]. Here we are interested in the envelope-soliton solution, so taking $G > 0$ (i.e. $q_1 < 0$), the solution of (16) is

$$A_s(x,\ t) = \left(\frac{C}{8J}\right)^{1/2} \operatorname{sech}\left[\frac{G}{4Ja}(x - vt)\right] \exp[i(kx - \omega t)] \tag{17}$$

where

$$k = \frac{\hbar v}{2Ja^2} \qquad \omega = \frac{E_0 - 2J + Ja^2k^2 - G^2(16J)^{-1}}{\hbar}. \tag{18}$$

Solutions $u(x,\ t)$ and $A(x,\ t)$ must satisfy the self-consistent condition (10), so we have

$$\frac{G}{8J}\operatorname{sech}^2\frac{G}{4Ja}(x - vt) = -q_1 u_0 \sqrt{\frac{\alpha}{2}} \operatorname{sech}^2 \sqrt{\frac{\alpha}{2}}(x - vt) \tag{19}$$

where $q_1 < 0$, so taking the antikink solution ($\sigma = -1$), corresponding to the compression area of the proton sublattice. From (19), we obtain

$$q_1 = -\frac{a}{2u_0} \tag{20}$$

$$v^2 = \frac{1}{2}\left[v_1^2 + v_0^2 \pm \sqrt{\left(v_1^2 - v_0^2\right) - \frac{J^2 g^2 a^4}{m_1 m_2 \chi^2}}\right] \tag{21}$$

where

$$v_1 = \left[1 - \frac{\chi a^2}{2m_1 u_0 c_0^2} - \frac{9J^2 a^2 \varepsilon_0}{m_1 u_0^4 c_0^2 \chi^2}\right]^{1/2} c_0 \tag{22}$$

is the velocity in the one-component soliton model. If $v_1 > v_0$, v corresponds to the upper sign in (21) and $v > v_0$, i.e. $q_2 > 0$. Then (14) and (15) show that if the proton sublattice produces an antikink, then the heavy-ion sublattice produces an antikink as well. They form a fast antikink–antikink pair. In this case, the influence of motion of the heavy ions is to decrease the velocity of the soliton. If $v_1 < v_0$, v corresponds to the lower sign in (21) and $v < v_0$, i.e. $q_2 < 0$. Then, the antikink in the proton sublattice and the kink in the heavy-ion sublattice will form a slow antikink–kink pair. In this case, the influence of motion of the heavy ions is to increase the velocity of the soliton. Here the antikink–antikink pair and antikink–kink pair are the lattice defects, i.e. the defects in proton and heavy-ion sublattices. These lattice defects correspond to the compression area of the proton sublattice, thus, they have positive fractional extra charge [11, 14].

From the above discussion, it can be concluded that one electron is trapped by the lattice defects (slow antikink–kink pair or fast antikink–antikink pair) with a fractional positive charge to form a bound state with a fractional negative charge. This electron trapped by the lattice defects is described by a bell-shaped electronic wave function (17) localized in the compression area of the proton sublattice and is called an electrosoliton in this paper. The lattice defects (solitons) and electrosoliton propagate along the hydrogen-bonded chain with the same velocity (given by (21)) in pairs, i.e. they form a bound state called the electrosoliton–soliton pair (or radical electron-soliton state [11]). Using the same way, we can obtain the dynamics of one electron hole in the chain, where the bell-shaped hole wave function is localized in the rarefaction area of the proton sublattice. One hole is trapped by another kind of lattice defect (slow kink–antikink pair of fast kink–kink pair) with a fractional negative charge to form a bound state with a fractional positive charge.

Using (6) and the continuum approximation model, we have the energy of the electrosoliton–soliton pair

$$E = \frac{1}{2}m^*v^2 + \left[E_0 - 2J + \frac{\sqrt{2}\alpha^{3/2}}{3\beta a}\left(m_1c_0^2 + q_2^2m_2v_0^2\right) + \frac{4\varepsilon_0}{3a}\sqrt{\frac{2}{\alpha}} - \frac{4}{3}gq_2u_0^3a^{-1} - \frac{u_0^2\chi^2}{4J}\right] \tag{23}$$

where

$$m^* = \frac{2\sqrt{2}\alpha^{3/2}}{3\beta a}\left(m_1 + q_2m_2\right) + \frac{\hbar^2}{2Ja^2} \tag{24}$$

is the effective mass of the electrosoliton–soliton pair. The binding energy of the pair is $u_0^2\chi^2/4J$. It is well known that the internal energy of an exciton is $E_0 - 2J$. From (23), it is obvious that the internal energy of the bound state is lower than the sum of internal energy of free lattice defects and free exciton.

