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Quantum-mechanical descriptions of proton transfer in biosystems containing hydrogen-bonded chains

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A mechanism of proton transfer along the proton channel of (F_0) ATP-synthetase of a membrane is suggested. In the small polaron model the charged fault (an excess of protons or a proton hole) transfer is considered in a longitudinal electric field along an assumed chain which is formed by hydroxyl groups connected by strong H-bonded chains. A number of kinetic parameters are estimated. The theoretical data are compared with the experimental results.

Introduction

The transmembrane proton conductivity plays an essential role in the functioning of bioenergetic [1,2] and receptor [3] systems. The experimental data on inorganic objects (ice [4], etc.) make it possible to assume that the proton transfer through a membrane is carried out not along a liquid-phase channel, but along a chain of H-bonds formed by the side-groups of amino acids (tyrosine, serine, etc.) of the protein crossing the membrane [5–9]. The possibility of the formation of H-bonded chains in proteins is demonstrated in a light-harvesting bacteriorhodopsin protein model [10]. But the mechanism of proton transfer along such a chain is hypothetical. Characteristic peculiarities of an H-bonded chain with regard to the biomembrane proton channel, i.e., the existence of a strong electric field, the connection between the protons and the chain framework vibrations, the protein dielectric properties, have not been taken into consideration in entirity in any models previously proposed, including those based on the ice crystal proton conductivity mechanisms [6–8] and the small polaron theory.

The mechanism of proton channel functioning suggested in this paper is free from the above-mentioned drawbacks, the theoretical results being in agreement with experiment. (The mathematical calculations of the theory in regard to the proton transfer in crystals $Li(N_2H_5)SO_4$ and $(NH_4)_3H(SO_4)_2$ are dealt with in more detail in another of our papers [12].)

Results

Energy operator for H-bonded chain

We assume that the movement of the ion state – a charge carrier (a proton or a proton hole in the system under consideration (Fig. 1)) – does not change the chain polarization, as a proton revolves round a proton-bonding atom due to the influence of electric field and side-bond asymmetry much more quickly than a charge carrier migrates along the chain [12]. In such a case, the energy operator, the Hamiltonian for the H-bonded chain (consider it formed by an O-H group) containing the charge carriers introduced by the electric field at the ends of the chain from water regions, can be written as:

$$\hat{H} = \hat{H}_0 + \hat{H}_1 + \hat{H}_2 + \hat{H}_E \qquad (1)$$

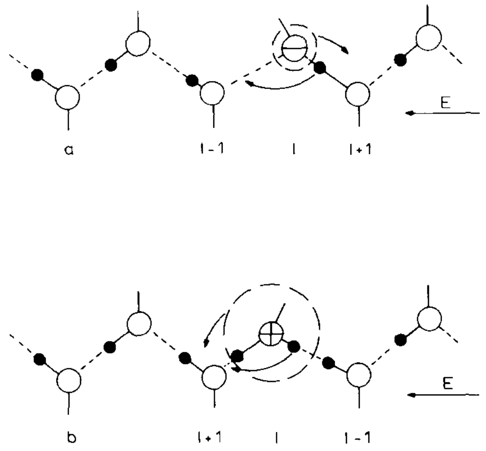

Fig. 1. (a) Ion state (−) moves to the right; it corresponds to the proton movement in the chain to the left; (b) ion state (+) moves to the left; it corresponds to the proton movement in the chain to the left, too. Symbols: ○, atom O; ●, proton; ▬, covalent bond; ···, H-bond.

Here $\hat{H}_0 + \hat{H}_1$ is the known polaron Hamiltonian [13] containing (i) $\hat{H}_0$, the energy operator of the charged fault, of the polarizational optical phonons (in this case we imply the proton vibrations on the H-bonds and the defect interactions, i.e., the charge carrier interactions with these optical phonons) and (ii) $\hat{H}_1 = \Sigma_l J \hat{a}^+_{l+1} \hat{a}_l$ is a tunnel Hamiltonian responsible for the charge carriers hopping among the nearest-neighbour sites; it contains the nearest-neighbour site carrier wave functions overlapping integral J (it is reasonable to suppose that $J \ll k_B T$ ($T \approx 300$ K) in view of the relatively large mass of a proton in comparison with that of an electron); the operator $\hat{H}_E$ takes into account the influence of the electric field on the charge carrier:

$$\hat{H}_E = -eE \sum_l R_l \hat{a}_l^+ \hat{a}_l \tag{2}$$

where $\hat{a}_l^+(\hat{a}_l)$ is the Fermi operator of charge carrier creation (annihilation) in the lth site, and $R_l = lg$ (g is the chain constant, i.e., the distance between the nearest-neighbour sites).

