Peierls Instabilities in Quasi-One-Dimensional Quantum Double-Well Chains

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Peierls-type instabilities in quarter-filled ($\bar{n} = 1/2$) and half-filled ($\bar{n} = 1$) quantum double-well hydrogen-bonded chain are investigated analytically in the framework of two-stage orientational-tunnelling model with additional inclusion of the interactions of protons with two different optical phonon branches. It is shown that when the energy of proton-phonon coupling becomes large, the system undergoes a transition to a various types of insulator states. The influence of two different transport amplitudes on ground states properties is studied. The results are compared with the pressure effect experimental investigations in superprotonic systems and hydrogen halides at low temperatures.

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I. INTRODUCTION

It is long been known that the formation of hydrogen bonds between molecules or ionic groups is responsible for a drastic changes in a wide variety of entire system properties such as structural phase transformations and proton ordering phenomena. In addition, proton transport phenomena in H-bonded materials and superionic properties discovered in some hydrogen-bonded crystals (for example, $M_3H(AO_4)_2$ class where $M=Rb$, Cs, NH$_4$; $A=$Se, S) are related closely to hydrogen-bonded network rearrangement. On heating these crystals transform into superionic conducting phase with statistically disordered hydrogen-bonded network (Fig. 1(a)). The protons can migrate through the two-dimensional conducting planes with low activation energy ($\sim 0.1$ eV). In this case protonic conductivity increases significantly to the value about $0.1$ $\Omega^{-1}$ cm$^{-1}$. It is generally accepted that the two-stage conduction mechanism is required to sustain proton transport. The intrabond proton tunnelling along the hydrogen bridge is connected with the transfer of ionic positive and negative charged defects, whereas the intermolecular proton transfer due to reorientational hopping and consequent feasibility of proton migration along the chain. Such a situation, as an example, is observed in superionic materials of $M_3H(AO_4)_2$-type which transform on cooling into dielectric state with dimerized structure.

Ions in hydrogen-bonded systems have been based generally on pseudospin Ising-type models with additional including of the pseudospin-phonon interactions to describe the coupling of protons with lattice vibration modes. In particular, the quantum double-well chain with quartic symmetric double-well potential has been used to model the transition from the symmetry-broken to the symmetry-restored ground state in hydrogen halides HX ($X=F$, Br, Cl) which consist of hydrogen-bonded chains with weak interchain coupling. The dynamics of both ionic and orientational defects created by the rotations of molecular groups in hydrogen halides has been studied in the framework of classic approach based on soliton model.

It must be emphasized that taking into account the two-stage transport mechanism renders the pseudospin formalism unsuitable for the proton subsystem description since the number of protons can differ from the number of possible (virtual) hydrogen bonds and the proton occupancy of each bond in principle can be other than unity due to reorientational hopping and consequent feasibility of proton migration along the chain. Such a situation, as an example, is observed in superionic materials of $M_3H(AO_4)_2$-type which transform on cooling into dielectric state with dimerized structure. It should be noted that such type of transitions to dielectric states is reminiscent of that of electronic systems in which the Peierls instabilities are observed. There have been many works to study the metal-insulator Peierls transitions in electron-phonon systems which are unstable against the electron-phonon interaction. It is common knowledge that the Peierls instabilities occur with the formation of Peierls gap at $k = \pm k_F$ ($k_F$ is the Fermi level) in the electronic energy band that connected with the electronic charge density waves condensation and structural lattice distortion modulations with $q = 2k_F$. The appearance of insulator state together with the structural transformation can be modelled in the framework of the Holstein electron-phonon model without additional in-
cluding the anharmonic terms in the lattice potential.

