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Macroscopic quantum tunneling of polarization in the hydrogen-bonded chain

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Abstract

The probability of macroscopic quantum tunneling of polarization in a finite H-bonded chain is treated theoretically with regard to the influence of chain anisotropy. It is shown that the anisotropy stipulated by different microscopical effects plays a major role in the tunneling rate of polarization. © 1997 Elsevier Science B.V.

Keywords: H-bonded chain; Macroscopic tunneling; Polarizability

1. Introduction

The existence of short hydrogen-bonded chains has been proved experimentally [1] in organic and bio-organic systems. It has been shown by Zundel and co-workers [1–6] that the H-bonded chain is characterized by large proton polarizability and its polarization fluctuates ceaselessly between two opposite directions. The H-bonded chain is now considered as a main structural unit of the proton channel in proton-conductive biomembranes [1,7]. Therefore knowledge of the mechanism of chain polarization fluctuations is very important as it should give the additional information needed for the detailed microscopic description of proton motion along the chain.

The physical properties of the H-bonded chain differ significantly from those of its nearest surroundings. Because of this the chain can be considered as a quasi-isolated and quasi-one-dimensional domain. In this paper we study the dynamics of such a domain and propose a macroscopic mechanism of polarization oscillations of the H-bonded chain. Our treatment is essentially based on our previous work [8] in which the polarized current caused by water domains adsorbed on a metal film was studied in detail.

2. H-bonded chain as a domain

We will consider the H-bonded chain shown in Fig. 1. We imply the chain is impressed in a condensed matter and two opposite configurations of the chain (a and b) have the same energy. The aim of the present paper is to show that repolarization of H-bonds, i.e. the transition $a \rightarrow b$ (or $b \rightarrow a$) in Fig. 1 for a finite chain can occur by virtue of macroscopic quantum tunneling of the chain polarization $\vec{P}$.

The motion of a proton in the strong or middle H-bond can be described in terms of a two-well potential. Let $\hat{a}_R^{\dagger}(\hat{a}_R)$ and $\hat{a}_L{}^{\dagger}(\hat{a}_L)$ be Fermi operators in the right

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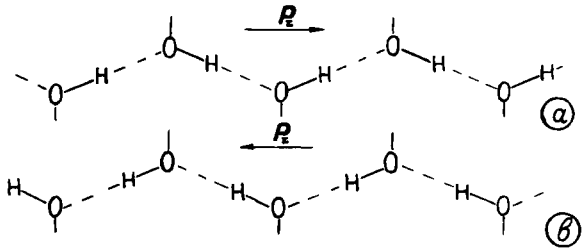

Fig. 1. The H-bonded chain. (*a*) OH groups are oriented to the right; (*b*) all OH groups are oriented to the left.

and left wells respectively. Then one can introduce the notion of pseudospin (see, e.g. Ref. [9]):

$$\hat{\sigma}_j^x = \tfrac{1}{2}\left\{\hat{a}_L^{j\dagger}\hat{a}_R^j + \hat{a}_R^{j\dagger}\hat{a}_L^j\right\} \tag{1a}$$

$$\hat{\sigma}_j^y = \tfrac{1}{2}\left\{\hat{a}_L^{j\dagger}\hat{a}_R^j - \hat{a}_R^{j\dagger}\hat{a}_L^j\right\} \tag{1b}$$

$$\hat{\sigma}_j^z = \tfrac{1}{2}\left\{\hat{a}_L^{j\dagger}\hat{a}_L^j - \hat{a}_R^{j\dagger}\hat{a}_R^j\right\} \tag{1c}$$

where j is the number of a two-well potential. Here the z component of pseudospin is given the dipole moment operator of the jth H-bond; the x component of the pseudospin is the tunneling operator (it describes oscillations of a proton in the H-bond); the y component is the operator of local current. In this case the Hamiltonian of an H-bonded chain can be written in the form