In order to show the validity of the continuum approximation mentioned above, we choose the experimental parameters, to estimate the soliton width $W = \sqrt{2\alpha}$, as follows [4, 12]: $a = 2.76$ Å, $u_0 = 0.37$ Å, $c_0 = 1.1 \times 10^5$ m s^{-1}, $v_0 = 0.1c_0$, $m_1 = 1.67 \times 10^{-27}$ kg, $m_2 = 17m_1$, $g = 1.0 \times 10^{-10}$ kg m s^{-2}, $\varepsilon_0 = 0.67$ eV, $J = 1.55 \times 10^{-22}$ J, $\chi = 1.0 \times 10^{-11}$ N. This gives soliton width $W \approx 2a$. Since the soliton width W remains much larger than the lattice spacing a, the continuum approximation is valid.

3. Stability of the electrosoliton–soliton pair

In order to show the stability of the solution, we present

$$A(x,\ t) = A_s + f(x,\ t) \qquad u(x,\ t) = u_k + p(x,\ t) \qquad \rho(x,\ t) = \rho_k + h(x,\ t) \tag{25}$$

where A_s, u_k and ρ_k are the solutions without perturbations, $f(x,\ t)$, $p(x,\ t)$ and $h(x,\ t)$ are perturbations. Substituting (25) into (7) and using (10), linearizing (7) with respect to $f(x,\ t)$, we derive

$$\mathrm{i}\hbar\frac{\partial f}{\partial t} - \left(E_0 - 2J\right)f + Ja^2\frac{\partial^2 f}{\partial x^2} + G\left(2f\left|A_s\right|^2 + f^*A_s^2\right) = 0. \tag{26}$$

Substituting the solution (17) into (26), we solve it to obtain

$$f(x,\ t) = -3\left(\frac{G}{8J}\right)^{1/2}\operatorname{sech}\frac{G}{4Ja}(x - vt)\tanh\frac{G}{4Ja}(x - vt)\ \exp[\mathrm{i}(kx - \omega t)]. \tag{27}$$

Consequently, since the solution (27) of the linearized equation (26) does not grow with time, the solution A_s is stable under small perturbations.

Substituting (25) into (8) and (9) and using (10), in the co-moving frame ($\xi \to x - vt,\ \tau \to t$), linearizing (8) and (9) with respect to $p(\xi,\ \tau)$ and $h(\xi,\ \tau)$, we derive

$$\frac{\partial^2 p}{\partial \tau^2} = 2v\frac{\partial^2 p}{\partial\tau\partial\xi} + \left(c_0^2 + \frac{\chi a q_1}{m_1} - v^2\right)\frac{\partial^2 p}{\partial \xi^2} + \frac{4\varepsilon_0}{m_2u_0^2}\left(1 - \frac{3u_k^2}{u_0^2}\right)p + \frac{2ga}{m_1}\left(\frac{\partial\rho_k}{\partial\xi}p + u_k\frac{\partial h}{\partial\xi}\right) \tag{28}$$

$$\frac{\partial^2 h}{\partial\tau^2} = 2v\frac{\partial^2 h}{\partial\tau\partial\xi} + \left(v_0^2 - v^2\right)\frac{\partial^2 h}{\partial\xi^2} - \frac{2ga}{m_2}\left(\frac{\partial u_k}{\partial\xi}p + u_k\frac{\partial p}{\partial\xi}\right). \tag{29}$$

We take here

$$p(\xi,\ \tau) = \sum_i \mathrm{e}^{\mathrm{i}\Omega_i\tau} p_i(\xi) \qquad h(\xi,\ \tau) = \sum_i \mathrm{e}^{\mathrm{i}\Omega_i\tau} h_i(\xi). \tag{30}$$

Substituting (30) into (28) and (29), we get

$$\Omega_i^2\Theta_i = -2\mathrm{i}\Omega_i v\frac{\partial\Theta_i}{\partial\xi} + \tilde{H}\Theta_i \tag{31}$$

where

$$\Theta_i = \begin{pmatrix} p_i \\ h_i \end{pmatrix} \tag{32}$$

$$\tilde{H} = \begin{pmatrix} -\left(c_0^2 + \frac{\chi a q_1}{m_1} - v^2\right)\frac{\partial^2}{\partial\xi^2} - \frac{4\varepsilon_0}{m_1 u_0^2}\left(1 - \frac{3u_k^2}{u_0^2}\right) - \frac{2ga}{m_2}\frac{\partial\rho_k}{\partial\xi} & -\frac{2ga}{m_1}u_k\frac{\partial}{\partial\xi} \\ \frac{2ga}{m_2}\left(u_k\frac{\partial}{\partial\xi} + \frac{\partial u_k}{\partial\xi}\right) & -\left(v_0^2 - v^2\right)\frac{\partial^2}{\partial\xi^2} \end{pmatrix}. \tag{33}$$