The term introduced in Eqn. 2 takes into account the interaction of the charged fault with acoustic phonons. This term is essential, as a proton hole is correct (Fig. 1a) and excess protons are strongly connected to a site by the covalent bonds (Fig. 1b). $\hat{H}_2$ appears as:

$$\hat{H}_2 = \sum_k \hbar \omega_{\mathrm{ac}}(k)\left(\hat{B}_k^+ \hat{B}_k + \tfrac{1}{2}\right) + \hbar \chi n \sum_l \sum_{q,k} \left[u_l(q) \hat{b}_q^+ + u_l^*(q) \hat{b}_q\right] \times \left[v_l(k) \hat{B}_k^+ + v_l^*(k) \hat{B}_k\right] \tag{3}$$

In Eqn. 3 $\hat{B}_k^+(\hat{B}_k)$ and $\hat{b}_q^+(\hat{b}_q)$ are the Bose operators of the creation (annihilation) of the acoustic and optical phonons with k and q momenta; $\omega_{\mathrm{ac}}(k)$ is the acoustic phonon frequency; $v_l(k)$ is the nondimensional acoustic vibration amplitude; χ is the acoustic and optical phonon interaction constant (in s^{-1}); n is the carrier concentration. The first term in Eqn. 3 corresponds to the sum of potential and kinetic energy of the chain sites' proper (discrete) vibrations, and the second describes the influence of the displaced protons (nondimensional value, $u_l(q)$, of the $(l-1)$th and $(l+1)$th sites) on the ion located in the lth site which has induced these displacements. The interaction results in the attraction of the ion itself to the $(l+1)$th site proton, Fig. 1).

The Hamiltonian (Eqn. 1) is diagonalized on the $\hat{b}_q$, $\hat{B}_k$ operators by the Bogolyubov-Tyablikov canonical transformation [14], which reflects the discrete and optical phonon spectral reorganization due to phonon interaction ($\omega_{\mathrm{ac}}(q)$ and $\omega_{\mathrm{opt}}(q) \rightarrow \tilde{\omega}_{\mathrm{ac}}(q)$ and $\tilde{\omega}_{\mathrm{opt}}(q)$. In this case, in the New Hamiltonian, the cross-members of the type $\hat{b}_q \hat{B}_k$ are lacking; it enables us to consider the problem from the point of view of the small polaron theory, and inasfar as the new Hamiltonian contains not only the polarizational optical phonons but also the acoustic ones (they become polarizational too), the operator should be named a polaron-condenson Hamiltonian.

Proton current calculation

At the temperatures of $T \approx 300$ K characteristic for biological systems, the hopping conductivity mechanism is the most significant one in the case of the samll polaron when phonons serve as the activating system [13]. While calculating the H-bonded chain proton current density, j, in this mechanism we apply the method based on the density matrix usage suggested in Ref. 15 for the other types of system. Insofar as the value J is assumed to satisfy the inequality, $J \ll k_BT$, reflecting the fact that a proton moving along the chain hops only to the nearest-neighbour sites, then according to Ref. 15, with an accuracy to the members J^2 (see also Ref. 12) ($\beta \equiv 1/k_BT$):

$$j = \frac{E}{\mathrm{Tr}\exp[-\beta(\tilde{H} - \hat{H}_E)]}\int_0^\infty \mathrm{d}\tau \int_0^\beta \mathrm{d}\lambda\, \mathrm{Tr}$$