Recent investigations of Peierls transitions in electronphonon systems have prompted us to study similar effects in several hydrogen-bonded solids. On the one hand, parallel sequences of plains (001) are formed in superionic state of M$_3$H(AO$_4$)$_2$ crystals. These hexagonal conducting plains consist of AO$_4$ groups connected by virtual hydrogen bonds (see Fig. 1(a)). In the low-temperature phases the frozen-in hydrogen bonds with only one index $f$ ($f = 1, 2, 3$) form well-defined sequences of dimers that involves the appearance of the parallel dimerized chain arrays consisting of ionic groups linked by the $f$th hydrogen bond (see Fig. 1(b)). To analyze the influence of the proton-ionic group displacements coupling we consider the simplified model, namely the quasi-one-dimensional quantum double-well chain along one of the proton pathways (for instance, the virtual hydrogen bond sequence $\ldots -1-3-1-3-\ldots$). As an initial step, we neglect of the interproton repulsion effect that is justified for the low proton concentration (in our case each proton is averaged over every three virtual hydrogen bonds). However, we take into account the possibility of proton exchange between our selected chain and surrounding. On the other hand, besides these superionic compounds we also analyze in this work the influence of ionic group displacements on the proton subsystem behavior in quasi-one-dimensional solid hydrogen halides. We reveal possible symmetry-broken phases with proton charge disproportionalities coming from a Holstein coupling to AO$_4$ ionic groups or X atoms. We compare our conclusions with the results of the pressure effect theoretical studies in M$_3$H(AO$_4$)$_2$ and hydrogen halides.$^{[4]}$ Although the first step of our analysis consists of the quasi-one-dimensional chain study, we believe our results can also be relevant for other hydrogen-bonded materials.

II. DESCRIPTION OF THE MODEL

The object of our consideration is the chain shown in Fig. 2(a). However, to avoid the geometric complexities introduced by the kinks in such an zig-zag chain, we consider in our model linear chain (see Fig. 2(b) where two neighboring chains are shown). The process of the proton transfer in the double-well H-bond potential is represented as the quantum tunnelling between two proton states with intrabond transfer integral $\Omega_0$

$$\Omega_0 \sum_{l} (c_{la}^+ c_{lb} + c_{lb}^+ c_{la}),$$

where $c_{la}^+$, $c_{lb}$ denote proton creation and annihilation operators in the position $(l, \nu = a, b)$ of the chain. Besides that, we describe the interbond reorientational proton hopping in two-level approximation as the quantum tunnelling effect with hopping amplitude $\Omega_R$

$$\Omega_R \sum_{l} (c_{l+1,a}^+ c_{lb} + c_{lb}^+ c_{l+1,a}).$$

In this way in the framework of orientational-tunnelling model proposed in Ref. 4, the two-stage proton migration mechanism can be considered as the sequential migration of the ionic and orientational defects.

As far as such a double-well chain is just a structural component of the system we also admit a possibility of proton exchange between the chain and surroundings by considering the system thermodynamics in the framework of the grand canonical ensemble with inclusion of the proton chemical potential

$$-\mu \sum_{l, \nu} n_{l\nu},$$

which is to be determined at the given proton concentration in the chain from corresponding equation for the chemical potential.

Our main interest is to analyze the influence of the longitudinal optical ionic group vibration modes on the proton subsystem ground state. However, it was noted in Ref. 4 that the interactions between protons of the neighboring chains can lead to appearance of three-dimensional ordering. The more detailed analysis of the interchain proton interaction effect in this model together with the determination of stability conditions for the existence of the phases with different ordering type at finite temperatures will be presented elsewhere. 5 We consider the anti-phase stretching vibration mode which causes a change of H-bond length in chain as indicated in Fig. 2(b) by solid arrows. Besides that, we also take into account the optical in-phase vibrations of ionic groups in chain
which induce their displacements with respect to surrounding chains as identified in Fig. 2(b) by dashed arrows. The coupling to the first type of displacements leads to the equal change of the potential well ($l$, $a$) and ($l$, $b$) depth within the H-bond

$$\sum_{l,q} \tau_1^{(1)}(q)(n_{l,a} + n_{l,b})(b_{q,1} + b_{q,1}^+),$$

whereas the coupling of protons to another optical mode causes the difference of these potential minima depth

