Volume 9, Number 2
1009-1963/2000/09(02)/0086-08

CHINESE PHYSICS

February, 2000
© 2000 Chin. Phys. Soc.

QUANTUM-MECHANICAL PROPERTIES OF PROTON TRANSPORT IN THE HYDROGEN-BONDED MOLECULAR SYSTEMS*

PANG XIAO-FENG(庞小峰)[a)b)†] and LI PING(李 萍)[b)]

[a)] *Institute of High-Energy Electronics, University of Electronic Science and Technology, Chengdu* 610054, *China*
International Centre for Material Physics, Chinese Academy of Sciences, Shenyang 110015, *China*

[b)] *Institute of Atomic and Molecular Physics, Sichuan University, Chengdu* 610065, *China*

(Received 2 November 1998; revised manuscript received 3 August 1999)

The dynamic equations of the proton transport along the hydrogen bonded molecular systems have been obtained by using completely quantum-mechanical method to be based on new Hamiltonian and model we proposed. Some quantum-mechanical features of the proton-solitons have also been given in such a case. The alternate motion of two defects resulting from proton transfer occurred in the systems can be explained by the results. The results obtained show that the proton-soliton has corpuscle feature and obey classical equations of motion, while the free soliton moves in uniform velocity along the hydrogen bonded chains.

PACC: 0365; 3150; 3320; 3176

I. INTRODUCTION

Hydrogen bonded systems in condensed matter, polymers and biological bodies have stimulated wide interest in recent two decades.[1−23] Such systems, as ice, imidazole, hydrogen halides, carbonhydrates, solid alcohol, bacteriorhodopsin, protein and others, exhibit considerable electrical conductivity,[1−4] even though electron transport through these systems is hardly supported. These systems are characterized by the formation of long chains of hydrogen bonded molecules $\cdots X$—H$\cdots X$—H$\cdots X$—H$\cdots\cdots$. This concept is illustrated for water molecular chains. A proton is transferred to a water molecule to form an ionic defect, a hydroxonium, H_3O^+, and another water molecule is dissociated by losing one of its protons to its neighbours, forming a hydroxy1, OH^-. Each proton (H^+) can be transferred inside the X—H$\cdots X$ bridge interchanging the role of the covalent (—) and the hydrogen ($\cdots$) bonds with the heavy ion group (X^-).[5−13] After such an intrabond proton transfer the chain is locally disturbing its neutral charge distribution, generating an ionic defect. An additional degree of freedom allows the group X—H to rotate in such a way that an interbond proton transfer is possible, generating a bonding (or Bjerrum, or orientational) defect. Any of the two defects could be the majority charge carriers through the chain. Both types of defects are also sensitive to the vibrations of the heavy ion substrate. Several scientists, trying to explain the protonic conductivity in ice, formulated theories based on the hopping migration of the ionic and bonding defects along the hydrogen-bonded networds in the crystals. However, these theories failed to reproduce the highly complicated dynamics in the system. In recent years, many scientists are inclined to believe that the structure and dynamics of ionic and bonding defects in these systems have been a collective behaviour stimulated by the dipole-dipole interaction between X—H groups. The collective effect could excite a kind of soliton, likely topological kink, to encourage motion of these defects.[5−23] Although the heavy ion sublattice does not change the qualitative picture of the defects dynamics, it has been proved that it may produce important "signatures" for experimental detection. For this reason, a two-component model has also been introduced,[10−15] trying to consider the main degrees of freedom of the hydrogen-bonded chain, it can only explain the motions of one pair of defect of each type, but cannot give the multi-defects dynamics. Others have also introduced an one-component protonic chain with a new two-parameter doubly periodic on-site potential.[19,20] In such a model the main charateristics of the systems are concentrated in the structure of the on-site potential, which is parametrized by two constants in order to have higher flexibility. Due to the flexibility of the potential the model can only be adapted to the hydrogen-bonded structure when the

*Project supported by the National Natural Science Foundation of China (Grant No. 19974034).
†E-mail: pangxf@mail. sc. cninfo. net

heavy ion sublattice is assumed "frozen". Therefore, in order to describe the main properties of the systems the two coupled degrees of freedom at each lattice site must be included, but this complicates also their investigation. Even when a continuum limit is taken, the equations of motion couple two fields so that they are difficult to solve in the above models. For instance, no exact analytical solution is known for an original Antonchenko model.[5] Another difficulty appears when one considers realistic parameters for hydrogen-bonded systems because then the solutions are narrow with respect to the lattice spacing and the continuum approximation fails. This is the case in ice in which the H_3O^+ or OH^- are almost point defects. Also, these models almost cannot explain theoretically the mutual conversion of the two types of defects in the transport processes along hydrogen-bonded chains.

Recently we proposed a new model,[24] in which a new Hamiltonian is introduced to study the classical properties of the proton transfer in a solitonic mechanism by using classical method. In the new Hamiltonian introduced we take into account not only the harmonic vibration of the proton with frequency ω_0 and the double-well potential which is similar to other models, but also the dipole-dipole interaction between the X—H groups and the change of the displacement of heavy ions resulting from this interaction. From this model we not only obtained an analytical solution of the equation of motion, but also gave a unitized explanation for the mutual conversion of the two types of defects in the proton transfer. Thus, this model overcame the difficulties existing in previous models.[5−16] However, we are more interested in the quantum mechanical properties of the proton soliton in this model because of many distinctions from the classical behaviours, which are not studied yet. The purpose of this paper is to study the quantum-mechanical properties of the proton-soliton in the systems by means of completely quantum-mechanical method in our model.[24] In Sec.Ⅱ we derive the equations of motion of the proton-solitons. The quantum-mechanical properties of the proton-soliton are given in Sec.Ⅲ.

