NONLINEAR DYNAMICS OF LOCALIZED STRUCTURES AND PROTON TRANSFER IN A HYDROGEN-BONDED CHAIN MODEL INCLUDING DIPOLE INTERACTIONS

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Abstract : The transport of energy in H-bonded chains is really an extremely important problem, because of its close connection with basic phenomena in biological systems. We consider a lattice model which is made of two one-dimensional harmonically coupled sublattices corresponding to the oxygens and protons, the two sublattices being coupled. The study becomes more interesting when we introduce the **dipole-dipole interactions**. As a microscopic dipole is created by the proton motion, it may affect the response of the nonlinear excitations propagating along the chain. We are looking for a solution for which the motion of oxygen ions can be neglected. A ϕ^6 **equation** is found , which admits nonlinear excitations of **solitary wave type**. We distinguish different classes of solutions for the description of the proton motion. Analytical expressions and the necessary conditions for the existence of these types of solutions are given. The introduction of the dipole interaction produces an influence on the electric field of the system which means that the proton motion is also affected and this makes the **proton conductivity** much easier. Numerical simulations are presented for special cases. Finally, possible further extensions of the work are discussed.

1.- INTRODUCTION.

Among the whole variety of condensed-matter systems where the soliton concept can be used are **quasi-one-dimensional molecular systems** in biology [1]. The transport of protons in H-bonded chains is a very interesting problem since it can explain fundamental properties of life [2]. It can be also used in order to explain **proton mobility and electric conductivity** in ice [5,9,10].
The aim of this work is to study the influences of the dipole-dipole interactions on protonic conductivity in H-bonded chains. At the same time an analytical study of the nonlinear dynamics of the proton motion is also proposed.
In order to reach our goal we construct a one-dimensional lattice model based on the **Antonchenko-Davydov-Zolotaryuk model** [3], for H-bonded chains. From previous scientific works [4,6,7,8], there is already a satisfactory number of results both analytical and numerical, which contribute to the validity of the ADZ model. This model was really a successful attempt to approximate and explain mechanisms which occur in

the atomic scale study. We also introduce the interatomic potentials involved in the model and we include -the important point of our work- the dipole interactions due to the proton motions. The existence of electric dipoles along the chain may affect the response of the system and the proton conductivity becomes much easier. Since the discrete system is not manageable, we are faced with the continuum approximation of the microscopic model.
After some calculations we find a Φ^6 equation. This means that now we have the possibility of many localized solutions, according to several selections and conditions. The protonic conductivity is caused by ionic and orientational defects as [1] explained in previous works. What is important to note here is also the possibility of many further extensions of the work.

2.- CONSTRUCTION OF THE MODEL.

The model consists of two one-dimensional interacting sublattices. These are the proton sublattice and the heavy-ion sublattice as shown in Fig.1. Protons and "oxygens" are harmonically coupled.

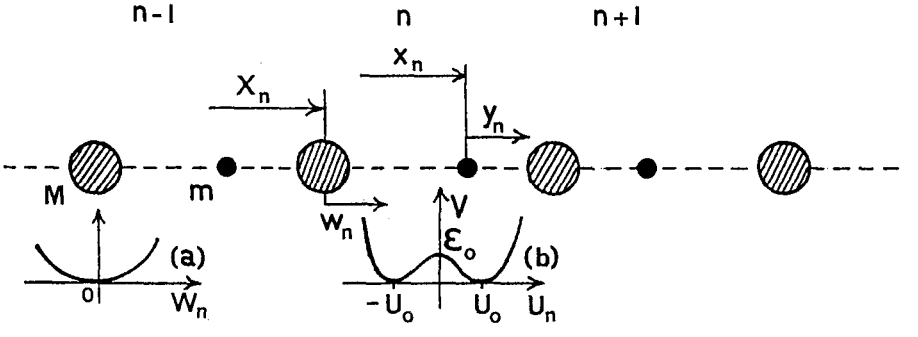

Fig. 1 : One-dimensional lattice model for a hydrogen-bonded diatomic chain. (a) harmonic potential for heavy ions and (b) double-well potential for protons.

