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## COMMENT

## Comment on ‘Dynamic properties of proton transfer in hydrogen-bonded molecular systems’

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### Abstract

A recent model for proton transfer in hydrogen-bonded chains given by Pang and Müller-Kirsten (Pang X F and Müller-Kirsten H J W 2000 *J. Phys.: Condens. Matter* **12** 885) is critically reconsidered. The model violates a basic symmetry of the system. The meaning of the model parameters is overinterpreted. The model can be applied only to describe the motion of ionic defects. The kink solutions corresponding to bonding defects obtained in this work by Pang and Müller-Kirsten are proven to be incorrect.

In a recent paper, Pang and Müller-Kirsten [1] have presented a model for use in investigating the mechanism of the formation of ionic and bonding defects and the interaction between the protons and heavy ions in hydrogen-bonded molecular systems. The authors of [1] claim that they have suggested for the first time a two-component model which simultaneously admits analytic soliton solutions of different types corresponding to two different kinds of defect.

However,

- (a) the physical motivation for the choice of some parameters in their discrete model Hamiltonian is not clear, and
- (b) the model *does not* describe both types of defect simultaneously.

In fact, models which allow for analytic solutions for a wide range of kink velocities were suggested soon after the pioneering work by Antonchenko *et al* [2]. It was realized [3–10] that in order to obtain the two-component model, which allows for analytic solution, one should consider the displacements of the heavy ions instead of their relative displacements. In at least two [5, 7] of these papers (not cited in [1]) a model has been investigated which gives in the continuum approximation exactly the same equations of motion as the ones treated in [1].

(a) The Hamiltonian of the system considered in [1] is  $H = H_p + H_{\text{ion}} + H_{\text{int}}$ . The proton, heavy-ion, and interaction terms are given by

$$H_p = \sum_n \left( \frac{1}{2m} p_n^2 + \frac{1}{2} m \omega_0^2 R_n^2 - \frac{1}{2} m \omega_1^2 R_n R_{n+1} + U(R_n) \right) \quad (1)$$

$$H_{\text{ion}} = \sum_n \left( \frac{1}{2M} P_n^2 + \frac{1}{2} \beta (u_n - u_{n-1})^2 \right) \quad (2)$$

$$H_{\text{int}} = \sum_n \left( \frac{1}{2} \chi_1 m (u_{n+1} - u_{n-1}) R_n^2 + m \chi_2 (u_{n+1} - u_n) R_n R_{n+1} \right) \quad (3)$$

with the proton on-site potential chosen to be the  $\phi^4$ -potential:

$$U(R_n) = U_0 [1 - (R_n/R_0)^2]^2. \quad (4)$$

Here  $R_n$  is the displacement of the  $n$ th proton from the middle of the bond between the  $n$ th and the  $(n + 1)$ th heavy ions in the static case.  $R_0$  is the distance between the central maximum and one of the minima of the double-well potential.  $U_0$  is the height of the potential barrier.  $u_n$  is the displacement of the  $n$ th heavy ion from its equilibrium position. Masses and conjugate momenta of the proton and the heavy-ion subsystems are given by  $m$ ,  $M$ ,  $p_n = m \dot{R}_n$ , and  $P_n = M \dot{u}_n$  respectively. The parameter  $\beta$  is the linear elastic constant for the heavy-ion sublattice. The quantity  $\omega_0$  is claimed to be the frequency of harmonic vibrations of the protonic sublattice, and the term  $\frac{1}{2} m \omega_1^2 R_n R_{n+1}$  is suggested to ‘show the correlation interaction between neighbouring protons caused by dipole–dipole interactions’.