$$\sum_{l,q} \tau_1^{(2)}(q)(n_{l,a} - n_{l-1,b})(b_{q,2} + b_{q,2}^+).$$

Here $\tau_1^{(1)}(q) = -2ig_1\sqrt{h/2M}N\omega_1(q)\sin \frac{q}{2}qd\exp[iq(l + 1/2)d]$ and $\tau_1^{(2)}(q) = g_2\sqrt{h/2M}\sqrt{\omega_2(q)}\exp[iqld]$ where $g_1$ and $g_2$ are corresponding coupling constants, $M$ is the effective ionic group mass, $N$ denotes the number of hydrogen bonds in chain and $d$ is a lattice spacing. Furthermore we take dispersionless approximation for the phonon frequencies: $\omega_1(q) = \omega_1$ and $\omega_2(q) = \omega_2$ and assume the harmonic approximation for the lattice vibration energies

$$\hbar\omega_1 \sum_q b_{q,1}^+b_{q,1} + \hbar\omega_2 \sum_q b_{q,2}^+b_{q,2}.$$  

First of all let us consider the case of the isolated chain without coupling to the phonon bath. Since the Hamiltonian can be exactly diagonalized, the proton energy spectrum

$$\varepsilon_{\nu}(k) = \pm |t_k|, \quad |t_k| = \sqrt{\Omega_0^2 + \Omega_R^2 + 2\Omega_0\Omega_R\cos kd}$$

forms two energy bands with the bandwidth $\Delta \varepsilon = \Omega_0 + \Omega_R - |\Omega_0 - \Omega_R|$. The energy gap in this case is $\Delta_{ab} = 2|\Omega_0 - \Omega_R|$. Eliminating one of the elementary transport process by setting hopping amplitude $\Omega_0 = 0$ or $\Omega_R = 0$ we can see that both the energy bands degenerate into two energy levels and the quantum fluctuations between these two system states could be derived. It is clear that in the case when $\tilde{n} = \frac{1}{N} \sum_{i\nu} n_{i\nu} = 1$ (one proton is averaged within the bond) the lower band is filled and the chemical potential $\mu$ is centered between bands - thus the material is in dielectric state. Such an situation can be observed in hydrogen halides. However, for $\tilde{n} = \frac{1}{2}$ only half of the lower band is filled and this corresponds to the case of protonic conductor that occurs for example in superionic phases of superprotonic crystals.

We will discuss afterwards the consequences of the proton-phonon coupling effect focusing on the analysis of the two physically different cases $\tilde{n} = \frac{1}{2}$ (1/4-filled two-band model) and $\tilde{n} = 1$ (half-filling case in two-band model).

### III. BROKEN-SYMMETRY SOLUTIONS

#### A. Case $\tilde{n} = \frac{1}{2}$

Let us now focus on the case of quarter filling when the half of the lower proton band is filled (one proton per two bonds). Then the macroscopic condensed phonon state is predominantly stabilized at $q^* = 2k_F = \pi/d$ and is characterized by the expectation values of the phonon creation and annihilation operators

$$\langle B_{q,1} \rangle = \langle b_{q,1} + b_{q,1}^+ \rangle = \frac{\Delta}{g_1}\sqrt{N} \delta_{q,q^*},$$

where $\Delta$ denotes the introduced distortion order parameter which should be determined from the stationarity conditions of the free energy. Since the condensation of displacements leads to the unit cell doubling, using the Fourier transformation $c_{\nu(i)} = \frac{1}{\sqrt{N/2}} \sum_k c_{k\nu(i)}e^{ikld}$ where the index $i = \{+, -\}$ denotes $(l = 2m)$ or $(l = 2m + 1)$th cell, the Hamiltonian in condensed state with static periodic distortions (adiabatic treatment) is given by

$$H = (-\mu + \tilde{\Delta}) \sum_{k\nu} n_{k\nu(+)} - (\mu + \tilde{\Delta}) \sum_{k\nu} n_{k\nu(-)} + \frac{1}{8} N \tilde{\Delta}^2 E_0 + \Omega_0 \sum_{k,i} (c_{k\nu(i)}^+c_{k\nu(i)} + c_{k\nu(i)}^+c_{k\nu(i)}^+) + \Omega_R \sum_k \sum_{i \neq i'} (c_{k\nu(i)}^+c_{k\nu(i')}e^{-ikd} + c_{k\nu(i')}^+c_{k\nu(i)}e^{ikd}),$$

