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Dynamics of a hydrogen-bonded linear chain with a new type of one-particle potential

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Abstract. The linear hydrogen-bonded chain with the new type of one-particle potential

$$V(u) = V_0 \left[\frac{1}{2} (A \cosh \alpha u - 1)^2 + B \sinh \alpha u \right]$$

is considered in the continuum limit. This double Morse potential might be a single- or double-well, symmetric or asymmetric one, depending on the parameters A and B. The solutions of the equations of motion in the form of oscillatory and solitary waves are derived and discussed. It is shown that in the asymmetric case there are no stable solitary waves.

1. Introduction

Linear chains of hydrogen bonds have attracted the interest of both physicists and chemists for a long time. Usually one assumes that the proton in a hydrogen bond 'lives' in a double-well potential, which might be of symmetric or asymmetric form. The former appears, for example, in the ice crystal, the latter in the acetanilide (ACN) crystal, in α-helical proteins and in formamide chains [1]. The chains of these two classes have the respective forms

$$\cdots \mathrm{A} \cdots \mathrm{H{-}A} \cdots \mathrm{H{-}A} \cdots \mathrm{H{-}A} \cdots \mathrm{H{-}A} \cdots \mathrm{H{-}A} \cdots \qquad (1a)$$

and

$$\cdots \mathrm{A} \cdots \mathrm{H{-}B} \cdots \mathrm{H{-}A} \cdots \mathrm{H{-}B} \cdots \mathrm{H{-}A} \cdots \mathrm{H{-}B} \cdots \qquad (1b)$$

where A and B are atoms or groups (like the O–H group in ice) and the H are protons. The understanding of the dynamics of such systems is of great importance. They play a significant role (especially the symmetric one) in the proton transfer phenomena which not only appear in such simple structures as ice crystal but also seem to be related to certain processes in the organic world [2]. The connection with proton transfer in biological systems makes this study even more appealing.

The theory of the dynamics of such chains was discussed in the fundamental paper by Antonchenko, Davydov and Zolotariuk [3] (see also [2] for details), where the ϕ^4-potential was used to represent the hydrogen bond. Extensive studies of the model and of its application to the explanation of the role played by solitons in proton transfer phenomena has been developed in the paper by Peyrard, Pnevmatikos and Flytzanis [4] (see also [5, 6]).

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Two kinds of approach to the dynamics of such a chain are possible. Either two linearly coupled sublattices are considered, one of which consists of heavy groups A and B and the other one of light H atoms [7], or the heavy groups are considered to be rigid and only the dynamics of the hydrogen protons is analysed. If the character of the heavy-group sublattice is harmonic and the coupling between the sublattices is linear, the results of the two approaches are essentially the same, except for the fact that in the former case a pair of excitations, one in each sublattice, appears.

The proton dynamics in such chains has been often described using the following quartic potential [8, 9]:

$$\mathcal{V}(u) = \frac{1}{2}Au^2 + \frac{1}{3}Bu^3 + \frac{1}{4}Cu^4.$$

Recent careful investigations have shown, however, that instead of this well known potential, a double Morse potential should be used [10, 11]. The main advantage of this potential is related to its physical origin: the Morse potential is a commonly accepted model for the description of a covalent bond [11–13], like that between hydrogen and oxygen atoms; the *ab initio* calculation proves that this choice is profoundly justified [14].

Such a potential is obtained as a sum of two Morse potentials (identical for a symmetric potential and different for an asymmetric one) put together 'back to back'. Following this prescription one obtains a potential which may be written in a compact form:

$$U(u) = U_0\left[\frac{1}{2}(A\cosh\alpha u - 1)^2 + B\sinh\alpha u\right] \tag{2}$$

where U_0 and A are constants assumed to be positive and B is an arbitrary constant.

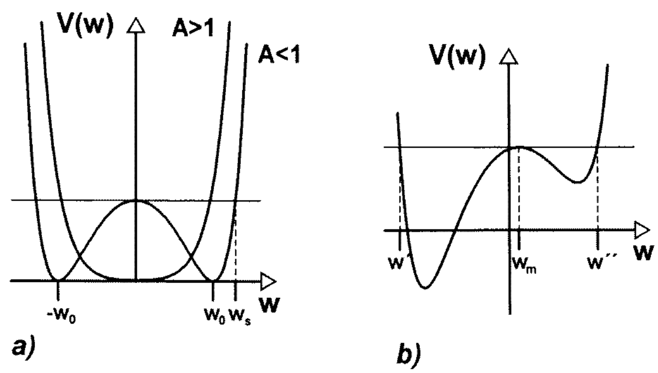

Figure 1. The symmetric double- and single-well potential (a) and the double-well asymmetric potential (b).