Now let us rewrite equation (1) in the following way:

$$H_p = \sum_n \left( \frac{1}{2m} p_n^2 + \frac{1}{4} m \omega_1^2 (R_{n+1} - R_n)^2 + U_{\text{on-site}}(R_n) \right) \quad (5)$$

with the effective on-site potential

$$U_{\text{on-site}}(R_n) = U'_0 [1 - (R_n/R'_0)^2]^2 + U''_0 \quad (6)$$

where

$$U'_0 = U_0 \left[ 1 - \frac{m R_0^2}{4 U_0} (\omega_0^2 - \omega_1^2) \right]^2, \quad R_0'^2 = R_0^2 - \frac{m R_0^4}{4 U_0} (\omega_0^2 - \omega_1^2)$$

and

$$U''_0 = \frac{m R_0^2}{2 U_0} (\omega_0^2 - \omega_1^2) \left[ 1 - \frac{m R_0^2}{8 U_0} (\omega_0^2 - \omega_1^2) \right].$$

While the authors of [1] insist on the great importance of the introduction of different  $\omega_0$  and  $\omega_1$  into the model, it is clearly seen that the proton–proton interaction is given solely by the second term of equation (5) with a spring constant  $m \omega_1^2/2$ . The single role of the parameter  $\omega_0^2$  is to change the parameters (not the shape<sup>3</sup>) of the double-well potential (4) through the difference  $(\omega_0^2 - \omega_1^2)$ . So the quantity  $\omega_0$  has nothing to do with the frequency of harmonic vibrations of the proton sublattice, and there is no need at all to introduce this parameter into the model Hamiltonian. In fact, to obtain the proton Hamiltonian of the form (5) it suffices to put  $\omega_0 = \omega_1$  in (1).

Now let us consider the interaction part (3) of the system Hamiltonian. First of all, it cannot be accepted for symmetry reasons. For the symmetric hydrogen-bonded chain which is described with the help of symmetric double-well on-site potential for the proton subsystem,

<sup>3</sup> In fact, for  $\omega_0^2 - \omega_1^2 > 4 U_0 / m R_0^2$  we get the single-well effective on-site potential, which is not the case of interest for the problem of proton transport in hydrogen-bonded chains.

the interaction of a particle with its neighbours to the left should be the same as the interaction with the neighbours to the right. But the first term in equation (3) describes the interaction of the  $n$ th proton with the *nearest* heavy ion to the right and with the *next-nearest* heavy ion to the left. Similarly, the second term in equation (3) has a contribution from the interaction of the spring between  $n$ th and  $(n + 1)$ th proton with the two heavy ions, one of which is located *between* the two protons, and another one *to the right* of the spring.

Secondly, the following definition of the coupling constants is not justified:

$$\chi_1 = \partial\omega_0^2/\partial u_n \quad \text{and} \quad \chi_2 = \partial\omega_1^2/\partial u_n.$$

If we accept this rationale, expression (3) should be expanded in a series in the relative heavy-ion displacement, namely  $\rho_n = (u_{n+1} - u_n)$ . The other question is why the parameter  $\chi_1$  has been chosen to be determined solely by the properties of  $\omega_0^2$  as a function of heavy-ion displacements. Instead, it has to be given by some *combination* of the derivatives of  $U'_0, R'_0$ , as well as of  $\omega_1^2$ .

Now let us consider more closely the term which comes from the spring interaction energy in (5). It is easy to see that the derivative of  $\omega_1^2$  contributes to the coupling constants  $\chi_1$  and  $\chi_2$ , constants with the same absolute value but of opposite sign. When we proceed with the continuum approximation, the sum of these two contributions vanishes. So the resulting interaction term depends only on the derivatives of the effective on-site potential parameters  $U'_0$  and  $R'_0$ .

(b) In the continuum approximation, equations of motion for the Hamiltonian (1)–(3) are given by

$$\begin{aligned} \frac{\partial^2 R(x, t)}{\partial t^2} &= v_1^2 \frac{\partial^2 R(x, t)}{\partial x^2} + \frac{4U'_0}{mR_0'^2} \left[ 1 - \left( \frac{R(x, t)}{R'_0} \right)^2 \right] R(x, t) \\ &\quad - 2(\chi_1 + \chi_2)u_0 \frac{\partial u(x, t)}{\partial x} R(x, t) \end{aligned} \quad (7)$$

$$\frac{\partial^2 u(x, t)}{\partial t^2} = C_0^2 \frac{\partial^2 u(x, t)}{\partial x^2} + \frac{(\chi_1 + \chi_2)u_0}{M} \frac{\partial R^2(x, t)}{\partial x} \quad (8)$$

where  $u_0$  is a lattice constant,  $nu_0 \rightarrow x$ , and the sound velocities for the proton and heavy-ion sublattices are given by  $v_1^2 = (\omega_1 u_0)^2/2$ ,  $C_0^2 = \beta u_0^2/M$ , respectively.