$$\times\Big\{\exp[-\beta(\tilde{H} - \hat{H}_E)]\exp[\lambda(\tilde{H} - \hat{H}_E)]\,\hat{j}\Big(-i\frac{\tau}{\hbar}\Big)$$

$$\times \exp[-\lambda(\tilde{H} - \hat{H}_E)]\,\hat{j}\Big\}$$

$$\hat{j}\Big(-i\frac{\tau}{\hbar}\Big) = \exp\Big[-i\frac{\tau}{\hbar}\Big]\,\hat{j}\exp\Big[i\frac{\tau}{\hbar}\tilde{H}\Big]$$

$$\hat{j} = \frac{e}{i\hbar}\sum_l Jg\hat{a}^+_{l+1}\hat{a}_l \tag{4}$$

Here the integration over the parameter λ between 0 and the value β^{-1} is due to the perturbation theory application, and the integration over time τ between 0 and ∞ defines the macroscopic current density according to the standard procedure.

After a quantum-mechanical termal averaging on the Fermi-operators with an accuracy to the linear carrier concentration terms in Eqn. 4 and then averaging on the phonon subsystem and calculating the integrals over τ and λ, we obtain:

$$j = 2^{3/2}\pi^{1/2}egnJ^2\hbar^{-2}\exp(-\beta E_a)$$

$$\times\left[\sum_{\nu=1}^{2}\sum_q |\Delta^{(\nu)}(q)|^2\tilde{\omega}_\nu^2(q)\,\mathrm{cosech}\big(\tfrac{1}{2}\beta\hbar\tilde{\omega}_\nu(q)\big)\right]^{-1/2}$$

$$\times\sinh\big(\tfrac{1}{2}\beta eEg\big) \tag{5}$$

where the polaron-condenson hopping activation energy is:

$$E_a = \beta^{-1}\sum_{\nu=1}^{2}\sum_q |\Delta^{(\nu)}(q)|^2\tanh\big(\tfrac{1}{4}\beta\hbar\tilde{\omega}_\nu(q)\big) \tag{6}$$

and $|\Delta^{(\nu)}(q)|$ is the polaron-condenson and phonon coupling function; it includes the Hamiltonian $\tilde{H}$ parameters.

If we assume that the membrane is really pierced by the proteins with H-bonded chains and not by water pores for protons, then it is a dielectric in view of the lack of free charge carriers in the system. But the water regions surrounding the membrane are conductors and contain unbonded protons which are assumed to be injected into the membrane by a protonmotive force created by the transmembrane potential difference and/or by the transmembrane proton concentration difference. The larger the value of the field, E (or of its equivalent), and the carrier concentration in the water region on the injection side, the larger should be the carrier's average concentration, n, all over the system, accounting for one chain (the number of carriers in different channels is unequal, it changes from zero to one or several units).

This is a case of the space-charge-limited injectional current. To calculate the density of the current mentioned, we proceed from the system of the equation [16]:

$$j = en\mu(E)E, \quad \frac{\mathrm{d}E}{\mathrm{d}x} = \frac{en}{\varepsilon_0\varepsilon} \tag{7}$$

Here $\mu(E)$ is the carrier's mobility (it is derived from the right-hand part of Eqn. 5, divided by enE); ε, ε_0 are the dielectric constants of the chain and free space, respectively. The dispension (i.e., the dependence of $\tilde{\omega}_\nu$ on q) being ignored, the solution of the system of Eqns. 7 appears as (in A/m^2):

$$j = \frac{2^{5/2}\pi^{1/2}\varepsilon_0\varepsilon J^2}{\hbar^2 e\beta L}\exp(-\beta E_a)$$

$$\times\left[\sum_{\nu=1}^{2}|\Delta^{(\nu)}|^2\tilde{\omega}_\nu^2\,\mathrm{cosech}\big(\tfrac{1}{2}\beta\hbar\tilde{\omega}_\nu\big)\right]^{-1/2}\left[\cosh\frac{\beta egV}{2L} - 1\right] \tag{8}$$

where $V = E/L$ is the difference in potentials at the chain ends. Eqn. 8 is true with $E \lesssim 10^8\ \mathrm{V\cdot m^{-1}}$. The proton current expression $i = j\pi R^2_{\mathrm{OH}}$ can be easily derived from Eqn. 8 where R_{OH} is an effective section of the proton channel; $R_{\mathrm{OH}} \approx 0.1$ nm is the characteristic dimension of the OH group.

