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Theory of proton transport along a hydrogen bond chain in an external field

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Abstract

The proton transport along a hydrogen bond chain in an external membrane field is described by means of the Pauli master equation with asymmetric rate constants. The analytic solution describing the proton motion is found and its properties are discussed.

1. Introduction

Natural processes are based on energy transformation and utilization. To obtain the energy necessary for their life living systems exploit external sources. There are two basic ways of getting energy in living organisms. Either they have chlorophyll molecules which make use of light energy in photosynthesis or they oxidize the products of cytoplasmic metabolism in the cell organelles in mitochondria. The primary sources of energy, i.e. light or substratum are used to create an electrochemical potential across the internal membranes of the organelles (thylakoid or inner membranes). In the next step the gradient of this potential is used by the enzyme F_1F_0 ATPase (the intrinsic protein) to synthesize ATP [1]. The process of ATP synthesis is based on the proton transport across the inner membrane of the organelle in the direction of the gradient of the membrane field.

There are, however, also opposite processes. For example, F_1F_0 ATPase can use the hydrolysis of ATP

for pumping protons against the membrane gradient. Another example is a membrane protein bacteriorhodopsin (bR) in *Halobacterium halobium* which can trap light energy and use it for proton pumping across the cell membrane against the gradient of the membrane potential. The proton pumping in the latter example exists because of the active site – rhodopsin – which supplies the energy the proton needs to overcome the external field. This protein creates local fields with gradients oriented in the direction of the proton motion. The rhodopsin is located in the middle of the transport path and is responsible for the proton motion from a low potential to a high potential. This transport is realized in three steps. First, the proton is transported from the intracellular space to the active site where it is bound to the active site. This motion is oriented in the direction of the gradient of the first local field. Second, the light absorption induces isomerization of the retinal. This process moves the proton from one position with a low potential to another position with a high potential. Finally, the proton is released from the active site after the isomerization and transported to the extracellular space

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[2] again in the direction of the gradient of the second local field.

It is known that proton transport is realized along hydrogen bond chains [3–5]. These chains existing in proteins are formed by amino acids having residues capable of forming hydrogen bonds (Asp, His, Arg, etc.). If we consider intrinsic proteins and the fact that almost any membrane has an electrochemical potential, the importance of the study of the proton transport along a hydrogen bond chain in such an external field gradient is obvious. The aim of this Letter is to suggest and discuss a simple model for this transport.

2. Model of transport

We assume that the proton can move with a certain probability between the neighbouring sites of a chain. We assume that due to the existence of the external field the rate constants describing the proton motion in the direction and against the direction of the field gradient are different. The proton motion is described by a simple Pauli kinetic equation

$$\frac{dP_m}{dt} = F(P_{m+1} - P_m) - F'(P_m - P_{m-1}). \quad (1)$$

Here, P_m is a probability of finding the proton at the m th site at time t . F or F' is the nearest-neighbour rate constant for the proton motion in the direction of decreasing or increasing m , respectively. We assume that $F, F' > 0$. The difference $F' - F$ determines the asymmetry of the motion. For the sake of simplicity we assume an infinite chain, $m = -\infty, \dots, +\infty$.

To solve Eq. (1) we assume a solution of the form

$$P_m(t) = \exp(\lambda t) h_m, \quad (2)$$

where λ is a constant and h_m is a time-independent coefficient which can be different for different sites. Substituting assumption (2) into (1) we get

$$\lambda h_m = F h_{m+1} - (F + F') h_m + F' h_{m-1}. \quad (3)$$

Eq. (3) is an ordinary difference equation for h_m with constant coefficients. It can be solved assuming

$$h_m = \mu^m, \quad (4)$$

where μ must fulfil the equation

$$\mu^2 - \frac{F + F' + \lambda}{F} \mu + \frac{F'}{F} = 0. \quad (5)$$

This quadratic equation has the solution

$$\mu_{1,2} = \sqrt{\frac{F'}{F} \left[\frac{F + F' + \lambda}{2\sqrt{FF'}} \pm \sqrt{\left(\frac{F + F' + \lambda}{2\sqrt{FF'}} \right)^2 - 1} \right]}. \quad (6)$$

Denoting

$$\frac{F + F' + \lambda}{2\sqrt{FF'}} = \cos(\vartheta), \quad (7)$$

Eq. (6) can be written in the form

$$\mu_{1,2} = \sqrt{\frac{F'}{F}} \exp(\pm i\vartheta). \quad (8)$$

We see that the solution of Eq. (1) is

$$P_m(t) = \exp(\lambda t) \left(\sqrt{\frac{F'}{F}} \right)^m \exp(\pm im\vartheta), \quad (9)$$

where

$$\lambda = -F - F' + 2\sqrt{FF'} \cos(\vartheta) \quad (10)$$

and $\vartheta \in (-\pi, \pi)$. The general solution of Eq. (1) is

$$P_m(t) = \exp[-(F + F')t] \left(\sqrt{\frac{F'}{F}} \right)^m \times \int_{-\pi}^{\pi} A(\vartheta) \exp[2\sqrt{FF'} \cos(\vartheta)t] \exp(im\vartheta) d\vartheta, \quad (11)$$

where $A(\vartheta)$ is an arbitrary function. We assume for simplicity that the proton is located at $t=0$ at site $m=0$,

$$P_m(0) = \delta_{m0}. \quad (12)$$

It follows from Eq. (12) that $A(\vartheta) = 1/2\pi$. Using the definition of the modified Bessel function $I_m(t)$ [6] the final expression for the probability $P_m(t)$ of finding the proton at time t at site m is

$$P_m(t) = \left(\sqrt{\frac{F'}{F}} \right)^m \exp[-(F + F')t] I_m(2t\sqrt{FF'}). \quad (13)$$