Ⅱ. EQUATIONS OF MOTION FOR PROTONSOLITONS

According to the features of collective excitation of the protons resulting from the localized fluctuation of protons and the deformation of structure of the heavy ionic sublattice in the hydrogen-bonded molecular systems, the Hamiltonian of the systems can be given by[24]

$$H = H_{\rm p} + H_{\rm h} + H_{\rm int} = \frac{m}{2}\sum_i p_i^2 + \frac{m\omega_0^2}{2}\sum_i r_i^2 - \frac{m\omega_1^2}{2}\sum_i r_1 r_{i+1} - \frac{U_0}{4}\sum_i (1 - r_i^2/r_0^2)^2 + \sum_i \left[\frac{M}{2}P_i^2 + \frac{\beta}{2}(R_i - R_{i-1})^2\right] + \frac{1}{2}m\chi_1\sum_i (R_{i+1} - R_{i-1})r_i^2 + m\chi_2\sum_i (R_{i+1} - R_i)r_i r_{i+1}, \quad (1)$$

where the proton coordinate r_i is the displacement of hydrogen from the middle of the bond between the ith and the $(i+1)$th heavy ions or OH^- in a static cases; r_0 is the distance between the local maximum and one of the minima of the potential well of $U = U_0(1 - r_i^2/r_0^2)^2$. U_0 is the height of the potential barrier, R_i is the displacement of heavy ion from the equilibrium position, χ_1 and χ_2 are coupled constants between the protonic and the heavy ionic sublattices due to the motion of the heavy ions. And ω_0 is the frequency of harmonic vibration of the protonic sublattice, $K = m\omega_0^2$ is the elastic constant of the protonic sublattice, ω_1 is a characteristic frequency of vibration of protons, β is a linear elastic constant of the heavy ionic sublattice. $V_0 = r_0(K/m)^{1/2}$ is the velocity of low amplitude sound waves in the protonic sublattice. $C_0 = R_0(\beta/M)^{1/2}$ is the sound velocity in the heavy ionic sublattice, p_i and P_i are the conjugate momenta of the coordinate r_i and the displacement R_i, respectively. $H_{\rm p}$ is the Hamiltonian for the protonic sublattice with an on-site double-well potential $U(r_i)$, $H_{\rm h}$ is the Hamiltonian for the heavy ionic sublattice, $H_{\rm int}$ is the Hamiltonian of interaction between protonic and heavy inoic sublattices, which takes into account the fact that with proton displacement from a stable equilibrium position the distances between the neighbour heavy ions changes.

Adopting the general transformation,[25−27] we have

$$r_i = (2m\omega_0/\hbar)^{-1/2}(a_i + a_i^+),$$
$$p_i = m\dot{r}_i = (\hbar m\omega_0/2)^{1/2}(-{\rm j})(a_i - a_i^+) \qquad ({\rm j} = \sqrt{-1}), \quad (2)$$

where $a_i^+(a_i)$ is the creation (annihilation) operator of the proton of number i, thus Eq.(1) becomes

$$H=\sum_i[\hbar\omega_0(a_i^+a_i+1/2)-(\hbar\omega_1^2/4)(a_i^+a_{i+1}+a_{i+1}^+a_i+a_i^+a_{i+1}^++a_{i+1}a_i)$$
$$-(U\hbar/2mr_0^2\omega_0)(a_i^+a_i+a_ia_i^++a_i^+a_i^++a_ia_i)+(\hbar^2U_0/m^2r_0^4\omega_0^2)(a_i^+a_i^+a_i^+a_i^+$$
$$+a_ia_ia_ia_i+4a_i^+a_i^+a_ia_i+4a_ia_i^+a_i^+a_i^++4a_i^+a_ia_ia_i)]$$
$$+\sum_i\left[\frac{M}{2}P_i^2+\frac{\beta}{2}(R_i-R_{i-1})^2\right]+(\hbar\chi_1/4\omega_0)\sum_i(R_{i+1}-R_{i-1})(a_i^+a_i+a_ia_i^++a_i^+a_i^+$$
$$+a_ia_i)+(\hbar\chi_2/2\omega_0)\sum_i(R_{i+1}-R_i)(a_{i+1}^+a_i+a_{i+1}a_i^++a_{i+1}^+a_i^++a_{i+1}a_i)+U_0/4. \quad (3)$$

According to the properties of collective excitation of the protons generated by the localized fluctuation and the deformation of conformation of heavy ionic sublattice, the trail wave function describing the state of collective excitation occurring in the systems should be of the form[25,26]

$$|\Phi\rangle=|\varphi\rangle|\beta_{\rm q}\rangle=(1/\lambda')(1+\sum_i\varphi_i(t)a_i^+)|0\rangle_{\rm pr}$$
$$\cdot\exp\left\{\sum_i(1/{\rm j}\hbar)[u_i(t)P_i-\pi_i(t)R_i]\right\}|0\rangle_{\rm ph}, \quad (4)$$

where $|0\rangle_{\rm pr}$ and $|0\rangle_{\rm ph}$ are the ground states of the proton and the vibrational excitation of the heavy ionic sublattice (phonons), respectively. We choose the normalization factor $\lambda'=1$ in the following calculation for convenience.

In Eqs.(3) and (4) we have the relations

$$\langle\Phi|R_i|\Phi\rangle=u_i(t),\qquad\langle\Phi|P_i|\Phi\rangle=\pi_i(t).$$

Thus we obtain

$$\frac{\partial u(t)}{\partial t}=\langle\Phi|[R_i,H]|\Phi\rangle,$$
$${\rm j}\hbar\frac{\partial}{\partial t}\pi_i(t)=\langle\Phi|[P_i,H]|\Phi\rangle. \quad (5)$$

Finally we can obtain from Eq.(5), in the continuum approximation,

$$M\frac{\partial^2}{\partial t^2}u(x,t)=\beta R_0^2\frac{\partial^2}{\partial x^2}u(x,t)$$
$$+\hbar(\chi_1+\chi_2)\frac{\partial}{\partial x}|\varphi(x,t)|^2. \quad (6)$$

Equation (6) is just the equation of displacement of the heavy ion in our classical model.[24]