where $E_0 = (\hbar g_1)^2/2M(\hbar\omega_1)^2$ is well known from polaron theory protonic polaron binding energy which
appears in the expression for the elastic energy per H-bond \( \frac{1}{2} \Delta P^{0} \) and \( \Delta = 4\Delta \sqrt{v_{y} / 2M} \omega_{1} = 4\Delta \sqrt{E_{0}/h\omega_{1}} / g_{1} \). The similar result can be obtained when we consider the second type of the ionic group displacements, in this case \( \langle B_{q,2} \rangle = \langle b_{q,2}^{+} b_{q,2} \rangle = \frac{1}{N} \sum N_{q,2}^{\prime} \) and the Hamiltonian in condensed state has the form similar to (5) with \( \tilde{\Delta} \) and the following notations are introduced:

\[
\langle \varepsilon \cdot \text{sgn}(\varepsilon) - \sqrt{t_{1} - t_{2}^{0}} \rangle
\]

(10)

\[
\text{where}
\]

\[
B_{1} = \sqrt{(t_{1} - \varepsilon^{2})^{2} - 4\Omega R^{2} \Delta^{2}},
\]

\[
B_{2} = \sqrt{4\Omega R^{2} \Delta^{2} + \Omega R^{2} - (t_{1} - \varepsilon^{2})^{2}}
\]

and the following notations are introduced: \( t_{1} = \Omega R^{2} + \Omega R^{2} + \Delta^{2}, t_{2}^{0} = 2\Omega R \sqrt{\Omega R^{2} + \Delta^{2}} \) and \( \Theta(x) \) is the Heaviside step function. The expression for the ground state energy can be obtained easily from (5) and (10):

\[
F = \frac{N \Delta^{2}}{8 E_{0}} - \sum_{k} \sqrt{t_{1} + 2\Omega R \sqrt{\Delta^{2} + \Omega R^{2} \cos^{2} kd}}.
\]

(12)

To determine the stable phase the equation \( \partial F / \partial \Delta = 0 \) should be solved. It appears that this equations has besides \( \Delta = 0 \), a nonzero additional solution \( \Delta \neq 0 \) for \( g_{1} > g_{p} \) where \( g_{p} \) is the crossover proton-phonon coupling strength. The solution \( \Delta \neq 0 \) corresponds to the global minimum of \( F \) and, as a result, implies the structural distortion stabilization with the amplitude \( u_{l} = \sqrt{h / 2M} \omega_{1} (B_{q}^{0})^{1 / 2} \) (see Fig. 3(a)). Let us discuss the proton position average occupancies on the bonds and the band structure. At \( g_{1} = g_{p} \) each proton band splits into two subbands

\[
\varepsilon_{a(+/-)}(k) = \pm \sqrt{t_{1} + 2\Omega R \sqrt{\Delta^{2} + \Omega R^{2} \cos^{2} kd}},
\]

\[
\varepsilon_{b(+/-)}(k) = \pm \sqrt{t_{1} - 2\Omega R \sqrt{\Delta^{2} + \Omega R^{2} \cos^{2} kd}}
\]

(13)

as shown in Fig. 3(b) where the proton density of states in the disordered and dimerized phases is represented. The Peierls energy gap between either of the two (lower and upper) subbands \( \Delta_{1} = \sqrt{t_{1} + 2\Omega R \Delta} - \sqrt{t_{1} - 2\Omega R \Delta} \approx 2\Omega R \Delta / \sqrt{\Omega R^{2} + \Omega R^{2} / \tilde{\Omega}} \) and tends to zero for \( \tilde{\Omega} \to 0 \). In this case \( \Delta = \pm \sqrt{4E_{0} - \Omega R^{2}} \) and the phase transition (change in the nature of the ground state) occurs when the localization energy \( E_{0} \approx (g_{1}^{0})^{2} = \frac{1}{4} \Omega R \). The energy gap between the second and third subbands increases at \( g_{1} > g_{p} \).

\[
\Delta_{ab} = 2 \sqrt{t_{1} - 2\Omega R \sqrt{\Delta^{2} + \Omega R^{2}}}.
\]