Each proton lies between a pair of heavy ions usually called as "oxygens". There are covalent and hydrogen bonds connecting proton with the two neighbouring oxygens. When a proton moves from a position closer to the one of the oxygens to a position closer to the next one, then the two bonds exchange their positions. The double-well acting on protons and allowing this jump can be approximated [11] by the expression

$$U(y_n) = \epsilon_0 \left(1 - y_n^2/y_0^2\right)^2 \quad . \tag{1}$$

A schematical representation is given in Fig.1. In Eq.(1), y_n denotes the displacement of the n-th proton with respect to the center of the oxygen pair in which it is located, ϵ_0 is the potential barrier and $2y_0$ is the distance between the two minima of the double-well potential. The coupling between oxygens and protons can provide a mechanism [6] which changes the potential barrier that protons have to overcome to jump from one molecule to the other and makes their motion easier.

3.- EQUATIONS OF THE MODEL.

The total Hamiltonian of the system is

$$H_{tot} = H_p + H_o + H_{int} + H_{dd} \quad . \tag{2}$$

The proton part of the Hamiltonian is

$$H_p = \sum_n \left[\frac{1}{2} m \dot{y}_n^2 + U(y_n) + \frac{1}{2} m \omega_1^2 (y_{n+1} - y_n)^2 \right] \quad . \tag{3}$$

The first term denotes the kinetic energy of each proton, the second is due to the double-well potential while the last term represents the harmonic coupling with the characteristic frequency ω_1 between neighbouring protons (m is the proton mass). The oxygen part of the Hamiltonian can be written as

$$H_o = \sum_n \left[\frac{1}{2} M \dot{w}_n^2 + \frac{1}{2} M \Omega_0^2 w_n^2 + \frac{1}{2} M \Omega_1^2 (w_{n+1} - w_n)^2 \right] \quad . \tag{4}$$

Here we consider only the relative displacement w_n of an oxygen pair, because a possible variation of the O-O distance can modulate the double-well undergone by the protons. The first term of H_o denotes the kinetic energy of oxygens, the second term denotes the coupling between oxygens of the same cell while the third term describes the harmonic coupling between neighbouring oxygen pairs and introduces in the model the dispersion of an optical mode (Ω_0 and Ω_1 are characteristic frequencies of the optical mode, M is the oxygen mass).
The Hamiltonian H_{int} is derived from the **dynamic interaction** between the two sublattices and describes how the double-well is modulated by the variation of the O-O distance. It is written as in ADZ model [6]

$$H_{int} = \sum_n \delta w_n \left(y_n^2 - y_0^2 \right) \quad . \tag{5}$$

Its physical meaning is the **lowering of the potential barrier** due to the oxygen displacements. (δ measures the strength of the coupling and determines the amplitude of the distortion in the oxygen sublattice).
The Hamiltonian H_{dd} is derived from the dipole interactions. The existence of electric dipoles in the chain, because of the electric charges, leads us to account for the **mutual interaction betweeen the dipoles.** In the present case, we assume that the distance r between neighbouring dipoles does not depend on the lattice displacement and all vectors of the dipole moment P_n are in the same direction (all are alligned). We find that

$$H_{dd} = \bar{\beta} \sum_{n} P_n P_{n+1} \ . \tag{6}$$

($\bar{\beta}$ is a constant which may account for the environment of the chain). The dipole moment induced by the proton motion must be zero when proton is at either position of the oxygens or when it is at the middle of the distance joining the oxygen pair where the interactions are opposite. The law which the dipole has to agree with is presented in Fig.2.

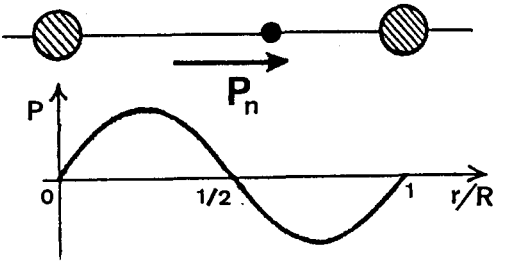

Fig. 2 : Dipole as a function of the proton position with respect to the neighbouring heavy ion positions.