Apart from its relatively simple form, this potential has several interesting features both from the formal and from the physical point of view. First, note that depending on the choice of parameters it may be a double-well potential, a strongly anharmonic one-well potential or a potential which is very flat at the bottom (for $A = 1$, $B = 0$). The potential (2) is symmetric when $B = 0$ (figure 1(a)) and asymmetric otherwise (figure 1(b)).

Another interesting feature of this model is that its quantum counterpart belongs to the class of so-called quasi-exactly solvable models [15–20]. It turns out to be related to its hidden symmetry (or hidden algebra), of a very special kind [21]. This allows one to find in a closed analytical form several energy levels for a certain set of potential parameters.

Though the double Morse potential is much less popular than the φ^4-model, some thermodynamical and dynamical properties of its one-dimensional (1D) version in the continuum limit have been discussed. Thermodynamical properties of its very special case—of a symmetric model, $B = 0$, corresponding to an exactly solvable version of its quantum mechanical counterpart—were discussed by Behera and Khare [22]. Using a well known method [23], the relationship with a ground-state energy of an appropriate quantum mechanical model, enabled the free energy of the 1D model to be determined. This led to the astonishing—but wrong—conclusion that kinks do not contribute to the thermodynamics in this case, in contrast to in the φ^4-model. The calculation of the free energy, usually done by means of the WKB method, can be accomplished in a reasonable way for this potential. It is due to the form of the potential hump, which is relatively flat, that the WKB approximation works well even for energies close to the hump. One finds that kinks do contribute to the thermodynamics (at low enough temperatures, of course), and that the contribution is even more substantial than in the case of the φ^4-model (thermodynamical properties will be considered in detail in a separate paper).

Babu and Baby [24] discussed the properties of solitary solutions in the Behera and Khare version. A rather advanced mathematical approach led to the conclusion of the presence of bell-shaped solitary-wave solution. This was for the following reasons.

(i) It is widely believed that non-trivial solitary solutions with zero topological charge do not exist in 1D one-component models [26].

(ii) It is hard to understand the physical origin of such a solitary solution in this symmetric double-well model.

This conclusion was extremely strange.

Recently, Kryachko [12] investigated the properties of the kink solution in a symmetric version ($B = 0$) of 1D model (2).

In this paper we present a simple approach to the problem of dynamics of the classical chain of atoms moving in the double-well on-site potential (2) and interacting via harmonic forces. This allows an elegant interpretation and classification of the solutions of the Euler–Lagrange equation to be achieved for the linear chain in the continuum limit, for both symmetric and asymmetric versions. Oscillatory pseudo-solitary and solitary waves are the two different types of solution. In the framework of the approach presented one avoids, in a rather natural way, mixing them up, which in fact caused the appearance of the bell-shaped solitary solution in the symmetric case [24]. It is shown that this excitation has some formal features of a solitary wave but cannot be considered as such because of its significantly different properties. On the other hand, a bell-shaped solitary solution is found in the case of an asymmetric potential ($B \neq 0$). It is shown, however, that this solution is unstable.

The paper is organized as follows: in section 2 the problem is formulated; in two subsequent sections 3 and 4 solitary and oscillatory solutions are discussed, respectively; the energy and topological charge of solitary excitations are considered in section 5 and a final discussion is provided in section 6; some calculations are given in the appendix.

2. Formulation of the problem

Let us consider particles (protons) of mass m placed in the sites of a one-dimensional chain with a constant interval a. The energy of a particle is a sum of its kinetic energy, its potential energy in the on-site potential (2) and the effective energy of interactions between the particles. We restrict the last component of the energy to the nearest-neighbour interaction and choose it in the simplest quadratic form.

Hence, the Hamiltonian of the model discussed can be written in the form

$$H = \sum_i \left[\frac{m\dot{u}_i^2}{2} + U(u_i) + f\frac{(u_i - u_{i-1})^2}{2} \right]$$

where $U(u_i)$ is the potential (2) and f is the spring constant describing the harmonic interaction of the atoms in the nearest lattice sites.

When the interaction between the sites is large compared to the on-site potential ($fa^2 \gg U_0$) it may be assumed that the displacements u_i at neighbouring sites do not differ considerably and we may pass to the continuum limit

$$x_i = ia \to x \qquad u_i - u_{i-1} \to a\frac{\partial u}{\partial x}.$$

The Hamiltonian of the system takes the form

$$H = \int \frac{\mathrm{d}x}{a} \left[\frac{m}{2}\left(\frac{\partial u}{\partial t}\right)^2 + \frac{fa^2}{2}\left(\frac{\partial u}{\partial x}\right)^2 + U(u) \right].$$

Obviously $u = u(x, t)$.