Discussion

Quantitative estimation of theory parameters

The values in Eqn. 8 are known [6,7] to be

$\varepsilon = 10$; $g = 0.25$–0.28 nm; the chain length, $L =$ 5–6 nm; the potential difference, $V = 0.1$–0.3 V. The values of the renormalized energies of optical ($\hbar\tilde{\omega}_1$) and acoustic ($\hbar\tilde{\omega}_2$) phonons and of the coupling functions$|\Delta^{(\nu)}|$ depend on a member of parameters and can be estimated if we set (i) the characteristic optical and acoustic vibration frequencies $\omega_{\mathrm{opt}} \lesssim 2\pi \cdot (2\text{–}6) \cdot 10^{12}$ s^{-1} [17], $\omega_{\mathrm{ac}} \approx 2\pi \cdot (1\text{–}10) \cdot 10^{10}$ s^{-1} (the frequencies (ω_{ac}) of the acoustic vibrations of the large-molecular particles are derived from half-quantitative theoretical estimations; they are in agreement with the estimations in Refs. 18,19); (ii) coupling constants:

$$S_{\mathrm{T},\nu} = \tfrac{1}{2}|\Delta^{(\nu)}|^2 \cosh\left(\tfrac{1}{2}\beta\hbar\tilde{\omega}_\nu\right) \tag{9}$$

(coupling constants of an ion with optical ($\nu = 1$) and acoustic ($\nu = 2$) vibrations, respectively), satisfying the conditions $S_{\mathrm{T},1}, S_{\mathrm{T},2} \gg 1$; at room temperature they are considered to be equal to 10–20 (compare with Ref. 13). The value J is the most uncertain in Eqn. 8; it is known to be $J \gg \beta^{-1}$. But comparison of the current i theoretical values with the experimental data on the conductivity of the proteins containing proton channels enables us to estimate the value J.

Let us compare the theoretical and experimental values of the proton current. In Ref. 20, the experimental data on the ATP-synthetase proton channel conductivity have been obtained from bacterium PS 3 in the case in which the electrochemical potential difference on the sides of the membrane is $V = 0.22$ V, the conductivity value depending on the pH of the water volumes has been obtained as $0.5 \cdot 10^{-18}$–$1.6 \cdot 10^{-16}$ $\Omega^{-1} \cdot \mathrm{m}^{-1}$ and, therefore, $i_{\mathrm{exp}} = 9.5 \cdot 10^{-18}$–$3.5 \cdot 10^{-17}$ A. Assuming that $i = i_{\mathrm{exp}}$ we obtain:

$$J = (0.4\text{–}1) \cdot 10^{-2}\beta^{-1} \tag{10}$$

This value is in agreement with the assumption that $J \ll \beta^{-1}$, adopted in our theory. The same values of the parameter J are obtained by the comparison of the expression for i with the experimental data on the chloroplast factor F$_0$ proton conductivity [21].

Estimation of polaron lifetime in a site

It should be noted that H-bonded chain proton current value dependent on the external electric field is restricted by the rate of injection and by the ion-state lifetime, τ_0, in the site.

Let us estimate the lifetime,' τ_0, of the ion state in the site. This value is connected with the probability of the polaron's hopping (in the time unit) between the nearest-neighbour sites in the following correlation:

$$\frac{1}{\tau_0} = W \tag{11}$$

Within the limit of the small overlapping integral resonance value. W is derived from the expression [13,22]:

$$W = \frac{\omega}{2\pi} \mathrm{e}^{-\beta E_{\mathrm{a}}} \eta_2 f(t_0) \tag{12}$$

where:

$$\eta_2 = \frac{J^2}{\hbar\omega\left(E_{\mathrm{a}}\beta^{-1}\right)^{1/2}}, \quad f(t_0) = \pi^{3/2} \tag{13}$$

ω is here the mean frequency of phonons.