The proton chemical potential \( \mu \) is centered between two lowest subbands with further increasing of \( g_{1} > g_{p} \) that points to the insulator state appearance. We see from inset in Fig. 3(a) that the distortion stability is accompanied by the formation of the charge-density-wave state in which \( \langle n_{a} \rangle = \langle n_{b} \rangle = \frac{1}{2} \) that means the forming of dimerized structure as shown in Fig. 4. Consider further the ground state phase diagrams \( (\tilde{g}_{1} = g_{1} / h\omega_{1}, \Omega_{0} = \Omega_{0} / h\omega_{1}) \) and \( (\tilde{g}_{1}, \tilde{\Omega}_{R} = \Omega_{R} / h\omega_{1}) \).
\[ \Omega_R/h\omega_1 \] represented in Fig. 5. We see the strong influence of the amplitude \( \Omega_R \) on the dimerized state stability. The increasing of \( \Omega_R \) suppresses dimerization. At \( \Omega_R \to 0 \) (without reorientational hopping) the system is brought immediately into the dimerized state. Only for the finite values of \( \Omega_R \) the uniform disordered phase begins to appear and the "metal"-insulator transition occurs.

It is necessary to mention that the hopping amplitudes \( \Omega_0 \) and \( \Omega_R \) depend strongly on external pressure. In particular, the \( \Omega_0 \) value decreases with pressure that deduces from quantum mechanical calculations, as well as from the experimental measurements. This is associated with the shortening of the distance between two potential minima (\( l, \nu \)) in the bond. Thus we can make a conclusion about pressure effect on the system state from the diagrams shown in Fig. 5. Using the obtained values for parameters \( \Omega_R, g_1 \) and \( \omega_1 \) (\( \Omega_R/h\omega_1 \approx 0.14 \) and \( h^2 g_1^2/2M(h\omega_1)^3 \approx 3.8 \)) we reveal that the dimerized state is always stable at \( T=0 \) under pressure for this set of parameters. It is interesting that the similar picture has been observed in \( \text{M}_3\text{H}(\text{AO}_4)_2 \) materials from experimentally measured baric dependencies at low temperatures. Nevertheless, we notice that as \( g_1 \) decreases and approaches the critical value \( g_1^c = \sqrt{\Omega_R/2} \), a transition from the dimerized to the uniform state occurs with pressure. This effect appears due to the more weak proton-phonon coupling and, as a result, to the tendency of the proton delocalization in chain.

**B. Case \( \bar{n} = 1 \)**

Let us discuss another case when one proton in average is placed in the bond. According to Peierls theory \[ \text{such a system is very susceptible towards lattice modulation at } g^* = 0. \] It should be noted that in this case only the second type of optical vibrations (interchain mode) contributes to the lattice distortions condensation. The Hamiltonian in condensed phase has the form

\[
H = \sum_k \left[ (\mu + \bar{\Delta}) n_{ka} - (\mu + \bar{\Delta}) n_{kb} \right] + \frac{1}{8} N \frac{\bar{\Delta}^2}{\epsilon_0} + \sum_k \left( t_k c_k^+ c_{kb} + t_k^* c_{kb}^+ c_{ka} \right).
\]

In this case the density of proton states

\[
\rho(\varepsilon) = \frac{2}{\pi} \frac{|\varepsilon|}{\sqrt{4\Omega_R^2 - (\varepsilon^2 - t_1^2)^2}} \times 
\left( \Theta(\varepsilon \cdot \text{sgn}(\varepsilon)) - \sqrt{\Delta^2 + (\Omega_0 - \Omega_R)^2} - \Theta(\varepsilon \cdot \text{sgn}(\varepsilon)) - \sqrt{\Delta^2 + (\Omega_0 + \Omega_R)^2} \right)
\]

points to the two-band structure

\[
\varepsilon_{\nu}(k) = \pm \sqrt{\Delta^2 + |t_k|^2}
\]

with the Peierls energy gap \( \Delta_{ab} = 2 \sqrt{\Delta^2 + (\Omega_0 - \Omega_R)^2} \). The chemical potential always is centered between two bands, i.e. \( \mu = 0 \). We present the equation for determination of \( \bar{\Delta} \neq 0 \) which follows from the stationary condition of \( F \):

\[
\frac{1}{4E_0} = \frac{1}{N} \sum_k \frac{1}{\sqrt{\Delta^2 + |t_k|^2}}
\]