When we derive the equation of $\varphi_i(t)$, the only assumption is that $|\Phi(t)\rangle$ satisfies the following time-dependent Schrödinger equation:

$${\rm j}\hbar\frac{\partial}{\partial t}|\Phi(t)\rangle=H|\Phi(t)\rangle. \quad (7)$$

Now substituting $|\Phi(t)\rangle$ in Eq.(4) into Eq.(7), and again product-lefting Eq.(7) with ${}_{\rm ex}\langle 0|\langle\beta|$, we get

$${\rm j}\hbar\dot\varphi_i=\Big[(3/2)\hbar\omega_0+\overline{W}-(1/2)\sum_k(u_k\dot\pi_k-\dot u_k\pi_k)+U_0/4-\hbar U_0/mr_0^2\omega_0\Big]\varphi_i$$
$$-(\hbar\omega_1^2/4\omega_0)(\varphi_{i+1}+\varphi_{i-1})+(\hbar\chi_1/2\omega_0)(u_{i+1}-u_{i-1})\varphi_i+(\hbar\chi_2/2\omega_0)[(u_{i+1}-u_i)\varphi_{i+1}$$
$$+(u_i-u_{i-1})\varphi_{i-1}]+(8\hbar^2U_0/m^2r_0^4\omega_0^2)\varphi_i\varphi_i^*\varphi_i+(8\hbar^2U_0/m^2r_0^4\omega_0^2)\varphi_i, \quad (8)$$

where

$$\overline{W}=\langle\beta_q|H_{\rm ph}|\beta_q\rangle. \quad (9)$$

To find out the explicit expression of $\overline{W}$ and $\sum_k(u_k\dot\pi_k-\dot u_k\pi_k)$, we should quantize further the low-frequency vibration of the heavy ionic sublattice. Thus, performing the transformation

$$R_i=\sum_q(\hbar/2NM\omega_q)^{1/2}(b_q+b_{-q}^+){\rm e}^{{\rm j}iqR_0},$$
$$P_i={\rm j}\sum_q(\hbar M\omega_q/2N)^{1/2}(b_{-q}^+-b_q){\rm e}^{{\rm j}iqR_0}, \quad (10)$$

where N is the number of the heavy ions in the hydrogen bonded chain, b_q^+ and b_q are creation and annihilation operators of the phonon with the wave vector q, $\omega_q=2(\beta/M)^{1/2}\sin(qr_0/2)$ is the frequency of phonon, substituting Eq.(10) and $H_{\rm h}$ into Eq.(9) yield

$$\overline{W}=\langle\beta_q|H_{\rm ph}|\beta_q\rangle$$
$$=\langle\beta_q|\sum_q\hbar\omega_q(b_q^+b_q+1/2)|\beta_q\rangle. \quad (11)$$

We know that the part of $|\Phi(t)\rangle$ depending on the dis-

placement and the momentum operators, R_i and P_i, is a coherent state of the normal mode with creation and anihilation b_q^+ and b_q. A coherent state for the model with wave vector q is

$$|\beta_q\rangle = \exp\Big\{-\sum_q \beta_q^*(t)b_q - \beta_q(t)b_q^+\Big\}|0\rangle_{\rm ph}. \quad (12)$$

We can obtain, from Eqs.(12) and (3),

$$\begin{aligned}&\sum_i (u_iP_i - \pi_iR_i) = \sum_q {\rm j}\hbar(\beta_q(t)b_q^+ - \beta_q^*(t)b_q),\\ &\beta_q(t) = (M\omega_q/2\hbar)^{1/2}u_q(t)\\ &\qquad + {\rm j}(1/2M\hbar\omega_q)^{1/2}\pi_q(t), \end{aligned} \quad (13)$$

where $u_q(t)$ and $\pi_q(t)$ are the spatial Fourier transform of $u_i(t)$ and $\pi_i(t)$, i.e.,

$$\begin{aligned}&u_q(t) = N^{-1/2}\sum_i {\rm e}^{-{\rm j}xq}u_i(t),\\ &\pi_q(t) = N^{-1/2}\sum_i \exp(-{\rm j}xq)\pi_i(t) \qquad (x = {\rm i}R_0). \end{aligned} \quad (14)$$

Utilizing Eq.(12), we can obtain

$$\begin{aligned}\langle\beta_q|b_q^+b_q|\beta_q\rangle =&|\beta_q(t)|^2 = ({\rm j}/2\hbar)(\pi_qu_{-q} - u_q\pi_{-q})\\ &+ \frac{m\omega_q}{2\hbar}|u_q|^2 + \left(\frac{1}{2m\hbar\omega_q}\right)|\pi_q|^2. \end{aligned} \quad (15)$$

Inserting again Eq.(15) into Eq.(11), we have

$$\overline{W} = \sum_q[(1/2M)|\pi_q|^2 + (\beta/2)|u_q|^2 + (1/2)\hbar\omega_q].$$

Using the Fourier transform relations in Eq.(14), we can rewrite $\overline{W}$ as

$$\overline{W} = \sum_i(\pi_i^2/2M + (\beta/2)(u_{i+1} - u_i)^2) + (1/2)\sum_q \hbar\omega_q. \quad (16)$$