The simplest form for the dipole moment P to approximate the structure of the curve in Fig.2 can be given [12] by a polynomial of the third degree

$$P_n = \bar{a}(x_n - X_n)(x_n - X_{n+1})\left[x_n - \frac{1}{2}(X_n + X_{n+1})\right]. \tag{7}$$

(Where $\bar{a}$ is a constant). The absolute positions x_n and X_n are shown in Fig.1 and we have

$$x_n = n\ell_0 + \frac{1}{2}\ell_0 + y_n \ , \quad X_n = n\ell_0 + w_n \ , \quad X_{n+1} = (n+1)\ell_0 + w_{n+1} \ . \tag{8}$$

We note that ℓ_0 is the lattice spacing. The equations of motion of the system form a set of coupled nonlinear differential-difference equations which derived from the Hamiltonian (1) and takes on the form

$$\frac{d^2 y_n}{dt^2} = \omega_1^2 (y_{n+1} - 2y_n + y_{n-1}) + \left(4\epsilon_0/m y_0^2\right)\left(1 - y_n^2/y_0^2\right)2y_n - (2\delta/m) w_n y_n$$
$$- \bar{\beta} \frac{\partial P_n}{\partial y_n} (P_{n+1} + P_{n-1}) \ , \tag{9a}$$

$$\frac{d^2 w_n}{dt^2} = \Omega_1^2 (w_{n+1} - 2w_n + w_{n-1}) - \Omega_0^2 w_n - (\delta/M)\left(y_n^2 - y_0^2\right)$$
$$- \bar{\beta} \frac{\partial P_n}{\partial w_n} (P_{n+1} + P_{n-1}) - \bar{\beta} \frac{\partial P_{n-1}}{\partial w_n} (P_n + P_{n-2}) \ . \tag{9b}$$

We study that case in which the heavy-ion sublattice can be considered as "frozen". The motion of the oxygens is not remarkable as the motion of the protons, which is very important. This approximation is related to the inertia of the oxygen sublat-

tice which cannot follow the fast proton motion especially for large velocities and suggests that a solution could involve only the proton displacement while oxygens stay at rest and do not participate in the motion. We can assume that w is very small compared to y. In the atomic lattice y is of the order of few Å and for this reason we can suppose that w is almost zero.

Now we consider only the Hamiltonians H_p and H_{dd}. We introduce the units E_0 for energy, t_0 for time and ℓ_0 for length. We find the derived units $m_0=E_0 t_0^2/\ell_0^2$ for mass and $f_0=\epsilon_0/\ell_0$ for force. We introduce the dimensionless parameters $\tilde{m}=m/m_0$, $\epsilon=\epsilon_0/E_0$, $\chi_1=-\tilde{\beta}\,\tilde{a}^{-2}\ell_0^6/E_0\tilde{m}$. We also consider $u_n=y_n/\ell_0$, $\tilde{H}=H/m\ell_0^2$. The expression for the energy of the system becomes

$$\tilde{H}=\sum_n\left[\frac{1}{2}\dot{u}_n^2+\frac{1}{2}\omega_1^2(u_{n+1}-u_n)^2+\frac{1}{4}G_0u_0^2\left(1-u_n^2/u_0^2\right)-\chi P_nP_{n+1}\right], \tag{10}$$

where the electric dipole is merely given by

$$P_n=u_n\left(u_n^2-1/4\right). \tag{11}$$

The equation of the discrete system describing the proton motion reduces to

$$\ddot{u}_n=\omega_1^2(u_{n+1}-2u_n+u_{n-1})+G_0u_n\left(1-u_n^2/u_0^2\right)$$

$$+\chi\left(3u_n^2-1/4\right)\left[u_{n-1}\left(u_{n-1}^2-1/4\right)+u_{n+1}\left(u_{n+1}^2-1/4\right)\right]. \tag{12}$$

Where we have previously set $G_0=4\epsilon_0/\ell_0^2u_0^2$ and $\chi=\chi_1E_0/m\ell_0^2$.

4.- CONTINUUM APPROXIMATION OF THE DISCRETE SYSTEM.