The nonzero solution, which appears for \( g_2 > g_P \), corresponds to the formation of a proton charge density wave in chain together with the distortions \( u_l = \Delta/2g_2 \) stabilization (see Fig. 6). The typical dependencies of the proton position average occupancies \( \langle n_{l\nu} \rangle \) are represented in

**Fig. 4.** Dimerized structure which appears in the case of quarter-filled chain.

**Fig. 5.** Ground-state phase diagrams (a) \( (\tilde{g}_1, \tilde{\Omega}_0) \) and (b) \( (\tilde{g}_1, \tilde{\Omega}_R) \). The notations PD and PU denote the dimerized and uniform phases respectively.

**Fig. 6.** Broken-symmetry structure which appears in the case of half-filled chain.
Fig. 7. It is interesting that the system now is invariable with respect to the interchanging $\Omega_0 \leftrightarrow \Omega_R$. Thus it is sufficiently to analyze the system behavior as a function of $\Omega_0$ for instance, with the given fixed value of $\Omega_R$. The ground state phase diagram ($\tilde{g}_2 = g_2/\hbar \omega_2$, $\Omega_0 = \Omega_0/\hbar \omega_2$) (see Fig. 8) differs essentially from the case $\bar{n} = \frac{1}{2}$. The phase equilibrium curve has the specific salient point at $\Omega_0 = \Omega_R$. The drastically decrease of $g_P$ in the vicinity of $\Omega_0 = \Omega_R$ is connected with the fact that the transfer anisotropy $|\Omega_0 - \Omega_R|$ forms the additional transverse field which competes with the ordering stabilization process. This anisotropy is vanished at $\Omega_0 = \Omega_R$ that leads to the lowering of the crossover proton-phonon coupling energy $g_P$ required for the ordering stabilization. The interpretation of the diagram ($\tilde{g}_2$, $\Omega_0$) with respect to the pressure effect is very interesting. The second-order transition from the uniform to ordered state occurs under pressure at $\tilde{g}_2 = \sqrt{\Omega_R}/2$. However, in the region $g_2 < g_2^*$ the additional reentrant transition from the symmetry-broken to the uniform state appears (see Fig. 9). In this case the region of symmetry-broken phase equilibrium narrows with $g_2$ decrease. We notice that the first-principle calculations confirm and the results of Monte Carlo simulations in quasi-one dimensional hydrogen halides show a transition from the symmetry-broken phase shown in Fig. 6 to the uniform symmetric phase under pressure at the low temperatures. Thus our results in the vicinity of $\Omega_0 \approx \Omega_R$ and for considerably large, the system undergoes a transition from disordered to broken-symmetry phases. The different cases of proton concentration have been analyzed: $\bar{n} = 1/2$ and $\bar{n} = 1$. It is shown that in the first case the Peierls transition to the dimerized phase occurs, whereas in the second one we obtain a transformation into the proton-ordered state. The influence of two different transport amplitudes on ground states properties is also studied. We compare our ground-state phase diagrams with the pressure effect experimental investigations in superprotonic systems and hydrogen halides at low temperatures.

IV. CONCLUSIONS

In the present work the lattice effect on the ground state properties of the quantum quasi-one-dimensional hydrogen-bonded chain is analyzed in the framework of the two-stage orientational-tunneling model. The interaction of protons with two different types of surrounding ionic group optical displacements is considered. We show that when the proton-phonon coupling energy becomes large, the system undergoes a transition from disordered to broken-symmetry phases. The different cases of proton concentration have been analyzed: $\bar{n} = 1/2$ and $\bar{n} = 1$. It is shown that in the first case the Peierls transition to the dimerized phase occurs, whereas in the second one we obtain a transformation into the proton-ordered state. The influence of two different transport amplitudes on ground states properties is also studied. We compare our ground-state phase diagrams with the pressure effect experimental investigations in superprotonic systems and hydrogen halides at low temperatures.
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