The Lagrangian corresponding to this system is

$$L = \int \frac{\mathrm{d}x}{a} \left[\frac{m}{2}\left(\frac{\partial u}{\partial t}\right)^2 - \frac{fa^2}{2}\left(\frac{\partial u}{\partial x}\right)^2 - U(u) \right].$$

The Euler–Lagrange equation derived from this Lagrangian has the form

$$\frac{\partial^2 w}{\partial \zeta^2} - \frac{\partial^2 w}{\partial \tau^2} = V'(w) = A \sinh w (A \cosh w - 1) + B \cosh w \tag{3}$$

where we have introduced the following notation that will be used further in this paper:

$$c_0^2 = \frac{fa^2}{m} \qquad \omega_0^2 = \frac{U_0 \alpha^2}{m} \qquad \tau = \omega_0 t \qquad \zeta = \frac{\omega_0}{c_0} x \qquad w = \alpha u \qquad V = \frac{U}{U_0}. \tag{4}$$

The zeros of the force on the right-hand side of equation (3) in the symmetric case ($B = 0$), corresponding to the minima of the on-site potential, are $\pm w_0$, where

$$w_0 = 2a \tanh \sqrt{\frac{1 - A}{1 + A}}.$$

Equation (3) is sometimes called a double-sinh–Gordon equation. In the present paper we will search for 'travelling' solutions of this equation, i.e. for the solutions of the form

$$w = w(\omega\tau - \kappa\zeta). \tag{5}$$

Inserting (5) into equation of motion (3), one obtains

$$(\kappa^2 - \omega^2)\frac{\mathrm{d}^2 w}{\mathrm{d}s^2} = V'(w) \tag{6}$$

where

$$s = \kappa\zeta - \omega\tau.$$

In this way the problem is reduced to the description of a single fictitious particle of mass

$$M = |\kappa^2 - \omega^2| \tag{7}$$

in: (i) an inverted potential, $-V(w)$, when $\kappa^2 - \omega^2 > 0$; or (ii) a potential $V(w)$ when $\kappa^2 - \omega^2 < 0$. For each of these cases, further considerations must be carried out in separate ways.

3. The solitary-wave solutions

First, let us consider the first case

$$\kappa^2 - \omega^2 > 0$$

where the motion of the fictitious particle takes place in the inverted potential. Integrating equation (6) we obtain

$$E \equiv -\frac{\varepsilon^2}{2} = \frac{\kappa^2 - \omega^2}{2}\left(\frac{\mathrm{d}w}{\mathrm{d}s}\right)^2 - V(w). \tag{8}$$

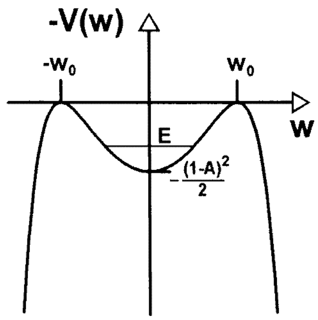

Figure 2. The inverted potential used for calculation of the kink solution.

In the symmetric case, $B = 0$, we are interested in the motion of the particle within the well (figure 2), since only such a case corresponds to the solutions of the field equation (3) having finite energy. The condition for the energy of the fictitious particle is therefore (cf. figure 2)

$$-\frac{1}{2}(1 - A)^2 < E \leqslant 0$$

and we see that ε is real and satisfies the relation

$$(1 - A) > \varepsilon > 0.$$

From figure 2 it is clear that there are two possible kinds of motion for such energies: the periodic anharmonic one for $E < 0$ and the aperiodic one for $E = 0$. The former may be approximated by harmonic motion when the amplitude of oscillations is small, i.e. E is close to $-(1 - A)^2/2$ (cf. figure 2) whereas the latter may be considered as its limit for large-amplitude motion.

The solution in the case where $E = 0$, obtained by integration of equation (8) (see the appendix), has the form

$$w = \pm 2a \tanh\left[\sqrt{\frac{1 - A}{1 + A}} \tanh(\gamma_1(s - s_0))\right] \tag{9}$$

where

$$\gamma_1 = \frac{1}{2}\sqrt{\frac{1-A^2}{\kappa^2-\omega^2}}.$$

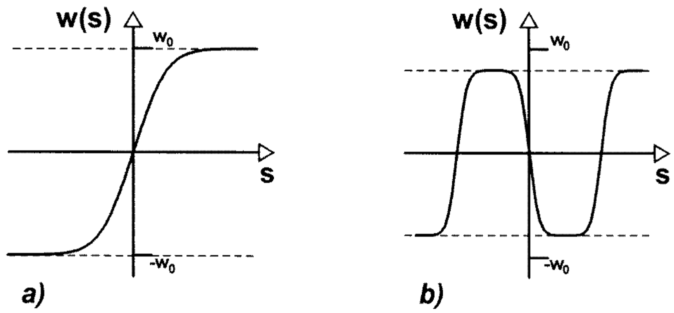

Figure 3. The kink solution (a) and a periodic solution (b) corresponding to the inverted potential.