Further step to the somewhat rough simplification consists of considering the **continuum approximation**. The equation of the proton motion -if we consider terms up to the second order- can be written as follows

$$u_{tt}-\left[1+\chi(3u^2-1/4)^2\right]u_{xx}-\alpha_1u+\beta_1u^3-\gamma_1u^5=0, \tag{13}$$

where we have set

$$\alpha_1=G_0+\chi/8, \qquad \beta_1=G_0/u_0^2+2\chi, \qquad \gamma_1=6\chi. \tag{14}$$

We can notice that all three parameters α_1, β_1, γ_1 depend on χ, which χ is also present in the factor accompanied u_{xx}. This last remark makes further investigation extremely difficult. In order to simplify the procedure we propose the following hypothesis : we set $1+\chi(3u^2-1/4)=\tilde{C}_0$ as a function of u. This function has two

minima. For certain value of χ we can find the mean value $\langle\tilde{C}_0\rangle$ and then we set $\langle\tilde{C}_0\rangle$ as the coefficient of u. This rough approximation can be done when there is no great difference between the greatest and the lowest values of the function. This occurs if the coefficient χ is considered small enough such that $|\chi|<<1$. We now set $\langle\tilde{C}_0\rangle=\omega^2$ and the equation for study becomes

$$u_{tt} - \omega^2 u_{xx} - \alpha_1 u + \beta_1 u^3 - \gamma_1 u^5 = 0 \ . \tag{15}$$

We use the change of variables $u = \alpha U$, $t = \gamma T$, $x = \beta X$. Then we select $\alpha = \sqrt{\beta_1/\gamma_1}$, $\gamma = \sqrt{\gamma_1}/\beta_1$, $\beta = \omega\sqrt{\gamma_1}/\beta_1$ (it must be $\gamma_1>0$, $\beta_1>0$). We also set $A=\alpha_1\gamma^2$. The equation for study takes on the following form

$$U_{TT} - U_{XX} = AU - U^3 + U^5 \ . \tag{16}$$

We are looking for localized solutions with constant profile, moving at a characteristic velocity v, that is for solutions $U=U(\xi)=U(X-vT)$. We do not dwell on the algebraic manipulations for finding out the different classes of solutions.

5.- DIFFERENT TYPES OF LOCALIZED SOLUTIONS.

The equation presents a symmetry, so when U is a solution then -U is also a solution. We can set $U_1 = U(\xi\to-\infty)$ and $U_2 = U(\xi\to\infty)$. We distinguish different types of solutions as we try to approach U_2 beginning by U_1, or the inverse.
For the solution of the type I (pulse), we have $U_1 = U_2 = 0$. We obtain the expression

$$U = \pm \frac{U_m}{[1 + P sinh^2(\Omega\xi/2)]^{1/2}} \ . \tag{17}$$

Where it is $U_m^2 = \pm 4A/\left(\sqrt{1 - A/A_0} \pm 1\right)$ and $P = 2\sqrt{1 - A/A_0}/\left(\sqrt{1 - A/A_0} \pm 1\right)$. The sign (+) corresponds to supersonic waves ($|v|>1$) and for this case we have also the condition $0<A<(3/16)$. The sign (-) corresponds to subsonic waves ($|v|<1$) and for this case it must be necessarily considered $A<0$. In both cases we have $A_0=(3/16)$ and $\Omega^2 = 4A/(v^2-1)$.
The solution of the type III presents a kink. In this case we have two opposite non zero values ($U_1=U_0$, $U_2=-U_0$). The expression becomes

$$U = \frac{\pm U_0 \, tanh z}{[1 + P(1-tanh^2 z)]^{1/2}} \ . \tag{18}$$

Where it is $z=(1/2)\Omega\xi$, $P = U_0^2/\left(2U_0^2 - 3/2\right)$, $\Omega^2 = 4U_0^2\left(U_0^2 - 1/2\right)/(v^2 - 1)$. U_0 is defined by $\left(U_0^{\pm}\right)^2 = (1\pm\sqrt{1 - 4A})/2$, where the sign (+) corresponds to supersonic waves (it must be additionally $A<(3/16)$ and $A\neq0$), and the sign (-) corresponds to subsonic waves (for the definition it must be additionally set $A<(1/4)$ with $A\neq0$, $A\neq(15/64)$).