For the travelling wave solutions of the form  $R(x, t) = R(x - vt)$  and  $u(x, t) = u(x - vt)$ , equation (8) gives

$$\frac{\partial u(x - vt)}{\partial x} = -\frac{m}{M} \frac{(\chi_1 + \chi_2)u_0}{C_0^2 - v^2} R^2(x - vt) + g$$

where  $g$  is an integration constant. To obtain the kink solution, one should apply the boundary conditions

$$\frac{\partial u(x - vt)}{\partial x} = 0, \quad \frac{\partial R(x - vt)}{\partial x} = 0 \quad \text{for } (x - vt) \rightarrow \pm\infty. \quad (9)$$

Then the integration constant is calculated as

$$g = \frac{R_0'^2 m u_0 (\chi_1 + \chi_2)}{M(C_0^2 - v^2)}$$

where  $R_0'^2$  has replaced  $R_0^2$  used in [1] (of course,  $R'_0 = R_0$  for  $\omega_1 = \omega_0$ ). The kink solution reads

$$R(x, t) = \pm R'_0 \tanh \left[ \frac{x - vt}{l(v)} \right] \quad (10)$$

and

$$u(x, t) = \frac{m(\chi_1 + \chi_2)u_0}{M(C_0^2 - v^2)} R_0^2 l(v) \tanh \left[ \frac{x - vt}{l(v)} \right] \quad (11)$$

where the kink width  $l(v)$  is given by

$$l^2(v) = \frac{mR_0^2(C_0^2 - v^2)(v_1^2 - v^2)}{2U'_0 v^{*2} - v^2}$$

and the third characteristic velocity  $v^*$  can be found from

$$v^{*2} = C_0^2 - \frac{m^2(\chi_1 + \chi_2)^2 u_0^2 R_0^4}{2MU'_0}.$$

The kink solutions of the form (10), (11) exist provided  $l^2(v) > 0$ . There are two possibilities for the ratio of the proton and the heavy-ion subsystem sound velocities.

- (1)  $v_1 > C_0$ . This is a commonly considered situation for hydrogen-bonded chains (since  $M \gg m$ ). In this case the kink solutions exist for

$$0 < v < v^* \quad \text{or} \quad C_0 < v < v_1.$$

The slow kink solutions are proven to be stable [3].

- (2)  $C_0 > v_1$  (the choice of parameters in [1]). The kink solutions exist for

$$0 < v < \min(v_1, v^*) \quad \text{or} \quad \max(v_1, v^*) < v < C_0.$$

It is clearly seen that the kink solutions (10) for both low- and high-velocity ranges have the same amplitude  $R'_0$  which depends neither on the coupling constants  $(\chi_1 + \chi_2)$  nor on the kink velocity  $v$ . These solutions correspond to the proton transition over the barrier of the double-well on-site potential (6), i.e., to the ionic defect.

The kink solutions with a variable amplitude of the proton displacements found in [1] have been derived with the incorrect application of the boundary conditions (9). The authors have not appreciated the shift of the minima of the on-site potential caused by the different values of  $\omega_0^2$  and  $\omega_1^2$ . As a result, expressions (18)–(20) in [1] do not satisfy equations of motion (7), (8). Thus, all the discussion (sections 4–6 of [1]) concerning the kink solutions with the protons being displaced beyond the heavy-ion positions has no physical meaning. The kink solutions of the form (10), (11) describe only *the ionic defects* and not the Bjerrum ones.

Furthermore, if there were solutions with the protons displaced beyond the heavy-ion positions<sup>4</sup>, it would be a great mistake to ascribe them some physics. By the very definition of the double-well on-site potential for the proton, it describes the hydrogen bond formed by two neighbouring heavy ions. This potential is not valid for the proton displaced to some position between another two heavy ions.

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<sup>4</sup> Figure 4(b) of [1] claiming to depict such a solution is absolutely wrong.

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