Let us consider the asymptotic behaviour of the solution (9), for definiteness with the sign '+'. We have

$$w \longrightarrow \pm 2a \tanh\sqrt{\frac{1-A}{1+A}} = \pm w_0 \qquad s \to \pm\infty.$$

It is the kink solution of the equation of motion (figure 3(a)).

The condition $\kappa^2 - \omega^2 > 0$ contains the case where $\omega = 0$. In other words, the kink solution may be a static one.

The periodic solutions of the equation (8), appearing for $E < 0$, have the form (see figure 3(b))

$$w(\zeta, \tau) = 2a \tanh\left[\sqrt{\frac{1-A-\varepsilon}{1+A-\varepsilon}}\ \mathrm{sn}(\gamma_{\varepsilon 1}(s-s_0), k)\right] \qquad (10)$$

where

$$\gamma_{\varepsilon 1} = \frac{1}{2}\sqrt{\frac{1-(A-\varepsilon)^2}{\kappa^2-\omega^2}} \qquad k = \frac{1-(A+\varepsilon)^2}{1-(A-\varepsilon)^2}.$$

In the limit $\varepsilon \to 0$ we have $k^2 \to 1$ and

$$\gamma_{\varepsilon 1} \to \gamma_1 = \frac{1}{2}\sqrt{\frac{1-A^2}{\kappa^2-\omega^2}}.$$

Owing to the relation

$$\mathrm{sn}(\vartheta, k=1) = \tanh\vartheta$$

we obtain the kink solution.

In the asymmetric case ($B \neq 0$), the solution has a rather complicated form (see the appendix). Nevertheless, some qualitative conclusions can be drawn easily. From figure 4(a) it is clear that the periodic oscillations will have the same character as in the symmetric case. The kink excitation, however, can no longer exist when the potential minima are not

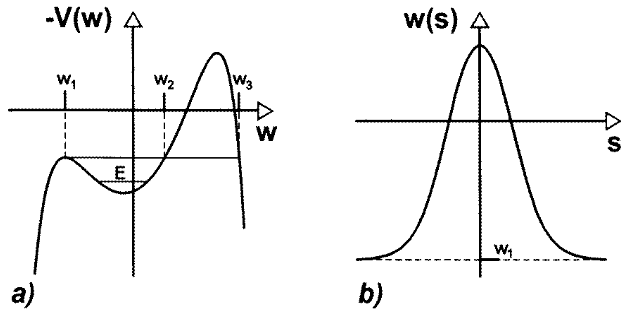

Figure 4. The asymmetric inverted potential in which a bell-shaped solution appears (a) and such a solution (b).

degenerate. Instead, a bell-shaped soliton-like excitation appears, which is given by the formula

$$w_B(\zeta,\tau) = w_1 + \frac{1}{a + b\cosh(\beta(\kappa\zeta - \omega\tau))} \tag{11}$$

(see figure 4(b)). Detailed calculation along with the formulae for the coefficients is given in the appendix.

Let us note that although this solution may form a static configuration, as in the previous case, it differs significantly from the kink. This is discussed in more detail in section 5.

4. Oscillatory solutions

Let us now consider the case where

$$\kappa^2 - \omega^2 < 0$$

in which the motion of the fictitious particle takes place in the simple potential.

In this case the first integral of motion is

$$E \equiv \frac{\varepsilon^2}{2} = \frac{\omega^2 - \kappa^2}{2}\left(\frac{\mathrm{d}w}{\mathrm{d}s}\right)^2 + V(w). \tag{12}$$

For the symmetric potential ($B = 0$), the possible forms of motion in this case include small-amplitude oscillations around the points $w = \pm w_0$ (see figure 1) for $E < (1-A)^2/2$ (they may be linearized to harmonic oscillations in the small-amplitude limit), large-amplitude oscillations around $w = 0$ for $E > (1-A)^2/2$, and aperiodic solutions separating them, which correspond to $E = (1-A)^2/2$.