If utilizing the relation

$$\sum_k (u_{k+1} - 2u_k + u_{k-1})^2 = -\sum_k (u_{k+1} - u_k)^2$$

and inserting the above results into Eq.(16), we can get

$$\begin{aligned}{\rm j}\hbar\dot{\varphi}_i =&\Big\{3\hbar\omega_0/2 + W_0 + U_0/4 - \hbar U_0/mr_0^2\omega_0 - (\hbar/4\omega_0)\sum_k[\chi_1(|\varphi_{k+1}|^2\\ &- |\varphi_{k-1}|^2)u_k + \chi_2((\varphi_{k-1}^* - \varphi_{k+1}^*)\varphi_k + \varphi_k^*(\varphi_{k-1} - \varphi_{k+1}))u_k]\Big\}\varphi_i\\ &- (\hbar\omega_1^2/4\omega_0)(\varphi_{i+1} - \varphi_{i-1}) + (\hbar\chi_1/2\omega_0)(u_{i+1} - u_{i-1})\varphi_i + (\hbar\chi_2/2\omega_0)[(u_{i+1} - u_i)\varphi_{i+1}\\ &+ (u_i - u_{i-1})\varphi_{i-1}] + 8(\hbar U_0/m^2r_0^4\omega_0^2)\varphi_i\varphi_i^*\varphi_i + (8\hbar U_0/m^2r_0^4\omega_0^2)\varphi_i, \end{aligned} \quad (17)$$

where $W_0 = (1/2)\sum_q \hbar\omega_q$ is the zero-point energy. If we assume that the terms contained in Eq.(17) which are independent of the site index i are $G(t)$, we have

$$G(t) = W_0 - (\hbar/4\omega_0)\sum_k[\chi_1(|\varphi_{k+1}|^2 - |\varphi_{k-1}|^2)u_k + \chi_2((\varphi_{k-1}^* - \varphi_{k+1}^*)\varphi_k + \varphi_k^*(\varphi_{k-1} - \varphi_{k+1}))u_k]. \quad (18)$$

Thus Eq.(17) becomes

$$\begin{aligned}{\rm j}\hbar\dot{\varphi}_i =&(3\hbar\omega_0/2 + G(t) + U_0/4 - \hbar U_0/mr_0^2\omega_0)\varphi_i + (\hbar\chi_1/2\omega_0)(u_{i+1} - u_{i-1})\varphi_i\\ &+ (\hbar\chi_2/2\omega_0)[(u_{i+1} - u_{i-1})\varphi_{i+1} + (u_i - u_{i-1})\varphi_{i-1}] + (8\hbar^2U_0/m^2r_0^4\omega_0^2)\varphi_i\\ &- (\hbar\omega_1^2/4\omega_0)(\varphi_{i+1} - \varphi_{i-1}) + (8\hbar^2U_0/m^2r_0^4\omega_0^2)|\varphi_i|^2\varphi_i. \end{aligned} \quad (19)$$

Obviously, Eq.(19) may turn into the following form in the continuum limit for low-frequency vibrations:

$$\begin{aligned}{\rm j}\hbar\frac{\partial}{\partial t}\varphi(x,t) =&(3\hbar\omega_0/2 + G(t) + U_0/4 - \hbar U_0/mr_0^2\omega_0 + \hbar\omega_1^2/2\omega_0)\varphi(x,t)\\ &- (\hbar\omega_1^2R_0^2/4\omega_0)\frac{\partial^2}{\partial x^2}\varphi(x,t) + (8\hbar^2U_0/m^2r_0^4\omega_0)\varphi(x,t)\\ &+ (\hbar(\chi_1 + \chi_2)R_0/\omega_0)\frac{\partial}{\partial t}u(x,t)\varphi(x,t) + (8\hbar^2U_0/m^2r_0^4\omega_0^2)|\varphi(x,t)|^2\varphi(x,t). \end{aligned} \quad (20)$$

This is a nonlinear Schrödinger equation, which is different from the equation of motion of the proton obtained in classical case for our model; the latter is a nonlinear Klein-Gordon equation, concretely speaking, φ^4-field equation. The above result is due to the linear Schrödinger equation (7) we here adopt.

Now we will find out the soliton solutions of Eqs.(6) and (20). The solution of the set of equations can be represented by the following form:[26,27]

$$Q(x,t)=Q(x-Vt),\qquad \varphi(x,t)=\varphi(x-Vt)\exp(-\mathrm{j}\theta(x,t)),\qquad Q(x,t)=-\frac{\partial}{\partial x}u(x,t). \tag{21}$$

Thus Eqs.(6) and (20) become[26,27]

$$Q(x,t)=[\hbar R_0(\chi_1+\chi_2)/MC_0^2\omega_0(1-s^2)]|\varphi(x,t)|^2+g', \tag{22}$$

$$\mathrm{j}\hbar\frac{\partial\varphi(x,t)}{\partial t}=\varepsilon\varphi(x,t)-JR_0^2\frac{\partial^2}{\partial x^2}\varphi(x,t)-g|\varphi(x,t)|^2\varphi(x,t), \tag{23}$$

where

$$\begin{aligned} s=&V/C_0,\qquad \varepsilon=3\hbar\omega_0/2-G(t)+U_0/4-\hbar U_0/mr_0^2\omega_0+g'\hbar(\chi_1+\chi_2)R_0/\omega_0\\ &-\hbar\omega_1^2/2\omega_0+8\hbar^2U_0/m^2r_0^4\omega_0^2,\qquad J=\hbar\omega_1^2/4\omega_0,\\ g=&\{8\hbar^2U_0/m^2R_0^4\omega_0^2-[\hbar^2r_0^2(\chi_1+\chi_2)^2/\omega_0^2MC_0^2(1-s^2)]\},\qquad \mu=g/4J. \end{aligned}$$

The exact solution of Eq.(23) normalized by the condition $\frac{1}{R_0}\int|\varphi(x,t)|^2\mathrm{d}x=1$ at $g>0$ and $\varepsilon>0$ has the form[25,27]

$$\begin{aligned}\varphi(x,t)=&\pm\sqrt{\mu/2}\tanh\left(\frac{\mu}{R_0}(x-x_0-Vt)\right)\\ &\cdot\exp\{\mathrm{j}[(-\hbar V/2JR_0^2)(x-x_0)-E_{\mathrm{sot}}t/\hbar]\},\end{aligned} \tag{24}$$

thus

$$\begin{aligned}u(x,t)=&\mp[\hbar R_0(\chi_1+\chi_2)\mu/MC_0^2\\ &\cdot(1-s^2)]\tanh\left(\frac{\mu}{R_0}(x-x_0-Vt)\right).\end{aligned} \tag{25}$$