$$\hat{\mathcal{H}} = -\hbar\Omega \sum_j \hat{\sigma}_j^x - \tfrac{1}{2}\sum_{jj'} J_{jj'}\hat{\sigma}_j^z\hat{\sigma}_{j'}^z - \tfrac{1}{2}\sum_{jj'} B_{jj'}\hat{\sigma}_j^x\hat{\sigma}_{j'}^x \tag{2}$$

here $\hbar\Omega$ is the tunneling energy of a proton in the H-bond potential well; $J_{jj'}$ is the energy of mutual interaction of the jth and j'th protons; $B_{jj'}$ is the energy of mutual interaction between the pseudospin and lattice vibrations. If $\vec{H}_j$ is the mean field, then the equation of motion of an average value of the pseudospin has the form [9]

$$\frac{\mathrm{d}\langle\vec{\sigma}_j\rangle_t}{\mathrm{d}t} = \langle\vec{\sigma}_j\rangle_t \times \vec{H}_j(t)\frac{1}{\hbar} \tag{3}$$

where

$$\vec{H}_j(t) = -\frac{\partial\langle\hat{\mathcal{H}}\rangle_t}{\partial\langle\vec{\sigma}_j\rangle_t} \tag{4}$$

Eqs. (3) and (4) are equivalent to the equations of free classical precession of the pseudospin round the momentary value of mean field in the present point. We assume that the dipole moment of each H-bond in the chain has the same value and direction. In this approximation the two sides of Eq. (3) can be multiplied by a factor corresponding to the quantity N of H-bonds in the chain. Then Eqs. (3) and (4) are transformed to the equation of motion for the vector polarization $\vec{P}$ of the chain (i.e. $\vec{P} = 2N\langle\vec{\sigma}\rangle_t d$ [9], where d is the dipole moment of one H-bond). So, one can write the following macroscopic equation for the motion of $\vec{P}$ in the H-bonded chain:

$$\frac{\mathrm{d}\vec{P}}{\mathrm{d}t} = -\vec{P}\times\frac{\delta E}{\delta\vec{P}}\frac{1}{\hbar} \tag{5}$$

Notice that Eq. (5) is wholly identical to the dynamic equation for magnetization $\vec{M}$ in ferromagnetics [10]:

$$\frac{\mathrm{d}\vec{M}}{\mathrm{d}t} = -\gamma\vec{M}\times\frac{\delta E}{\delta\vec{M}} \tag{6}$$

where $E(\vec{M})$ is the energy of anisotropy and γ is the gyromagnetic coefficient.

Within the last ten years there has been considerable interest in the phenomenon of macroscopic tunneling of magnetization which takes place in single-domain magnetic particles [11–17]. In the spherical coordinate system the vector $\vec{M}$ has the components: $\{M_0\sin\theta\cos\phi,\ M_0\sin\theta\sin\phi,\ M_0\cos\theta\}$. In this case according to Refs. [13,18] Eq. (6) can be derived from the action:

$$I = \int \mathrm{d}t\left[\frac{M_0}{\gamma}\dot{\phi}\cos\theta - E(\theta,\phi)\right] \tag{7}$$

with the Lagrangian of the system

$$L = p\dot{q} - E \tag{8}$$

where

$$q = \phi,\ p = \frac{M_0}{\gamma}\cos\theta \tag{9}$$

Eq. (6) is equivalent to the equation of motion obtained from the Lagrangian Eq. (8)

$$\dot{\theta}\sin\theta = \frac{\gamma}{M_0}\frac{\partial E}{\partial\phi} \tag{10}$$

$$\dot{\phi}\sin\theta = -\frac{\gamma}{M_0}\frac{\partial E}{\partial\theta} \tag{11}$$

If there are the two or several equilibrium directions of the magnetization vector $\vec{M}$ which correspond to minima of the energy then calculation of the probability of tunneling transition from one to another equilibrium direction can be performed by passing in Eqs. (10) and (11) to an imaginary time $\tau = it$. Along trajectories connecting two minima the action is implicit and its extremals should give an expression for tunneling rate $\mathcal{P}$ in the quasiclassical (WKB) approximation:

$$\mathcal{P} \propto \exp(iI/\hbar) \tag{12}$$

Analysis based on techniques of spin-coherent states [17] has given the possibility of acquiring tunneling-rate prefactors.

