THE CONTRIBUTION OF SUPERSONIC DAVYDOV SOLITONS TO THE VALUE OF KINETIC COEFFICIENT OF ELECTRON TRANSFER ALONG A BIOPOLYMER CHAIN

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Abstract

In this paper we deal with statistical calculation of kinetic coefficient characterizing the process of electron transfer from the donor molecules to the acceptor molecules in a molecular chain with cubic anharmonicity.

1. INTRODUCTION

The basic idea of Davydov's soliton theory |1| is that vibrational energy becomes self trapped through interaction with low-frequency phonons. In the case of one-dimensional molecular chain, where the lattice have the cubic nonlinear vibrations, the supersonic Davydov solitons appears. In distinction to ref. |2| where the probability of the individual act of the electron transfer by a supersonic soliton is derived, here we deal with the kinetic process by using the method of nonequilibrium statistical mechanics. The mentioned phenomena may play a significant role in biochemical process where electrons are transferred from the donor molecules to the acceptor ones via long biopolymer molecules.

2. THE HAMILTONIAN OF THE SYSTEM

Let us consider a specimen of molecular chain with a large number of identical molecules ($N >> 1$) separated by equilibrium distance R_0.

We emphasize that ν_D donors and ν_A acceptors are statisticaly tied to the chain.

We start from the Hamiltonian of the system as follows

$$H = H^{ex-ph}_{anh} + H\,(A, D) + H_{int} \tag{2.1}$$

The part of Hamiltonian describing the exciton and anharmonic phonon degrees of freedom has the form

$$H^{ex-ph}_{anh} = \Delta \sum_n B^+_n B_n - \frac{L}{2} \sum_n B^+_n (B_{n+1} + B_{n-1}) + \sum_n \Big[\frac{1}{2M} p^2_n + \frac{k}{2} (u_n - u_{n-1})^2 + \frac{k_1}{3} (u_n - u_{n-1})^3 \Big] + \chi \sum_n B^+_n B_n \, (u_{n+1} - u_{n-1}), \tag{2.2}$$

where we introduce the set of denotations;

— B_n and B^+_n are annihilation and creation operators satisfying Bose commutation relations and describing presence and absence of an extraelectron at the site n with corresponding energy Δ;

— L is the resonance interaction between excited nearest-neighbour molecules of the chain;

— P_n denotes the conjugated momentum to the displacement u_n of molecule (n) with the mass M;

$$[\, u_n, p_m \,] = i \hbar \delta_{nm} \tag{2.3}$$

— k and k_1 are the coeficient of elasticity of the chain, and the parameter of anharmonicity, respectively;

— χ is the extra electron-phonon coupling interaction.

The role of donor and acceptor molecules joined statisticaly to the chain is given by the Hamiltonian H(A, D) as follows

$$H(A,D) = \sum_{l=1}^{\nu_A} \epsilon_A A^+_l A_l + \sum_{m=1}^{\nu_D} \epsilon_D D^+_m D_m + \sum_{\sigma, l} \hbar\omega_{\sigma l} a^+_{\sigma l} a_{\sigma l} + \sum_{\gamma, m} \hbar\omega_{\gamma m} d^+_{\gamma m} d_{\gamma m} \tag{2.4}$$

— A_l, A_l^+ and D_m, D_m^+ are, respectively, annihilation and creation Fermi operators of an electron in the acceptor ground state with energy ϵ_A, and in the donor ground state with energy ϵ_D;

— $a_{\sigma l}$ $a^+_{\sigma l}$ and $d_{\gamma m}$ $d^+_{\gamma m}$ are, respectively, annihilation and creation Bose operators of vibronic levels of acceptor (σ) with energy $\hbar\omega_{\sigma l}$, and of donor (γ) with energy $\hbar\omega_{\gamma m}$.

Finally, the interaction between the chain and donor and acceptor molecules has the form

$$H_{int} = \sum_{n,l,\sigma} [V^{(\sigma)}_{nl} B^{+}_{n} A_l a_{\sigma l} + V^{(\sigma)*}_{nl} a_{\sigma l} A^{+}_{l} B^{+}_{n}] + \qquad (2.5)$$

$$+ \sum_{n,m,\gamma} [W^{(\gamma)}_{nm} B^{+}_{n} D_m d_{\gamma m} + W^{(\gamma)*}_{nm} d^{+}_{\gamma m} D_m B^{+}_{n}]$$

— $V^{(\sigma)}_{nl}$ and $W^{(\gamma)}_{nm}$ are the matrix elements of the interaction of an extra electron on the site n with the vibronic level (σ) of the acceptor at site l, and with the vibronic level (γ) of the donor at site m, respectively.