If $g<0$ and $\varepsilon<0$, the solution of Eq.(23) is in the following form:

$$\begin{aligned}\varphi(x,t)=&\sqrt{|\mu|/2}\mathrm{sech}\left(\frac{|\mu|}{R_0}(x-x_0-Vt)\right)\\ &\cdot\exp\{\mathrm{j}[(-\hbar V/2JR_0^2)(x-x_0)-E_{\mathrm{sot}}t/\hbar]\},\end{aligned} \tag{26}$$

$$\begin{aligned}u(x,t)=&[\hbar R_0(\chi_1+\chi_2)|\mu|/MC_0^2\\ &\cdot(1-s^2)]\tanh\left[\frac{|\mu|}{R_0}(x-x_0-Vt)\right].\end{aligned} \tag{27}$$

If inserting Eqs.(24) and (25) into the formula of $G(t)$, we can get, in the continuum limit,

$$\begin{aligned}G(t)=&(4\hbar N/\pi)(\beta/M)^{1/2}\\ &-\hbar^2R_0^2(\chi_1+\chi_2)^2|\mu|/6\omega_0^2MC_0^2(1-s^2).\end{aligned} \tag{28}$$

From the above results we see clearly that an analytical solution of soliton for proton transfer is again obtained from the new model in quantum case. This is an advantage of this model as compared with others. Thus we may suppose that this model could overcome the difficulties occurring in other models. Owing to the fact that the nonlinear interaction, g, in this model comes from the double-well potential U and proton-heavy ions coupling interaction, the nature of the proton soliton can be determined by the competition between the two kinds of nonlinear interactions. When the double-well patential is dominant, the solutions (Eqs.(24),(25)) show the motions of ionic defects. When the coupling interaction dominates, the solutions, Eqs.(26),(27) show the motions of bonded defects. Therefore, our solutions can completely explain the combined and alternate motions of the two kinds of defects along hydrogen-bonded systems. For detailed explanation for the phenomenon, please refer to Ref.[24]. On the other hand, although the form of the above solition in the quantum mechanical theory is the same as that in the classical case,[24] its amplitude and shape and velocity are all changed as compared with the classical case. This shows that the quantum-mechanical properties of the soliton are different from those in the classical case in the new model. Therefore, the quantum-mechanical properties of the soliton excited in the systems are worthwhile to further study. In the following section we shall study the properties by means of the above equation of motion obtained, Eq.(23), and the completely quantum-mechanical method. Meanwhile, we here should point out that the equations of motion of the proton transfer in quantum mechanics can also be obtained from the Heisenberg equations of operators b_i and a_i, but the latter is φ^4-field equation which is the same as the one in the classical model.[24] This is a quite interesting result, and is also quite worthwhile to study thoroughly.

Ⅲ. THE QUANTUM-MECHANICAL PROPERTIES OF THE PROTON-SOLITON IN THE SYSTEMS

A. The motion of the soliton satisfies the conventional conservation laws of mass, momentum and energy

First of all, we write down Langrangian and effective Hamiltonian of the system corresponding to Eq.(23),

$$L = \frac{1}{R_0}\int [(\mathrm{j}\hbar/2)(\varphi\varphi_t^* - \varphi^*\varphi_t) - J|\varphi_x|^2 + (g/2)|\varphi|^4 - \varepsilon|\varphi|^2]\mathrm{d}x \qquad (\text{here}\,\varphi = \varphi(x,t)), \tag{29}$$

$$H = \frac{1}{R_0}\int [-J|\varphi_x|^2 + (g/2)|\varphi|^4 - \varepsilon|\varphi|^2]\mathrm{d}x, \tag{30}$$

respectively, where $\varphi_x = \dfrac{\partial}{\partial x}\varphi(x,t), \varphi_t = \dfrac{\partial}{\partial t}\varphi(x,t)$. Thus we can determine the number density, number current, momentum and energy of the proton-soliton. They are

$$\left.\begin{aligned} &\rho = |\varphi|^2, \qquad p = -\mathrm{j}(\varphi^*\varphi_x - \varphi\varphi_x^*), \\ &\mathcal{J} = \mathrm{j}(\varphi^*\varphi_x - \varphi\varphi_x^*), \varepsilon = -J|\varphi_x|^2 - \frac{g}{2}|\varphi|^4 + \varepsilon|\varphi|^2, \end{aligned}\right\} \tag{31}$$

respectively. From Eqs.(23),(29),(31) and the conjugate equation of Eq.(23)

$$-\mathrm{j}\hbar\varphi_t^*(x,t) = \varepsilon^*(x,t) - J\varphi_{xx}^*(x,t) - \frac{g}{2}|\varphi^*(x,t)|^2\varphi^*(x,t), \tag{32}$$

we can obtain

$$\frac{\partial\rho}{\partial t'} = \frac{\partial\mathcal{J}}{\partial x'}, \frac{\partial p}{\partial t'} = \frac{\partial}{\partial x'}\left[2\left(\frac{\partial\varphi}{\partial x'}\right)\frac{g}{2}|\varphi|^4 + 2\varepsilon|\varphi|^2 - \left(\varphi^*\frac{\partial^2}{\partial x'^2}\varphi + \varphi\frac{\partial^2}{\partial x'^2}\varphi^*\right) + 2\mathrm{j}\varepsilon\left(\varphi^*\frac{\partial\varphi}{\partial x'} - \varphi\frac{\partial\varphi^*}{\partial x'}\right)\right],$$

$$\frac{\partial\varepsilon}{\partial t'} = \frac{\partial}{\partial x'}\left[\rho p + \mathrm{j}\left(\frac{\partial\varphi^*}{\partial x'}\frac{\partial^2\varphi}{\partial x'^2} - \frac{\partial\varphi}{\partial x'}\frac{\partial^2\varphi^*}{\partial x'^2}\right) - \mathrm{j}\varepsilon\left(\varphi^*\frac{\partial\varphi}{\partial x'} - \varphi\frac{\partial\varphi^*}{\partial x'}\right)\right]. \tag{33}$$