3. Polarization tunneling

Let us present the polarization along the principal axis of the H-bonded chain in the form

$$P_z = 2Nd\langle\hat{\sigma}^z\rangle = 2dS^z \tag{13}$$

where the designation

$$S^z = N\langle\hat{\sigma}^z\rangle \tag{14}$$

means that S^z is the z component of the pseudospin $\vec{S}$ of the whole H-bonded chain. The module of $\vec{S}$ is equal to

$$S = N\sqrt{\langle\hat{\sigma}^x\rangle^2 + \langle\hat{\sigma}^y\rangle^2 + \langle\hat{\sigma}^z\rangle^2} \tag{15}$$

To know the dynamics of the pseudospin $\vec{S}$ we need to know the mean field $\langle\vec{H}_{\text{tot}}\rangle$ as it follows from Eq. (2) the Hamiltonian of the pseudospin system can be present [9] as a product $\vec{H}_{\text{tot}}\vec{S}$ where the field 'vector' $\vec{H}_{\text{tot}}$ has following components:

$$\vec{H}_{\text{tot}} = \left\{ -\left(\hbar\Omega + \tfrac{1}{2}\sum_{jj'} B_{jj'}\langle S^x\rangle\right),\ 0,\ -\tfrac{1}{2}\sum_{jj'} J_{jj'}\langle S^z\rangle \right\} \tag{16}$$

The first term of the x component of the 'vector' $\vec{H}_{\text{tot}}$ in Eq. (16), i.e. Ω, does not depend on $\vec{S}$. This term can be considered as a transversal 'magnetic' field H applied to the chain. All other nonlinear dynamics, that is the terms dependent on $\vec{S}$ one can simulate by the term $K\sin^2\theta$ where the anisotropic constant $K < 0$. This type of model is the most simple but it enables investigation of the nature of macroscopic tunneling. With regard for these circumstances we can put the energy of anisotropy in the form

$$E(\theta,\phi) \equiv \mathcal{H} = \langle\vec{H}_{\text{tot}}\rangle\vec{S} = K\sin^2\theta - HS\sin\theta\cos\phi + \frac{H^2S^2}{4K} \tag{17}$$

The first term on the right hand side of Eq. (17) corresponds to the z component of the field 'vector' Eq. (16) (we believe that $J_{jj'} > 0$), the second term corresponds to the x component of the vector Eq. (16) (we keep only $\hbar\Omega$ because we assume that $\hbar\Omega \gg \sum_{jj'} B_{jj'}\langle S^x\rangle/2$) and the last term in Eq. (17) has been introduced for convenience (see below). Notice that the energy Eq. (17) has the form wholly similar to that proposed in Refs. [13,14]. To input the angle θ_0 by the formula

$$\sin\theta_0 = \frac{HS}{2K} = \frac{\hbar\Omega}{2\tilde{J}} \tag{18}$$

where

$$\tilde{J} = -K/S \tag{19}$$

one can rewrite the energy Eq. (17) as

$$E(\theta,\phi) = K(\sin\theta - \sin\theta_0)^2 + 2K\sin\theta\sin\theta_0(1-\cos\phi) \tag{20}$$

It will readily be seen that the energy Eq. (20) has two minima: $E = 0$ at $\phi = 0$, $\theta = \theta_0$ and $E = 0$ at $\phi = 0$, $\theta = \pi - \theta_0$. Tunneling from the minimum with coordinates $\{\theta = \theta_0, \phi = 0\}$ to the minimum with coordinates $\{\theta = \pi - \theta_0, \phi = 0\}$ means the substitution $S^z \rightarrow -S^z$ (Fig. 2), i.e. the repolarization of H-bonded chain.