3. THE SUPERSONIC SOLITON SOLUTION

Let us consider now the problem by introducing the normal mode expansion for extra-electron and phonon variables

$$B_n = N^{-1/2} \sum_k B_k \exp(ikR_o n) \qquad (3.1)$$

$$u_n = \sum_k [\frac{\hbar}{2M\omega(k)}]^{1/2} (a^{+}_{-k} + a_k) \exp(ikR_o n) \qquad (3.2.a)$$

$$p_n = i \sum_k [\frac{\hbar M\omega(k)}{2}]^{1/2} (a^{+}_{-k} - a_k) \exp(ikR_o n) \qquad (3.2.b)$$

where we have well-known dispersion relation

$$\omega^2(k) = k \frac{k}{M} \sin^2 (\frac{kR_o}{2}) \qquad (3.2.c)$$

We first transform the Hamiltonian (2.1) by using the expansions (3.1)..(3.2). On the other hand, we introduce the Davydov's Ansatz state vector in the coherent state representation

$$|D_{sol}> = \prod_k |\beta_k>|\alpha_k>, \qquad (3.3)$$

where the eigenfunctions $|\beta_k>$ and $|\alpha_k>$ satisfy the definitions

$$a_k(t) |\alpha_k> = \alpha_k(t) |\alpha_k> \qquad (3.4.a)$$

$$B_k(t) |\beta_k> = \beta_k(t) |\beta_k> \qquad (3.4.b)$$

In order to determine the amplitudes of extra-electron β_k (t) and of anharmonic phonons α_k (t) we form the expectation value of Hamiltonian (2.1) (in the invese lattice) in the state (3.3), see ref. |3|.

$$\mathcal{H}^{ex-ph}_{anh} = \langle D_{sol} \mid H^{ex-ph}_{anh} \mid D_{sol} \rangle =$$

$$= \sum_{k} \mathcal{E}_k |\beta_k|^2 + \sum_{k} \hbar\omega(k) \left(|\alpha_k|^2 + 1/2\right) + N^{-1/2} \sum_{k,\, k'} F(k')\, \beta^*_{k+k'} \beta_k \left(\alpha^*_{-k'} + \alpha_{k'}\right) +$$

$$+ N^{-1/2} \sum_{k_1, k_2, k_3} \phi(k_1, k_2, k_3) \left(\alpha^*_{-k_1} + \alpha_{k_1}\right) \left(\alpha^*_{-k_2} + \alpha_{k_2}\right) \left(\alpha^*_{-k_3} + \alpha_{k_3}\right) \delta(k_1 +$$

$$+ k_2 + k_3), \qquad (3.5)$$

where we introduce the new energy parameters

$$\mathcal{E}_k = \Delta - L \cos kR_o \qquad (3.5.a)$$

$$F(k) = 2\, i\, \chi \left[\frac{\hbar}{2M\omega(k)}\right]^{1/2} \cdot \sin kR_o \qquad (3.5.b)$$

$$\phi(k_1, k_2, k_3) = \frac{k_1}{3} \left(\frac{\hbar}{2M}\right)^{3/2} (2i)^3 N^{-1/2} \exp - \left[\frac{iR_o}{2} (k_1 + k_2 + k_3)\right]$$

$$\sum_{j=1}^{3} \frac{\sin\left(\frac{k_j R_o}{2}\right)}{\sqrt{\omega(k_j)}} \qquad (3.5.c)$$

The parameters α_k (t) and β_k (t) are treated as generalized coordinates with corresponding generalized momenta $i\hbar\alpha_k^*$ (t) and $i\hbar\beta_k^*$ (t). The equations of motion for these generalized dynamical variables are taken to be classical Hamilton equations in which the expectation value of the quantum Hamiltonian (3.5) appears as the Hamilton function.