(31) has the form of a Schrödinger equation. The stability of the solution u_k and ρ_k is guaranteed if no eigenvalues Ω_i^2 of (31) are negative. Here we treat the operator $(-2\mathrm{i}\Omega_i v\partial/\partial\xi)$ as a perturbation to the Hamiltonian $\tilde{H}$. In the case without the perturbation (i.e. let $v = 0$), as is known [15],

$$\tilde{H}\Theta_0 = 0 \tag{34}$$

where Θ_0 is the Goldstone mode,

$$\Theta_0 = \begin{pmatrix} \mathrm{d}u_k/\mathrm{d}\xi \\ q_2\,\mathrm{d}u_k/\mathrm{d}\xi \end{pmatrix}. \tag{35}$$

It is clear that the eigenfunction $\mathrm{d}u_k/\mathrm{d}\xi$ is nodeless, i.e. Θ_0 is the ground state of the system, corresponding to the ground state eigenvalue $\tilde{\Omega}_0^2 = 0$. In the case with the perturbation (i.e. $v \neq 0$), according to the perturbation theory, we obtain

$$\Omega_0^2 = \tilde{\Omega}_0^2 + \left(2\Omega_0 v\right)^2 \sum_{i\neq 0}\frac{|W_{0i}|^2}{\tilde{\Omega}_0^2 - \tilde{\Omega}_i^2} \tag{36}$$

where

$$W_{0i} = \left\langle\Theta_0\middle|\left(-\mathrm{i}\frac{\partial}{\partial\xi}\right)\middle|\Theta_i\right\rangle. \tag{37}$$

From (36), we can find $\Omega_0^2 = 0$. It follows that the ground state eigenvalue of (31) is zero. Then, all the other eigenvalues are therefore positive. Since all solutions (30) of the linearized equations (28) and (29) do not grow with time, the solutions u_k and ρ_k are stable.

Thus, the electrosoliton–soliton pair is stable. The pair may be responsible for the cooperative transport of electron and lattice defects in hydrogen-bonded chains.

4. Cooperative transport of proton and electron

When an external electric field is applied to hydrogen-bonded chains the solitonic defects propagate along the chains and, if one can close the circuit from outside, a permanent charge conduction is established. However, the protons are unable to leave the sample which, indeed, is a finite length system. The conduction mechanism of the solitonic defect in a finite-length hydrogen-bonded chain has been discussed by some authors [11, 14]. In their papers, the solitonic defects (i.e. the solitons in the proton sublattice, they do not consider the motion of heavy ions) play the role of a ferryboat for electrons. Based on the concept of the electrosoliton–soliton pair, the conduction mechanism in a finite-length hydrogen-bonded chain can be given qualitatively as follows.

When a constant electrical field is applied to a finite-length hydrogen-bonded chain, a lattice defect with a fractional positive charge starts moving to the negative electrode (see [11] and [14]). When this defect arrives at the corresponding boundary, it will trap one electron from the negative electrode and become an electrosoliton–soliton pair with a negative fractional charge. The pair under the influence of the electrical field immediately starts moving to the positive electrode. When this pair arrives at the corresponding boundary, it will release the electron at the positive electrode and return to the lattice defect with fractional positive charge. Thus this defect with a fractional positive charge under the influence of the electrical field will move to the negative electrode again. The electrons are transported by the electrosoliton–soliton pairs from the negative electrode to the positive electrode and can close the circuit from outside, but the solitonic defects perform only a back and forth shuttling motion in the hydrogen-bonded chain and do not leave the sample.

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References

[1] Horne R A and Axelrod E H 1964 *J. Chem. Phys.* **40** 1518
[2] Zolotaryuk A V, Spatschek K H and Laedke E W 1984 *Phys. Lett.* **101A** 517
[3] Halding J and Lomdahl P S 1988 *Phys. Rev.* A **37** 2608
[4] Zhou B and Xu J-Z 1997 *Phys. Lett.* **236A** 322
[5] Xu J-Z 1991 *Solid State Commun.* **78** 439
[6] Xu J-Z 1992 *Phys. Lett.* **172A** 148
[7] Glasser L 1975 *Chem. Rev.* **75** 21
[8] Seanor D A 1968 *J. Polym. Sci.* **6** 463
[9] Umeyama H, Imamura A, Nagata C and Hanano M 1973 *J. Theor. Biol.* **41** 485
[10] Abdullaev F Kh, Flytzanis N and Zolotariuk A V 1990 *J. Mol. Electron.* **6** 75
[11] Zolotaryuk A V, Pnevmatikos St and Savin A V 1991 *Phys. Rev. Lett.* A **67** 707
[12] Davydov A S 1991 *Soliton in Molecular Systems* 2nd edn (Dordrecht: Reidel)
[13] Flytzanis N, Pnevmatikos St and Remoissenet M 1985 *J. Phys. C: Solid State Phys.* **18** 4603
[14] Xu J-Z 1993 *Phys. Lett.* **183A** 301
[15] Currie J F, Krumhansl J A, Bishop A R and Trullinger S E 1980 *Phys. Rev.* B **22** 477