Finally, the solution of the type IV corresponds to a case in which it is $U_1=U_2\neq 0$. It is found

$$U = \pm \frac{U_0}{[P(tanh^2 z - 1) + tanh^2 z]^{1/2}} . \qquad (19)$$

Where it is $P = U_0^2/(2U_0^2 - 3/2)$, $\Omega^2 = 4U_0^2[U_0^2 - 1/2]/(v^2 - 1)$. For the constant value U_0 we have $(U_0^{\pm})^2 = (1 \pm \sqrt{1 - 4A})/2$. The sign (+) corresponds to supersonic waves which can be defined when we also consider $(3/16)<A<(1/4)$. The sign (-) corresponds to subsonic waves. (Now we have to consider $A<(1/4)$ with $A\neq 0$, $A\neq(15/64)$). Finally, a particular case (type II) occurs for which $A=(3/16)$ and the solution represents a kink describing a transition from the state $U_1\neq 0$ to the state $U_2=0$.

6. NUMERICAL RESULTS.

We present numerical simulations corresponding to the solutions of the types I and III. We examine the evolution of a localized solution in time and we consider a certain number of particles in each case. The numerical simulations are performed directly by means of the set of discrete equations (12).
The kink-like solution of the type III corresponds to a proton displacement from the state $-U_0$ to the state $+U_0$ which are wells of the Φ^6 potential. This solution is remarkably **stable** as it is shown in Fig.3a. On the contrary, the pulse solution of the type I shown in Fig.3b presents an **instability**. After a short lapse of time, the pulse splits into two pulses travelling in opposite directions accompanied with rather large perturbations behind them. This makes difficult further investigations.

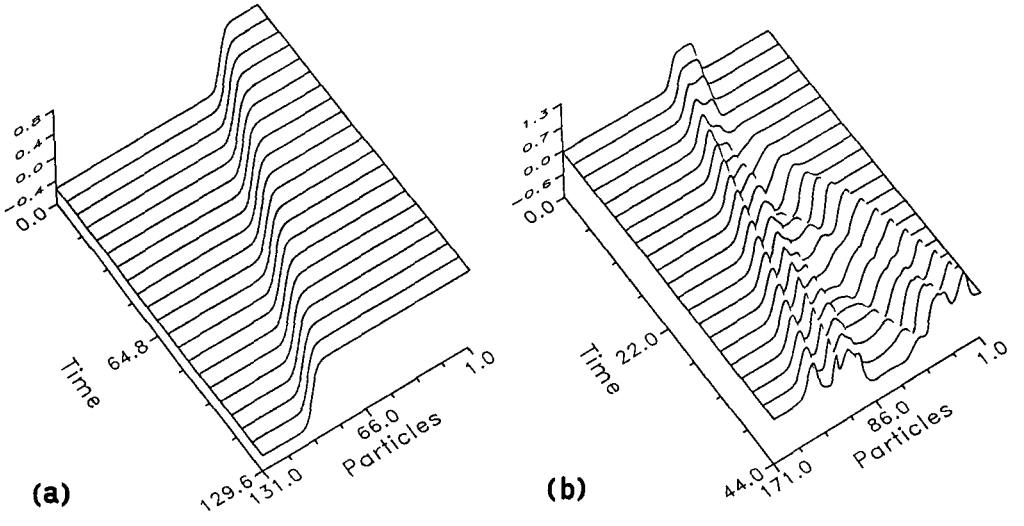

Fig. 3 : Numerical simulations of the proton motion on the lattice, (a) stable kink-like solution (type III) and (b) unstable pulse solution (type I).

7.CONCLUSIONS.

We have studied the influence of the dipole-dipole interaction on the proton motion. This kind of interaction produces an influence on the electric field of the system which affects to the proton motion and proton conductivity becomes much easier. The description of **ionic and orientational defects associated with the protonic conductivity** remains the same as in Φ^4 case, previously studied by other scientists [6]. It is necessary to remark that in our case we obtain many possibilities for the solution according to the values of the parameters, since the resulting equation possesses **stable, unstable and metastable steady states.** Another important point of the whole study is that we have to return to the problem of the continuum approximation and examine in detail all the possible cases. The model can be extended by the introduction of an external electric field applied on protons and also the introduction of damping. We can additionally consider a **rotational motion of the dipoles,** something which is closer to the real system, especially if we deal with nonlinear atomic chain. We can also examine the influence of second nearest-neighbouring interactions and more. At length, discreteness effects can be a source of very fascinating phenomena occuring at the microscopic scale.

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