Going over to the continuum approximation and having in mind that the functions α (ξ) and β (ξ) and their derivatives tend to zero when $|\xi| \to \infty$, after calculation explicitely given in |3| we obtain well-known bel shaped solitonic solution which describe the solitonic localization of extra-electron transported along the chain with velocity v; ($\xi = x - x_o - vt$).

$$\beta(x, t) = G^{1/2} \frac{\exp\left[\, i\, (\bar{k}x - \omega_{sol}\, t)\, \right]}{ch^2 \left[\frac{\tilde{\mu}}{Ro} (x - x_o - vt)\right]} \qquad (3.6)$$

where we have the set of denotations

$$G^{1/2} = \frac{\mu \Gamma(5/2)}{\sqrt{\pi}\,\Gamma(2)} \; ; \quad \Gamma(X) \text{ is gamma function} \tag{3.6.a}$$

$$\mu = [3(s^2 - 1)]^{1/2} ; \; s = \frac{v}{v_o} > 1 ; \; v_o \text{ is the sound velocity} \tag{3.6.b}$$

$$\bar{k} = \frac{\hbar}{LR^2_o} v ; \quad x_o \text{ is the center of soliton} \tag{3.6.c}$$

4. THE STATISTICAL CALCULATION OF THE KINETIC COEFFICIENT FOR THE SUPERSONIC SOLITONS

The statistical formalism for description of the electron transfer along the one-dimensional molecular chain is generally given in our previous paper |4|. Here we use only final result of this theory.

In this sense the kinetic coefficient is given as follows(*)

$$L(\dot{N}_A ; \dot{N}_A) = \int_{-\infty}^{o} dt \; e^{\epsilon t} \int_{o}^{1} d\tau < \dot{N}_A e^{-\hat{M}\tau} \dot{N}_D(t)\, e^{\hat{M}\tau} >_q \tag{4.1}$$

ϵ is small parameter including the time; the corresponding population of particles are

$$N_A = \sum_{l=1}^{\nu_A} A^+_l A_l ; \qquad N_D = \sum_{m=1}^{\nu_D} D^+_m D_m \tag{4.1.a}$$

and N_A, N_D are the corresponding curents. The part of Hamiltonian which play the effective role in statistical tretman is

$$\hat{M} = \tilde{\beta} [\sum_n (\Delta - \mu_B) B^+_n B_n + \sum_r (\epsilon_A - \mu_A) A^+_l A_l + \sum_m (\epsilon_D - \mu_D) D^+_m D_m +$$

$$+ \sum_{\sigma, l} \hbar\omega_{\sigma l} a^+_{\sigma l} a_{\sigma l} + \sum_{\gamma, m} \hbar\tilde{\omega}_{\gamma m} d^+_{\gamma m} d_{\gamma m}]$$

$$\tilde{\beta} = (k_B T)^{-1} \tag{4.1.b}$$

(*) The dot represents the derivation with respect to time

μ_B, μ_A and μ_D are the corresponding chemical potentials.

The subscript $< \ >_q$ denote the correspondent average value with respect quasi reversible matrix

$$\rho_q = e^{-\hat{M}} [Sp e^{-\hat{M}}]^{-1} \tag{4.1.c}$$

The expression (4.1) may be transformed into Onsager's formula by using a boson retarded Green's function. In the next step the correlators of the Green's function may be averaged over the Bose operators B_n (t) taken in the coherent state description (3.4.b) [5].

Finally we obtain

$$L(\dot{N}_A ; \dot{N}_A) = \sum_{\substack{n, n_1 \\ \sigma, l}} \frac{V_{nl}^{(\sigma)} V_{n_1 l}^{(\sigma)*}}{\beta E_\sigma} \int_{-\infty}^{0} dt \exp \left[\epsilon t - \left(\frac{\epsilon_A}{\hbar} + \omega_{\sigma l}\right) t\right] \times$$

$$\times \frac{\theta(-t)}{\hbar^2} \beta_n(0) \beta^*_{n_1}(t) \bar{N} \bar{n} \exp[-\tilde{\beta}(\Delta - \mu_B)], \tag{4.2}$$

where

$$E_\sigma = \Delta - \epsilon_A - \hbar\omega_{\sigma l} - \mu_B + \mu_A \tag{4.2.1}$$

$$\bar{N} = \left\{\exp[\tilde{\beta}(\epsilon_A - \mu_A)] + 1\right\}^{-1} \tag{4.2.2}$$

$$\bar{n} = \left\{\exp(\beta\hbar\omega_{\sigma l}) - 1\right\}^{-1} \tag{4.2.3}$$

$\theta(-t)$ is the step function

Let us now consider the contribution of supersonic Davydov solitons to the value of kinetic coefficient. In this sense we take into account that the functions β_n (0) and $\beta^*_{n_1}$ (t) in the formula (4.2) are the solitonic amplitudes given by the expression (3.6).