In the case where $E = \frac{1}{2}(1-A)^2$, the solution obtained by integrating the first integral of the equation of motion is

$$w = \pm 2a \tanh\left[\frac{\sqrt{1-A}}{\cosh(\gamma_2(s - s_0))}\right] \tag{13}$$

where

$$\gamma_2 = \sqrt{\frac{A(1-A)}{\omega^2 - \kappa^2}}.$$

The solution is presented in the figure 5(a).

This excitation reminds one of a bell-shaped solitary solution (11). However, unlike the kink solution (9) or the soliton-like solution (11), it cannot be made stationary.

In order to obtain periodic solutions we must integrate equation (12) for a general value of the energy parameter ϵ. This may be done in three separate ranges of energy.

For $\varepsilon < (1 - A)$ the solution is

$$w = 2a \tanh\left[\sqrt{\frac{1 - A + \varepsilon}{1 + A + \varepsilon}}\ \mathrm{dn}(\gamma_{\varepsilon 2}(s - s_0), k)\right] \tag{14}$$

where

$$\gamma_{\varepsilon 2} = \frac{1}{2}\sqrt{\frac{1 - (A - \varepsilon)^2}{\omega^2 - \kappa^2}} \qquad k^2 = \frac{4A\varepsilon}{1 - (A - \varepsilon)^2}.$$

The period of the function $\mathrm{dn}(\vartheta, k)$ is $2K(k)$, where $K(k)$ is the complete elliptic integral of the first kind with the modulus k.

In the limit

$$\varepsilon \to (1 - A) \Rightarrow k^2 \to 1 \qquad \gamma_{\varepsilon 2} \to \gamma_2.$$

Taking into account

$$\mathrm{dn}(\vartheta, k = 1) = \frac{1}{\cosh \vartheta}$$

the solution (14) may be written in the form (13).

When $1 - A < \varepsilon < 1 + A$, the solution is

$$w = 2a \tanh\left[\sqrt{\frac{1 - A + \varepsilon}{1 + A + \varepsilon}}\ \mathrm{cn}(\gamma_{\varepsilon 3}(s - s_0), k)\right] \tag{15}$$

where

$$\gamma_{\varepsilon 3} = \sqrt{\frac{A\varepsilon}{\omega^2 - \kappa^2}} \qquad k^2 = \frac{1 - (A - \varepsilon)^2}{4A\varepsilon}.$$

The period of the function $\mathrm{cn}(\vartheta, k)$ is equal $4K(k)$.

In the limit $\varepsilon \to (1 + A)$ we have $k \to 0$ and due to the relation

$$\mathrm{cn}(\vartheta, k = 0) = \cos \vartheta$$

the solution takes the form

$$w(\zeta, \tau) = 2a \tanh\left[\frac{\cos(\gamma_3(s - s_0))}{\sqrt{1 + A}}\right] \tag{16}$$

with

$$\gamma_3 = \sqrt{\frac{A(1 + A)}{\omega^2 - \kappa^2}}.$$

Finally, for $\varepsilon > (1 + A)$ we get

$$w = 2a \tanh\left[\sqrt{\frac{\varepsilon - A + 1}{\varepsilon + A + 1}}\ \mathrm{sn}(\gamma_{\varepsilon 4}(s - s_0), k)\right]$$

where

$$\gamma_{\varepsilon 4} = \frac{1}{2}\sqrt{\frac{(\varepsilon + A)^2 - 1}{\omega^2 - \kappa^2}} \qquad k^2 = \frac{(\varepsilon - A)^2 - 1}{(\varepsilon - A)^2 - 1}.$$

The period of the function $\mathrm{sn}(\vartheta, k)$ is equal $4K(k)$.

In the limit $\varepsilon \to (1 + A)$,

$$\mathrm{sn}(\vartheta, k = 0) = \sin\vartheta$$

and we obtain the solution (16) up to a phase shift.

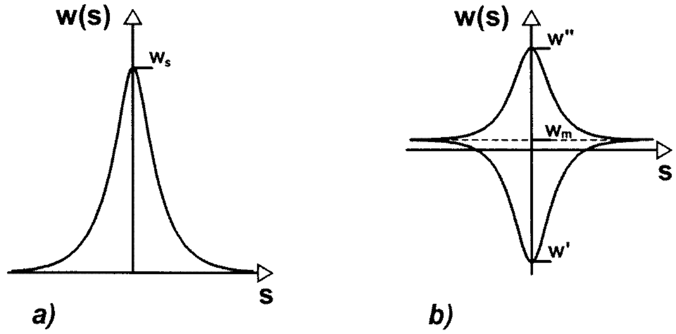

Figure 5. The fast-travelling soliton-like solution of the symmetric problem (a) and the soliton and antisoliton solutions of the asymmetric case (b).