Thus we have the following forms of integrals:

$$\frac{\partial}{\partial t'}M = \frac{\partial}{\partial t'}\int\rho\mathrm{d}x' = 0, \qquad M = \text{const.},$$
$$\frac{\partial}{\partial t'}P = \frac{\partial}{\partial t'}\int p\mathrm{d}x' = 0, \qquad \frac{\partial E}{\partial t'} = \frac{\partial}{\partial t'}\int\varepsilon\mathrm{d}x' = 0 \qquad (t' = t/\hbar, x' = x/\sqrt{J}). \tag{34}$$

These formulae are just the conservation laws of mass, momentum and energy of the proton-solitons in such a case. This shows that the particles (solitons) in nonlinear systems still obey the general rules of conservation which are the same as those in linear quantum systems.

B. The mass, momentum and energy of the proton-soliton

When the proton-soliton is formed in the hydrogen-bonded chains, the chain deformation energy is

$$\overline{\varepsilon}_0 = \frac{1}{2R_0}\int_{-\infty}^{\infty}(M(u_t)^2 + \beta(u_z))\mathrm{d}x = \beta(s^2+1)\hbar^3R_0^2(\chi_1+\chi_2)^4/6\beta^3\omega_0^3(1-s^2)^3\omega_1^2.$$

Taking the chain deformation energy into account the energy of transfer by the proton-soliton along the molecular chains is

$$E = \frac{1}{R_0}\int_{-\infty}^{\infty}H\mathrm{d}x = \int_{-\infty}^{\infty}\left(\varepsilon|\varphi|^2 - J|\varphi_x|^2 - \frac{g}{2}|\varphi|^4\right)\mathrm{d}x + \overline{\varepsilon}_0 = \overline{E}_0 + M_{\mathrm{sol}}V^2/2, \tag{35}$$

where the rest energy of the soliton is

$$\overline{E}_0 = 3\hbar\omega_0/2 + \frac{4\hbar N}{\pi}(\beta/M)^{1/2} - \frac{\hbar\omega_1^2}{2\omega_0} + \frac{U_0}{4} - \frac{\hbar U_0}{2mr_0^2\omega_0} - \frac{\hbar^2(\chi_1+\chi_2)^4(2\omega_1^2+3\hbar R_0^2)}{12\beta^2\omega_1^2\omega_0^3} + \left[1 - \frac{4\hbar(\chi_1+\chi_2)R_0^2}{6\omega_0^2MC_0^2} + \frac{8\hbar^2U_0}{m^2r_0^4\omega_0^2}\right]\left[\frac{8\hbar^2U_0}{m^2r_0^4\omega_0^2}\right], \tag{36}$$

the effective mass of the soliton is

$$M_{\mathrm{sol}} = m_{\mathrm{ex}} + \frac{[(4\hbar R_0^2\omega_0 - 4\omega_0^2 - 6\hbar R_0^2) + (3s^2-s^4)(2\omega_1^2+3\hbar R_0^2+2\hbar^2\omega_0^2)](\chi_1+\chi_2)^4 + (5s^2-1-s^4)(8\hbar^2r_0^{-2}\omega_0^{-1}\omega_1^2U_0Mm^{-2}\beta(\chi_1+\chi_2))}{6\omega_0^3\omega_1^2(1+s^2)^3\beta^3M}. \tag{37}$$

The momentum of the soliton is

$$P(V) = \frac{\hbar}{2\mathrm{j}R_0}\int(\varphi^*\varphi_x - \varphi\varphi_x^*)\mathrm{d}x - \frac{M}{R_0}\int u_iu_x\mathrm{d}x = \left[m_{\mathrm{ex}}^* + M\left(\frac{\hbar^4R_0^2(\chi_1+\chi_2)^4}{3\omega_0^4\beta^4(1-s^2)^3}\right)\right]V. \tag{38}$$

From the above formulae we see that the energy, momentum and the effective mass of the proton-soliton increase as velocity of the soliton increases. However, at all finite values of the rest energy, Eq.(38), the soliton velocity is always less than that of the longitudinal sound in the hydrogen-bonded molecular chains ($V < C_0$). When $V \to C_0$, the amplitude, energy and momentum and the effective mass of the proton-soliton go to infinity and the distances between the adjacent heavy ions tend to zero. This means that the above approximation method is in applicable as the velocity, V, is near the longitudinal sound C_0. This is a shortcoming of this theory. However, if considering further the anharmonic vibration of the heavy ionic sublattice, the above difficulty can be completely ruled out. Furthermore, according to the rule of the minimum energy for the stability of soliton, i.e., their energy is less than the conduction band bottom of the proton, we can obtain from Eq.(36) that the proton-soliton is stable only under the conditions of $s < 1/\sqrt{5}$ or $V < C_0/\sqrt{5}$ and $\mu < 1$. On the other hand, when the proton-soliton velocity is lower, i.e., $V \ll C_0$, $s \ll 1$, we have

$$E = \overline{E}_0 + M_{\rm sol}V^2/2, \qquad P = [m^*_{\rm pr} + (\hbar^4 R_0^2 M(\chi_1+\chi_2)^4/3\omega_0^4\beta^4)]V = \text{const.}V,$$
$$M_{\rm sol} = m^*_{\rm pr} + \frac{(4\hbar R_0^2\omega_0^2 - 4\omega_1^2 - 6\hbar R_0^2)(\chi_1+\chi_2)^4 + 8\hbar^3 r_0^{-2}\omega_0^{-1}\omega_1^2 U_0 M m^{-2}\beta(\chi_1+\chi_2)}{6\omega_0^3\omega_1^2\beta^3 M} = \text{const.} \tag{39}$$

This shows that the dependences of the soliton energy and momentum on its velocity are analogous to those of the general macroparticle's in the proton transfer in the systems. These results also show that the proton solitons determined by the nonlinear wave equations, Eqs.(6) and (20), have obviously corpuscle feature.