Substituting (3.6) into (4.2) we get

$$L(\dot{N}_A ; \dot{N}_A) = \frac{\tilde{\mu}}{\hbar^2 \tilde{\beta}} \sum_{\sigma l} \frac{[V_0^{\sigma}]^2}{E_\sigma} \frac{\bar{N} \bar{n}}{ch^2[\tilde{\mu}(1 - l_0)]} I_{\sigma l}(\Omega); \tag{4.3}$$

$$I_{\sigma l}(\Omega) = \int_{-\infty}^{0} dt \; \frac{e^{\epsilon t}\cos \Omega t}{ch^2\left[\tilde{\mu}\left(l - l_0 - \frac{V}{R_0}t\right)\right]} \exp\left[-\tilde{\beta}(\Delta - \mu_B)\right]; \tag{4.3.a}$$

$$l = \frac{x}{R_0}; \qquad l_0 = \frac{x_0}{R_0}; \qquad \Omega = \omega_{sol} - \omega_{\sigma l} - \frac{\epsilon_A}{\hbar} \tag{4.3.b}$$

The above time integration (4.3.a) will be approximately performed so that we have

$$I_{\sigma l} = \frac{\pi\Omega R_0^2}{2\tilde{\mu}^2 v^2} \; \frac{1}{ch^2\left[\tilde{\mu}(l - l_0)\right] sh\left(\frac{\pi\Omega R_0}{2\tilde{\mu} v}\right)} \left\{1 - 2\, th\left[\tilde{\mu}(l - l_0)\right]\left[\frac{\tilde{\mu} v}{o} - \right.\right.$$

$$\left.\left. - \frac{\pi^2 \Omega R_0}{\tilde{\mu} v} th\left(\frac{\pi\Omega R_0}{2\tilde{\mu} v}\right) - \frac{\pi\Omega^2 R_0^2}{\tilde{\mu}^2 v^2} B_2\right] + th^2\left[\tilde{\mu}(l - l_0)\right]\left(1 - \frac{\Omega^2 R_0^2}{2\tilde{\mu}^2 v^2}\right)\right\} \tag{4.4}$$

(B_2 is the Bernoulli's number)

If we consider the case where the concentration of the donor and acceptor molecules is high enough the sum over to l in formula (4.3) may be replaced by the integration $\sum_l \rightarrow \int_{-\infty}^{+\infty} dz$. Finally, we take into account the fact that the quantities N, n and E_σ have constant values independent of the sites l. After all, the expression (4.3) becomes

$$L(\dot{N}_A; \dot{N}_A) = \frac{\left[V_0^{(\sigma)}\right]^2 \bar{N}\,\bar{n}}{\tilde{\beta} E_\sigma} \cdot \frac{\pi\Omega R_0^2}{\hbar^2\tilde{\mu}^2 v^2} \; \frac{\exp\left[-\beta(\Delta - \mu_B)\right]}{sh\left(\frac{\pi\Omega R_0}{2\tilde{\mu} v}\right)} \tag{4.5}$$

5. CONCLUSIONS AND DISCUSSION

We see that the kinetic coefficient decrease with increasing of solitonic velocity. It is a consequence of the fact that the probability of capture of an extra-electron by a fast soliton is smaller than that of a slow soliton.

The time dependence of average curent of acceptors (reaction rate) may be represented by the accustomed relation

$$< \dot{N}_A > = \text{const} \cdot \exp\left(-\frac{t}{\tau_{rel}}\right) \tag{6.1}$$

where the relaxation time τ_{rel} is related with the kinetic coefficient by simple relation

$$\tau_{rel} \sim [L(\dot{N}_A; \dot{N}_A)]^{-1} \tag{6.2}$$

If we wish to estimate the value of the kinetic coefficient (4.5) we suppose that inequality $\Omega R_o << \mu v$ hold. In this case we easily obtain

$$L(\dot{N}_A; \dot{N}_A) = \frac{2 [V_o^{(\sigma)}]^2 R_o}{\tilde{\beta} E_\sigma \hbar^2 \tilde{\mu}} \bar{N} \bar{n} \frac{1}{v} \exp [-\tilde{\beta}(\Delta - \mu_B)] \tag{6.3}$$

At last, we conclude that the combination of energy parameters containable in E_σ tend to zero then the corresponding kinetic coefficient may increase enough and then mentioned mechanism play significant role in electron transport.

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