3. Discussion

Using the properties of Bessel functions [6] it can be shown that the probabilities $P_m(t)$ fulfil the normalization condition $\sum_{m=-\infty}^{\infty} P_m(t) = 1$. It is obvious from Eq. (13) that for $F' > F$ and $m > 0$ we get $P_m(t) > P_{-m}(t)$. This means that the proton moves in the direction of increasing m . The motion in the opposite direction has for a large difference $F' - F$ a low probability. The asymmetry of the motion is given by the factor $\sqrt{F'/F}$. At time $t=0$ the proton is at site $m=0$. With increasing time, the probability of finding the proton at neighbouring sites increases (see Fig. 1). At the same time, the proton moves in the direction of increasing m . The delocalization of the proton increases with increasing time and the actual position of the proton becomes less and less determined. In other words, the ‘wave’ or better the ‘probability’ packet describing the proton motion moves in the direction of increasing m and spreads at the same time.

The proton ‘center of mass’ is given by the expression

$$\langle m \rangle = \sum_{m=-\infty}^{\infty} m P_m(t). \quad (14)$$

It follows from Eq. (1) that the proton ‘center of mass’ moves linearly in the direction of increasing m ,

$$\langle m \rangle = (F' - F)t. \quad (15)$$

The speed of this motion equals $F' - F$. The width of the ‘probability packet’ can be characterized by the quantity

$$\langle (m - \langle m \rangle)^2 \rangle = \sum_{m=-\infty}^{\infty} (m - \langle m \rangle)^2 P_m. \quad (16)$$

It follows from these equations that

$$m^2 P_{m-1} = (m-1)^2 P_{m-1} + 2m P_{m-1} - P_{m-1}, \quad (17)$$

$$m^2 P_{m+1} = (m+1)^2 P_{m+1} - 2m P_{m-1} - P_{m-1}, \quad (18)$$

and from Eq. (15) that

$$\langle (m - \langle m \rangle)^2 \rangle = t(F' + F). \quad (19)$$

We see that the width of the ‘packet’ $\sqrt{\langle (m - \langle m \rangle)^2 \rangle}$ increases as the square root of t . It is obvious that $\langle (m - \langle m \rangle)^n \rangle$, $n > 2$ can be calculated analogously.

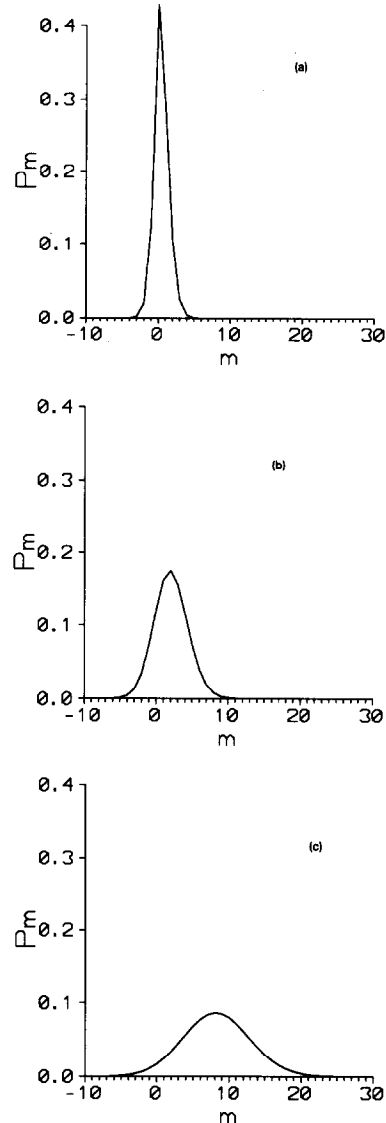


Fig. 1. Probability $P_m(t)$, Eq. (13), describing the proton motion as a function of m . Here, $F=1/3$, $F'=3/4$ and time $t=1$ (a), $t=5$ (b) and $t=20$ (c).

4. Conclusions

Eq. (1) is the transport equation describing the hopping of an arbitrary particle along a chain of discrete sites. In this sense, it can be applied to an arbitrary ion or other particle moving in a homogenous external field. The asymmetry of the field is given by $F' - F$.

We have found the exact analytic solution of this

transport equation in terms of Bessel functions in a similar way as was done in the symmetric case (see, e.g., Ref. [7]). The motion of the 'center of mass' of the proton and the width of the corresponding 'probability packet' have been calculated. The quantities $\langle (m - \langle m \rangle)^n \rangle$ can be calculated analytically also for $n > 2$. In general, the proton moves in the direction for which the nearest-neighbour hopping probability is larger and the corresponding 'probability packet' spreads out at the same time. A detailed description of the form of the 'packet' is given by $\langle (m - \langle m \rangle)^n \rangle$.

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