In the asymmetric case ($B \neq 0$), the periodic solutions will have the same character as in the symmetric case. For some range of energies two kinds of periodic solution will appear for one value of energy, corresponding to the motion in two inequivalent wells. Instead of the soliton-like solution (13), identical to the corresponding antisoliton-like solution up to the sign, we obtain two different solutions (figure 5(b)). For $B > 0$ they are small-amplitude soliton-like and large-amplitude antisoliton-like solutions.

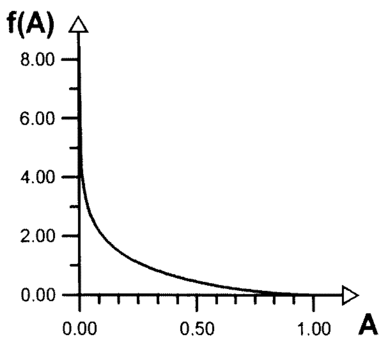

Figure 6. A plot of the function $f(A)$ defining the mass of the kink.

5. Energy and topological charge of solitary solutions

The energy of the kink and antikink in the symmetric potential is given by the expression (written in the original variables)

$$\mathcal{E} = \int_{-\infty}^{\infty} \frac{\mathrm{d}x}{a}\ \varepsilon(x)$$

where $\varepsilon(x)$ is the density of energy:

$$\varepsilon(x) = \frac{m}{2}\left(\frac{\partial u}{\partial t}\right)^2 + \frac{mc_0^2}{2}\left(\frac{\partial u}{\partial x}\right)^2 + V\left(u(x,t)\right).$$

Substituting the kink solution (9) into the above formula we obtain

$$\varepsilon(x) = \frac{V_0(1-A^2)}{\kappa^2-\omega^2}\cosh^4\left(\frac{\omega_0}{c_0}\gamma_1(\kappa x - \omega c_0 t)\right) \times \left[1 - \tanh^2\frac{\alpha u_0}{2}\tanh^2\left(\frac{\omega_0}{c_0}\gamma_1(\kappa x - \omega c_0 t)\right)\right]^{-2}.$$

This expression shows that

$$\varepsilon = \varepsilon(\kappa x - \omega c_0 t)$$

and that the energy density is localized around the point x such that

$$\kappa x - \omega c_0 t = 0.$$

This point moves along the x axis with the velocity

$$v = \frac{\omega}{\kappa}c_0 < c_0$$

i.e. the solution represents a solitary wave. The evaluation of the energy $\mathcal{E}$ leads to the result

$$\mathcal{E} = \frac{2V_0 c_0 f(A)}{a\kappa\omega_0\sqrt{1-v^2/c_0^2}}$$

where

$$f(A) = \ln\left[\frac{1}{A}(1+\sqrt{1-A^2})\right] - \sqrt{1-A^2}.$$

From the expression for energy it follows that the mass of the kink is equal to

$$M_k = \frac{2V_0}{ac_0\kappa\omega_0}f(A).$$

The mass of the kink depends substantially on the parameter A, $0 < A < 1$, of the on-site potential $V(w)$. For small A, i.e. for a high potential barrier, the mass is large—the kink is heavy. For values of A approaching 1 the mass becomes small and we have a light kink. The plot of the function $f(A)$ is presented in figure 6. For $v \ll c_0$ the 'classical approximation' holds:

$$\mathcal{E} = \frac{M_k c_0^2}{\sqrt{1-v^2/c_0^2}} \approx M_k c_0^2\left(1+\frac{v^2}{2c_0^2}\right) \approx M_k c_0^2 + \frac{1}{2}Mv^2.$$

The situation is different in the case of bell-shaped excitations, both slow (11) and fast (13) ones. In these cases in the limit where $t \to \infty$ the chain (or field) takes the value corresponding to the local minimum (slow excitations) or local maximum (fast ones) of the potential. The resulting energy of the whole chain is infinite in the limit of infinite length of the chain.

Let us define the topological current for a solitary solution of a non-linear field equation given, up to a multiplicative factor, by the expression

$$J^\mu = \epsilon^{\mu\nu}\frac{\partial u}{\partial x^\nu}$$

where $x^0 \equiv t$, $x^1 \equiv x$ and $\epsilon^{\mu\nu}$ is the antisymmetric tensor for the given dimension of the space. If we assume the solutions to be smooth, the derivatives with respect to any coordinates commute and one obtains the following local conservation law for the current defined above:

$$\sum_{\mu} \frac{\partial J^{\mu}}{\partial x^{\mu}} = 0.$$

The globally conserved topological charge is obtained by integration of the zeroth (time) component of the topological current over the space. In one dimension this may be performed in a general case, yielding (still up to a multiplicative factor)

$$Q = \int_{-\infty}^{\infty} J^0 \,\mathrm{d}x = \int_{-\infty}^{\infty} \frac{\partial u}{\partial x} \,\mathrm{d}x = u(\infty) - u(-\infty).$$

Thus, the topological charge for a solitary solution in one dimension is just proportional to the difference of the field values in plus and minus infinity.