C. The proton-soliton obeys a classical rule of motion

Now let $t' = t/\hbar, x' = x/\sqrt{J}$ and $\overline{U} = \varepsilon - G(t)$. Utilizing Eqs.(23) and (33), we can obtain

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t'}\int_{-\infty}^{\infty}\varphi^*\varphi_{x'}\mathrm{d}x' &= \int_{-\infty}^{\infty}\varphi^*_{t'}\varphi_{x'}\mathrm{d}x' + \int_{-\infty}^{\infty}\varphi^*(\varphi_{t'})_{x'}\mathrm{d}x' = \mathrm{j}\int_{-\infty}^{\infty}\Big\{\varphi^*\frac{\partial}{\partial x'}[\varphi_{x'x'} + g\varphi^*\varphi^2 \\ &\quad - \overline{U}\varphi] - [\varphi^*_{x'x'} - g\varphi(\varphi^*)^2 - \overline{U}\varphi^*]\varphi_{x'}\Big\}\mathrm{d}x' \\ &= \mathrm{j}\Big\{\int_{-\infty}^{\infty}(\varphi^*\varphi_{x'x'x'} - \varphi_{x'}\varphi^*_{x'x'})\mathrm{d}x' \\ &\quad + \int_{-\infty}^{\infty}\Big[g(\varphi^{*2}\varphi\varphi_{x'} + \varphi^*\varphi^2\varphi^*_{x'}) - \varphi^*\frac{\partial\overline{U}}{\partial x'}\varphi\Big]\mathrm{d}x'\Big\} \\ &= \mathrm{j}\int_{-\infty}^{\infty}\varphi^*\frac{\partial\overline{U}}{\partial x'}\varphi\mathrm{d}x',\end{aligned}$$

where

$$\int_{-\infty}^{\infty}(\varphi^*\varphi_{x'x'x'} - \varphi^*_{x'x'}\varphi_{x'})\mathrm{d}x' = \varphi^*\varphi_{x'x'}\Big|_{-\infty}^{\infty} - \int_{-\infty}^{\infty}\varphi^*_{x'}\varphi_{x'x'}\mathrm{d}x' - \varphi_{x'}\varphi_{x'}\Big|_{-\infty}^{\infty} + \int^{\infty}\varphi^*_{x'}\varphi_{x'x'}\mathrm{d}x' = 0,$$
$$\int_{-\infty}^{\infty}g(\varphi^{*2}\varphi\varphi_{x'} + \varphi^*\varphi^2\varphi^*_{x'})\mathrm{d}x' = \frac{1}{2}\int_{-\infty}^{\infty}g(\varphi^{*2}\varphi^2)_{x'}\mathrm{d}x' = -\frac{1}{2}\int_{-\infty}^{\infty}\varphi^{*2}(g)_{x'}\varphi^2\mathrm{d}x' = 0.$$

Using the boundary conditions

$$\lim_{|x'|\to\infty}\varphi(x',t') = \lim_{|x'|\to\infty}\varphi_{x'}(x',t') = 0 \quad \text{and} \quad \int_{-\infty}^{\infty}\varphi^*\varphi\mathrm{d}x' = \text{const.},$$
$$\lim_{|x'|\to\infty}\varphi^*x'\varphi_{x'} = \lim_{|x'|\to\infty}\varphi^*_{x'}x'\varphi = 0,$$

we can get

$$\frac{\mathrm{d}}{\mathrm{d}t'}\int_{-\infty}^{\infty}\varphi^*x'\varphi\mathrm{d}x' = \int_{-\infty}^{\infty}\Big(\frac{\partial\varphi^*}{\partial t'}x'\varphi + \varphi^*x'\frac{\partial\varphi}{\partial t'}\Big)\mathrm{d}x' = \mathrm{j}\int_{-\infty}^{\infty}\Big\{\varphi^*x'[\varphi_{x'x'} + g\varphi^*\varphi^2 - \overline{U}\varphi]$$
$$- \varphi x'[\varphi^*_{x'x'} + g\varphi^{*2}\varphi - \overline{U}\varphi^*]\Big\}\mathrm{d}x' = \mathrm{j}\int_{-\infty}^{\infty}(\varphi^*x'\varphi_{x'x'} + \varphi^*_{x'}(\varphi x')_{x'})\mathrm{d}x' = -2\mathrm{j}\int_{-\infty}^{\infty}\varphi^*\varphi_{x'}\mathrm{d}x'.$$

The average position (or mass centre) of the proton-soliton $\varphi(x,t)$ can be represented by[27] $< x' >= \int_{-\infty}^{\infty} \varphi'^{*}\varphi \mathrm{d}x \Big/ \int_{-\infty}^{\infty} \varphi^{*}\varphi \mathrm{d}x'$, and the average velocity (or velocity of the mass centre) of the proton-soliton $\varphi(x',t')$ is defined as

$$\frac{\mathrm{d}}{\mathrm{d}t'} < x' >= \frac{\partial}{\partial t'}\Big\{ \int_{-\infty}^{\infty} \varphi^{*} x' \varphi \mathrm{d}x' \Big/ \int_{-\infty}^{\infty} \varphi^{*}\varphi \mathrm{d}x' \Big\} = -2\Big\{ \int_{-\infty}^{\infty} \varphi^{*}\varphi_{x'} \mathrm{d}x' \Big/ \int_{-\infty}^{\infty} \varphi^{*}\varphi \mathrm{d}x' \Big\}.$$