In our case $E_{\mathrm{a}} \simeq (4\text{–}5)\beta^{-1}$ ($S_{\mathrm{T},1} = 15$–20), $J \simeq (0.7\text{–}0.4) \cdot 10^{-2}\beta^{-1}$, $T \simeq 300$ K. Substituting these data into Eqns. 11 and 12, we obtain $W \approx (1\text{–}2) \cdot 10^6$ s^{-1} and according to Eqn. 9, the estimation of the polaron lifetime in a located state $\tau_0 \approx (0.5\text{–}1) \cdot 10^{-6}$ s.

The lifetime of the charge transfer along the chain containing 20 sites cannot be less than $2 \cdot 10^{-5}$ s. If the injection is not a rate-limiting step, the maximally possible proton current value, i_{max}, should be 10^{-14} A under the same conditions. But the real maximum proton current value should be less. This is caused by the fact that the movement of protons one after the other is hindered by Coulomb repulsion. The considerable carrier population in a chain is possible only in the case of the extremely high electric field, E. (The influence of the Coulomb correlations and the local inhomogeneity of the electric field, E, on the proton conductivity will be considered in a subsequent publication.)

Proton mobility quantitative estimation

The current density by Eqn. 8 is an average characteristic for one channel of the protein system under investigation, where the proton chennels are supposed to be H-bonded chains.

Eqn. 5 corresponds to one concrete channel current density, j, and in addition, it is connected with the proton mobility $\mu(E)$ by the relation $j = en\mu(E)E$, as has been stated above.

In the case of the adiabatic approach under consideration, the phonon-phonon coupling constant, χ, is small; therefore, the renormalization of the phonon spectra initial frequencies is insignificant and it can be neglected in the first instance. The dispersion being neglected, the coupling function, $|\Delta^{(\nu)}|$, in $\mu(E)$ is expressed by means of coupling constants (Eqn. 9). Then the mobility expression can be written as:

$$\mu(E,T) = \frac{2\sqrt{\pi}\,gJ^2}{\hbar^2\omega_{\mathrm{opt}}}\left[S_{\mathrm{T,1}}\,\mathrm{sech}\left(\tfrac{1}{2}\beta\hbar\omega_{\mathrm{opt}}\right)\right]^{-1/2}$$

$$\times\exp\left[-2S_{\mathrm{T,1}}\left(1-\mathrm{sech}\left(\tfrac{1}{2}\beta\hbar\omega_{\mathrm{opt}}\right)\right)\right]\frac{1}{E}\sinh\left(\tfrac{1}{2}\beta eEg\right) \quad (14)$$

The acoustic phonon conditions are omitted here, as their contribution in $\mu(E)$ is small. But the fact of strong coupling between the charge carriers in an H-bonded chain and its framework vibrations is of primary importance by itself. It enables us to perceive the influence of an external impact (of a hypersound in particular, which plays a significant role in cell life [18]) upon the proton conductivity of a biosystem if the latter contains H-bonded chains. (This question will be considered in subsequent publications.)

Eqn. 14 is available within the room temperature range and it can be used experimentally. The values g and ω_{opt} in Eqn. 14 are known (see above). In the polaron theory the coupling constant is $S_{\mathrm{T,1}} = 10$–20 ($T \simeq 300$ K); as has been stated above, the resonance integral $J \ll \beta^{-1}$ and its value is apparently in good agreement with the estimate [10]. The electric field $E = V/L$, where V is a transmembrane potential. In particular, with $g = 0.28$ nm, $\omega_{\mathrm{opt}} = 2\pi \cdot 6 \cdot 10^{12}$ s^{-1}, $T = 300$ K, $S_{\mathrm{T,1}} = 15$, $J = 10^{-2}\ k_{\mathrm{B}}T$ and $E = 10^7$ V $\cdot$ m^{-1} for the mobility we obtain $\mu \simeq 10^{-6}$ cm$^2 \cdot$ V$^{-1} \cdot$ s^{-1}.

The dependence of mobility Eqn. 14 on temperature is discussed in the Appendix.