Using this fact we may conclude that the topological charge of the kink appearing as the low-velocity (or stationary) solution for the symmetric problem is non-zero (it may be normalized to be, e.g., unity), whereas the topological charge of any of the bell-shaped solutions is zero.

6. Discussion

We have shown here how the excitations in a linear chain of double-well hydrogen bonds might be classified into solitary and oscillatory waves. According to the generally accepted interpretation, the former one is characterized by spatially localized energy. In the case of a Morse-originated double-sinh–Gordon potential, solutions have a rather complicated form, compared with φ^4-model. Due to the proposed method of treatment, one can easily recognize all of the interesting properties of the excitations in this (and similar) cases.

Among the oscillatory solutions one finds small- and large-amplitude ones, corresponding to oscillations around local minima and local maximum, respectively. They are separated by a bell-shaped-like excitation (13), which tends to zero, $w \to 0$, as time $t \to \pm\infty$ (see figure 5(a)). In the case of the asymmetric potential, two different solutions of that type are present (figure 5(b)). These solutions of course cannot be made static. In [24], a certain type of symmetric potential (2) has been investigated. By using a rather sophisticated mathematical method the solution (13) was found and called a solitary wave. It was assumed, mistakenly, that it might be made static, and even the problem of stability of its static version was investigated.

Among the solitary waves (9)–(11), the best known one is kink solution (9). Its energy is spatially localized and it carries a topological charge equal to 1. Snoidal solutions (10) are periodical functions, so they will naturally appear when a finite chain with periodic boundary conditions is considered.

The bell-shaped solution (11) (a similar one was found in φ^4-model in [25]) requires additional discussion due to certain aspects. On the one hand it may form a stationary configuration of the chain like the kink solution; on the other hand its topological charge is equal to zero, which is extremely strange in this one-dimensional case (see, e.g., [26]). Let us note that the energy of the sector of this excitation lies above the energy of the vacuum sector by the term $\epsilon_0 L$, which tends to infinity as the length of the chain $L \to \infty$. It also turns out that the bell-shaped solution, unlike solitons or kinks, is unstable. In fact, studying the stability of (11) in the static case, one looks at the small oscillations, $\psi(x,t) = e^{i\omega t}\phi(x)$, around static $w_B(x)$:

$$w(x,t) = w_B(x) + \psi(x,t). \tag{17}$$

Linearizing in $\phi(x)$ the equation of motion (3), the eigenvalue problem is obtained:

$$-\phi''(x) + V''(w_B(x))\phi(x) = \omega^2\phi(x). \tag{18}$$

Because $w_B(x)$ breaks translational symmetry, the Goldstone mode exits in this case. Similarly to what is found in the case of the kink solution, this zeroth or *translational mode* (see, e.g., [23]) is $w'_B(x)$, which satisfies (18) with the eigenvalue $\omega^2 = 0$. In the case of a kink solution, one can easily verify that this zeroth mode is nodeless, so it corresponds to the lowest eigenvalue and eventually the kink is stable. In this case however, $w'_B(x)$ has got one node (cf. figure 4(b)), so there exists a nodeless solution of (18), corresponding to a lower eigenvalue, $\omega^2 < 0$. Therefore, the bell-shaped solution is unstable. This may change if the bell-shaped soliton moves. In this case one may observe a relative dynamical stabilization of this solution: the characteristic decay time becomes longer. The discussion of the stability also gets more complicated if two-component chains are considered. More detailed analysis of these problems will be contained in a separate paper.

The phenomena discussed formally in this paper are related, among other features, to the proton transfer process in hydrogen-bonded chains. The kink solution moving along a chain of the type (1*a*) or (1*b*) corresponds to the transition of the protons from one potential minimum to the other, which is equivalent to transferring a single proton along the chain. Another effect—the Bjerrum defect which restores the chain to its original state allowing the next proton transfer to take place [2]—may also be viewed as a transition between two equivalent positions of the group A propagating along the chain. Discussion of both of these processes requires a more complex model, as considered, for example, in [6].