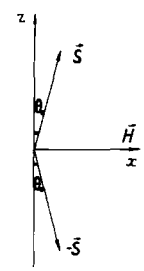

Fig. 2. The two possible orientations of the pseudospin ($\vec{S}$), which characterized the polarization vector of the H-bonded chain.

By analogy with Eq. (7), we can introduce the following action for the H-bonded chain:

$$I = \int \mathrm{d}t[\hbar S\dot{\phi}\cos\theta - E(\theta,\phi)] \tag{21}$$

Then instead of Eqs. (10) and (11) one has

$$\dot{\theta} = H\sin\phi \equiv \hbar\Omega\sin\phi \tag{22}$$

$$\hbar\dot{\phi} = \Omega\cot\theta\cos\phi - 2\frac{\tilde{J}}{\hbar}\cos\theta \tag{23}$$

As the tunneling occurs along the trajectory with $E = 0$, we find (from the condition $E = 0$)

$$\cos\phi = \frac{\sin^2\theta + \sin^2\theta_0}{2\sin\theta\sin\theta_0} \tag{24}$$

Now from (24):

$$\sin^2\phi = -\frac{(\sin^2\theta - \sin^2\theta_0)^2}{4\sin^2\theta\sin^2\theta_0} \tag{25}$$

that is with the tunneling through the barrier $\sin\phi$ is pure imaginary. Substituting $\sin\phi$ from Eq. (25) into Eq. (21) and passing on to imaginary time one has

$$\dot{\theta} = i\frac{\mathrm{d}\theta}{\mathrm{d}\tau};\ i\frac{\mathrm{d}\theta}{\mathrm{d}\tau} = i\Omega\frac{\sin^2\theta - \sin^2\theta_0}{2\sin\theta\sin\theta_0} \tag{26}$$

(hereinafter the dot over a symbol defines the derivative with respect to t). The solution of Eq. (26) is

$$\cos\theta = -\cos\theta_0\tanh(\omega_b\tau) \tag{27}$$

where

$$\omega_b = \tfrac{1}{2}\Omega\cot\theta_0 \tag{28}$$

It seen from Eq. (27) that $\theta = \theta_0$ at $\tau \longrightarrow -\infty$ and $\theta = \tau - \theta_0$ at $\tau \longrightarrow \infty$, i.e. the extremal trajectory connects both minima.

To substitute $\cos\phi$ from Eq. (24) into Eq. (23) one gains

$$\dot{\phi} = \frac{\Omega}{2}\frac{\sin^2\theta_0 - \sin^2\theta}{\sin^2\theta_0\sin^2\theta}\cos\theta \tag{29}$$

Determining from Eq. (26) $\mathrm{d}\tau$ by $\mathrm{d}\theta$ with regard for Eq. (29) one obtains

$$\dot{\phi}\mathrm{d}\tau = -\frac{\cos\theta}{\sin\theta}\mathrm{d}\theta \tag{30}$$

Now we can calculate the action along the imaginary (i.e. subbarrier) trajectory:

$$iI = i\int \mathrm{d}t[\hbar S\dot{\phi}\cos\theta - E] = \hbar\int_{-\infty}^{\infty}\mathrm{d}\tau\dot{\phi}\cos\theta$$

$$= -\hbar S\int_{\theta_0}^{\pi-\theta_0}\mathrm{d}\theta\frac{\cos^2\theta}{\sin\theta} = -2\hbar S\int_{\theta_0}^{\pi/2}\frac{\cos^2\theta}{\sin\theta} \tag{31}$$

that is

$$iI = -\hbar S\left\{-\cos\theta_0 + \frac{1}{2}\ln\left(\frac{1+\cos\theta_0}{1-\cos\theta_0}\right)\right\} \tag{32}$$