Conclusion

The theory developed is applicable to various biological systems containing H-bonded chains in a longitudinal electric field irrespective of the mechanism of the proton injection into the system. In particular, the theoretical estimations of proton current are in agreement with the value i_{exp} in the $\mathrm{F_0}$ and $\mathrm{F_0F_1}$ factors of bacterium PS 3, in which protons are injected by the transmembrane potential and the ATP chemical energy, respectively ($3.5 \cdot 10^{-17}$ A for $\mathrm{F_0}$ [21] and $2.8 \cdot 10^{-17}$ A for $\mathrm{F_0F_1}$ [23] at ΔpH = 2, and with the value for bacteriorhodopsin where injection is caused by the proton energy (10^{-8}–10^{-6} A $\cdot$ cm^{-2} [24]).

The theory predicts the maximum (10^{-14} A) velocity value of a proton moving along a channel constructed as an H-bonded chain. It predicts the nonlinear behavior of the proton mobility (Eqn. 14) at large values of the field, E. The theory also gives a complicated dependence of mobility on temperature. Thus, the theory advances directions for the experimental differentiation of the a priori assumed proton-transfer mechanisms in the biosystems.

Appendix

An ice model is usually applied for the theoretical analysis, and to explain their various features it is necessary to assume the availability of H-bonded chains (see Ref. 7). But this approach is inadequate for a number of reasons. Extensive regular H-bonded chains are lacking in ice, and the chains availabel are branched. Proton vibrations in H-bonds strongly interact with those in branches. For this reason, a clearly distinguished longitudinal mode of optical phonons is lacking. The lack of strong proton vibration coherence in a chain gives rise to Bjerrum faults.

H-bonded chain sites in the other solid body systems ($\mathrm{Li(N_2H_5)SO_4}$, some biopolymers and others), unlike those in ice crystals, are formed by OH groups, which are the final links of massive radicals, and the positions of these sites are rather rigidly fixed by chemical bonds. The chain rigidity and, therefore, the relative independence of the vibrations of the hydrogen atom on the H-bond located inside the O–H $\cdots$ O complex from the high-frequency ones inside of -OH groups in crosswise covalent bonds (the frequency relations 10) is the reason for significant differences between the mechanism of proton transfer in these solid body systems and that in ice. Bjerrum faults in such a chain are impossible in that proton coherent vibrations contribute to considerable chain polarization, and this does not allow local reorientation of protons on the sites. The proton vibrations arise from a single optical polarizational mode. Hence it is necessary to construct the proton transfer theory on a small polaron model.

The polaron theory presents nonmonotonous dependence of conductivity on the temperature and predicts two intervals over which the mobility decreases with temperature increase and one interval with reverse dependence (Fig. 2). In the small polaron theory, an approximation $T > T_2$ corresponds to our case where $T_2 = \hbar\omega_{\rm opt}/2k_{\rm B}$ i.e., the hopping mechanism of charge transfer when phonons serve as an activating system. In particular, with $T > T_2$, the experimental dependence $\mu\exp(T)$ for ice can also be presented in terms of the hopping conductivity (compare Fig. 2 with the results of the Ch. VI of Ref. 25, and with Fig. 2 of Ref. 26). But to construct this theory it is necessary to go beyond the scope of a one-dimensional chain model and to take into account additional optical modes. (The application of the low temperature polaron formula in Ref. 4 characterizing band conductivity is incorrect for the description of experimental dependence $\mu\exp(T)$ for ice, as the values of the applied parameters (of the phonon spectrum frequencies) are not suitable for theoretical description over this temperature range. It appears that the consideration of a heavy semiclassical particle such as a proton in terms of band conductivity is physically unreal.)

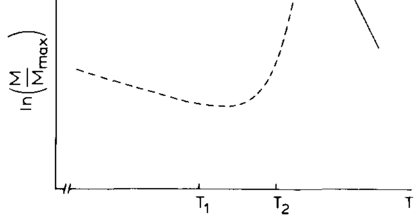

Fig. 2. Temperature dependence of the small polaron mobility (qualitatively), with $T < T_1$ band conductivity can be found: over the range $T_1 < T < T_2$, tunneling conductivity; at $T > T_2$, hopping conductivity (our case is outlined).

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