Finally, let us mention that, although quasi-exact solvability of the potential (2) in the quantum limit does not influence dynamical properties of the classical one-dimensional chain, in the studies of thermodynamical properties it might be of great importance. This problem will be discussed in our next paper where also an exactly solvable—in a thermodynamic limit—version of the above model will be presented.

Appendix

In this appendix we will briefly describe the way in which the integration of the equations of motion may be performed.

The key substitution used to carry out the integration is

$$z = \tanh\frac{w}{2}.$$

Introducing this new variable into the equations (8) and (12) one obtains, after some algebra,

$$\left(2\frac{dz}{ds}\right)^2 = \pm F(z) \tag{A1}$$

where

$$F(z) = \left[(1+A)^2 - \varepsilon^2\right]z^4 + 2Bz^3 - 2(1-A^2-\varepsilon^2)z^2 - 2Bz + (1-A)^2 - \varepsilon^2$$

and the plus and minus sign corresponds to the cases $\kappa^2 - \omega^2 > 0$ and $\kappa^2 - \omega^2 < 0$ respectively (note the difference in the definition of ε in these two cases). The classical motion takes place in the regions where $\pm F(z) > 0$, with the proper sign chosen.

Now, there are two general ways of solving equation (A1). One may transform it in the standard way to the form

$$s = \int \frac{\mathrm{d}z}{\sqrt{\pm F(z)}} \tag{A2}$$

and calculate the integral. Alternatively, it may be possible to transform it to the form defining Jacobi elliptic functions.

In the case of a symmetric potential, the second method is used. For example, in the range where $\kappa^2 - \omega^2 > 0$, as considered in section 3, we may use the substitutions

$$\vartheta = \frac{1}{2}\sqrt{1-(A-\varepsilon)^2}\, s \qquad \text{and} \qquad \tilde{z} = \sqrt{\frac{1+A-\varepsilon}{1-A-\varepsilon}}\, z$$

to obtain the equation

$$\left(\frac{\mathrm{d}\tilde{z}}{\mathrm{d}\vartheta}\right)^2 = (1-\tilde{z}^2)(1-k^2\tilde{z}^2) \qquad \text{where} \qquad k^2 = \frac{1-(A+\varepsilon)^2}{1-(A-\varepsilon)^2}.$$

This equation is known in the theory of elliptic functions as the equation defining the Jacobi sine amplitude function with modulus k [27]. Thus, we have at once

$$\tilde{z} = \mathrm{sn}(\vartheta, k)$$

which leads to the solution (10).

In the limit $\varepsilon \to 0$ this solution takes the form (9).

For the asymmetric potential ($B \neq 0$), the solution in the general case is technically more difficult. One needs to write the solution in the form of the integral (A2) and integrate it. The solutions for any kind of such an integral are given in [27] in terms of the zeros of the polynomial $F(z)$. These, in turn, may be found analytically if this is desirable. On the other hand, the number and the character of the zeros may be deduced from the qualitative analysis of the motion. As an example, we will derive the bell-shaped solution (11).

In this case, the value of the constant ε is chosen equal to the lower maximum of the inverted potential (see figure 4). Hence, there is one negative double root and two single positive roots of the polynomial $F(z)$. It may be therefore written in the form

$$F(z) = D^2(z-z_1)^2(z-z_2)(z-z_3)$$

where

$$D^2 = (1+A)^2 - \varepsilon^2.$$

ε is the value of the potential corresponding to the lower minimum and z_1, z_2, z_3 are the roots of the polynomial F arranged in increasing order. To find the solution we must calculate the integral

$$t = \frac{1}{D}\int \frac{\mathrm{d}z}{(z-z_1)\sqrt{(z-z_2)(z-z_3)}} = \frac{1}{D}\int \frac{\mathrm{d}\zeta}{\zeta\sqrt{(\zeta-\zeta_2)(\zeta-\zeta_3)}}$$
$$= \frac{1}{D}\frac{1}{\sqrt{\zeta_2\zeta_3}}\, a\cosh\left[\frac{2\zeta_2\zeta_3}{\zeta_3-\zeta_2}\left(\frac{1}{\zeta} - \frac{\zeta_2+\zeta_3}{2\zeta_2\zeta_3}\right)\right]$$

where we performed the shift

$$\zeta = z - z_1 \qquad \zeta_{2,3} = z_{2,3} - z_1 > 0 \qquad \zeta_2 < \zeta_3.$$

Upon inverting, this yields the solution (11) with

$$a = \frac{z_2+z_3-2z_1}{2(z_2-z_1)(z_3-z_1)} \qquad b = \frac{z_3-z_2}{2(z_2-z_1)(z_3-z_1)}$$
$$\beta = D\sqrt{(z_2-z_1)(z_3-z_1)}.$$

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