Thus the average acceleration (or the acceleration of the mass centre) of the soliton $\varphi(x',t')$ is

$$\begin{aligned} \frac{\mathrm{d}^2}{\mathrm{d}t'^2} < x' > &= -2\mathrm{j}\frac{\mathrm{d}}{\mathrm{d}t'}\Big\{ \int_{-\infty}^{\infty} \varphi^{*}\varphi_{x'} \mathrm{d}x' \Big/ \int_{-\infty}^{\infty} \varphi^{*}\varphi \mathrm{d}x' \Big\} \\ &= -2 \int_{-\infty}^{\infty} \varphi^{*} \overline{U}_{x'} \varphi \mathrm{d}x' \Big/ \int_{-\infty}^{\infty} \varphi^{*}\varphi \mathrm{d}x' = -2\Big\langle \frac{\partial \overline{U}}{\partial x'} \Big\rangle. \end{aligned} \tag{40}$$

This shows that the motion of the soliton (or its mass centre) $\varphi(x,t)$ determined by Eq.(23) obeys Newton-type equation of motion. Thus it exhibits clearly the classical property of the proton-soliton. We see from Eqs.(34), (39) and (40) that the proton-soliton has wave-corpuscle duality. On the other hand, if substituting $\overline{U} = \varepsilon - G = 3\hbar\omega_0/2 - \hbar\omega_1^2/2\omega_0 + U_0/4 + 8\hbar^2 U_0/m^2 r_0^4 \omega_0^2 + g'\hbar(\chi_1+\chi_2)r_0/\omega_0 - \hbar U_0/m\omega_0 r_0^2 - G$=const. (notice that G is a const., see Eq.(28)) into Eq.(40), we can get $\dfrac{\mathrm{d}^2 < x' >}{\mathrm{d}t'^2} = 0$. This shows that the kind of proton-soliton formed in such a case moves with a uniform velocity (i.e., V =const.) along the hydrogen-bonded chains. This result has important meaning in the biological systims, if appling this theory to the protein and DNA, because these are a kind of special hydrogen-bonded systems. The above property of the proton-soliton in the protein and DNA ensures that the energy and momentum and charge transported by the proton-soliton can be kept without any decay and dissipation, which is very important for the development of living bodies.

REFERENCES

[1] G. Zundel, Hydration and Intermolecular Interaction (Mir. Moscow, 1972), p.1.

[2] P. Schuster, G. Zundel and C. Sandorfy (eds.), The Hydrogen Bond, Recent Developments in Theory and Experiments (North Holland, Amsterdam, 1976).

[3] W. C. Homilton and J. A. Ibers, Hydrogen Bonding in Solids (Benjamin, New York, 1969).

[4] R. P. Bell, The Proton in Chemistry (Chapman and Hall, London, 1973).

[5] V. Ya. Antonchenko *et al.*, *Phys. Stat. Sol.*(*b*), **115**(1983), 631.

[6] A. V. Zolotaryuk *et al.*, *Phys. Lett.*, **A101**(1984), 517.

[7] E. W. Laedke *et al.*, *Phys. Rev.*, **A20**(1985), 1161.

[8] M. Peyrared, St. Pnevmatikos and N. Flytzanis, *Phys. Rev.*, **A36**(1987), 903.

[9] H. Weberpals, R. H. Spatschek, *Phys. Rev.*, **A36**(1987), 2946.

[10] D. Hochstrasser *et al.*, *Phys. Rev.*, **A38**(1988), 5332.

[11] H. Desfontaines, M. Peyrared, *Phys. Lett.*, **A142**(1989), 128.

[12] St. Pnevmatikos, *Phys. Rev. Lett.*, **60**(1988), 1534; *Phys. Lett.*, **A112**(1987), 249.

[13] J. Halding, P. S. Lomdahl, *Phys. Rev.*, **A37**(1988), 2608.

[14] J. M. Braum and Yu. S. Kivshar, *Phys. Lett.*, **A149**(1990), 119; *Phys. Rev.*, **B43**(1991), 1060.

[15] T. Fraggs *et al.*, *Phys. Lett.*, **A142**(1989), 361.

[16] M. Buttiker and R. Ladauer, *Phys. Rev.*, **A23**(1981), 1397; F. Marcheson, *Phys. Rev.*, **B34**(1986), 6536.

[17] J. F. Nagle and S. Tritram Nagle, *J. Membr. Biol.*, **74**(1983); 1; J. F. Nagle, H. J. Morowitz, *Proc. Natl. Acad. Sic. USA*, **75**(1978), 1298; J. F. Nagle, M. Mille and H. J. Morowitz, *J. Chem. Phys.*, **72**(1980), 3958.

[18] G. P. Tsironis, St. Pnevmatikos, *Phys. Rev.*, **B39**(1989), 7161.

[19] St. Pnevmatikos *et al.*, *Phys. Rev.*, **A43**(1991), 5518.

[20] St. Pnevmatikos *et al.*, *Phys. Lett.*, **A173**(1993), 43.

[21] T. Mitani *et al.*, *Phys. Rev. Lett.*, **60**(1988), 2299.

[22] B. Brzezinski *et al.*, *J. Phys. Chem.*, **91**(1987), 3077.

[23] G. P. Johar, S. J. Jones, *J. Chem. Phys.*, **82**(1985), 1019; S. F. Fischar *et al.*, *J. Chem. Phys.*, **226**(1970), 842.

[24] X. F. Pang, G. Zundel. *Acta Physics Sinica*, **46**(1997), 625(in Chinese); *Acta Physica Sinica*(*Overseas Edition*), **7**(1998), 70; *J. Phys. Cond. Mat.*, (2000), 1.

[25] X. F. Pang, *J. Phys. Condens. Matter*, **2**(1990), 9541; *Acta Math. Scienties*, **13**(1993), 437; *Chinese Phys. Lett.*, **10**(1993), 381 and 437 and 517; *Phys. Rev.*, **E49**(1994), 4747; *Chinese Science Bulletin*, **38**(1993), 1557 and 1665.

[26] X. F. Pang, Theory for Non-Linear Quantum Mechanics (Chinese Chongqing Press, Chongqing, 1994), pp.427 and 795.

[27] X. F. Pang, *J. Low. Temp. Phys.*, **58**(1985), 334.