The solution of Eq. (32) gives the tunneling rate Eq. (12) of polarization $\vec{P}$ in an H-bonded chain. Simple expressions are obtained in two limiting cases: 1) $\theta \longrightarrow 0$ and 2) $\theta \longrightarrow \pi/2$. In the first case $\sin\theta_0 \approx \theta_0 = \hbar\Omega/2\hat{J} \ll 1$ and from Eqs. (12) and (32) we derive

$$\mathcal{P} \propto \theta_0^{2S} \equiv (\hbar\Omega/2\tilde{J})^{2S} \tag{33}$$

with

$$S \approx S^z = P_z/2d \tag{34}$$

Hence Eq. (33) transforms into

$$\mathcal{P} \propto (\hbar\Omega/2\tilde{J})^{P_z/2d} \tag{35}$$

In the second case, $\theta_0 \longrightarrow \pi/2$, it is convenient to introduce a small parameter

$$\epsilon = 1 - \hbar\Omega/2\tilde{J} \ll 1 \tag{36}$$

Then $\sin\theta_0 = \hbar\Omega/2\tilde{J}$ and $\cos\theta_0 \approx \sqrt{2\epsilon}$; putting these values into Eqs. (12) and (32) we derive

$$\mathcal{P} \propto \exp\left\{-\tfrac{2}{3}(2\epsilon)^{3/2}S\right\} = \exp\left\{-\tfrac{2^{5/2}}{3}(1-\hbar\Omega/2\tilde{J})^{3/2}S\right\} \tag{37}$$

4. Discussion

Experimental estimation of the tunneling rate of H-bonded chain polarization has been achieved by Zundel and co-workers [5,6,19,20]. In line with their data $\mathcal{P}_{\text{experim.}} > 10^{12}$ Hz. Of the parameters contained in the expression for $\mathcal{P}$ the value $P_z \sim Nd$, where the dipole moment d of H-bond is known [21] and the quantity N of H-bonds in the chain one may estimate in principle.

We can recognize from Eqs. (35) and (37) that the tunneling rate depends very significantly on the values of polarization P_z and total pseudospin S. For a

short H-bonded chain these parameters are not very large. Consequently the value of the tunneling rate $\mathcal{P}$ (Eqs. (35) or (37)) is not very small and in this case it enables spontaneous repolarization. Thus the Bjerrum defects (see, e.g., Ref. [22]) are not typical in a short chain because it can restore itself. Elsewhere [7] we have considered spontaneous fluctuations of the short chain in bacteriorhodopsin as original polarized optical phonons; utilizing these specific phonons made it possible to study the motion of protons in the outlet channel of the protein molecule.

The increase of P_z in Eq. (35) and S in Eq. (37) leads to a sharp decrease of tunneling rate $\mathcal{P}$. As is seen from Eqs. (13), (14) and (15) P_z and S are proportional to the quantity N of H-bonds in the chain. So the longer the H-bonded chain, the smaller the value of $\mathcal{P}$. That is why for the long chain $\mathcal{P}$ is so small that macroscopic tunneling of polarization must be suppressed. For instance, it should be realized in the $LiN_2H_5SO_4$ crystal which includes very long H-bonded chains [23]. This hard H-bonded chain was used by us [22] as a basis for the construction of small protonic polaron conductivity along the chain.

With the variation of length of the H-bonded chain the interaction between the chain and its surrounding can be changed. The anisotropy can influence on the value of parameters Ω and $2\tilde{J}$ which are included in Eqs. (35) and (37) for $\mathcal{P}$.

Notice that the microscopic theory of one-dimensional proton sublattice vibrations which interact with vibrations of the frame has been studied by Davydov and co-workers [24,25]. For these two sublattices they have suggested the interaction Hamiltonian and obtained the effect of repolarization of H-bonds in a soliton model. That is, in their theory the chain repolarization occurs classically, i.e. protons cross over the barriers. They assumed that the rate of repolarization was a constant but its value was not defined. However, in the model proposed in Refs. [24,25] one can pass on to the second quantization and to the pseudospin formalism. Then in the mean field approximation for a finite H-bonded chain one may derive an explicit form of the constant K contained in our theory. Notwithstanding our approach is essentially wider than the concept described in Refs. [24,25], because our theory admits the existence of other microscopic mechanisms which can influence on the behavior of protons.

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