THE PERTURBATIVE INFLUENCE OF DONORS AND ACCEPTORS ON THE VALUE OF THE KINETIC COEFFICIENT OF ELECTRON TRANSFER ALONG A ONE-DIMENSIONAL MOLECULAR CHAIN ACHIVED BY DAVYDOV SOLITONS

By
Z. Ivić (a), M. Satarić (b) and R. Žakula (a)
Boris Kidrič Institute of Nuclear Sciences, Institute of Theoretical
Physics, Belgrade (a)
Faculty of Technical Sciences, Institute of Applied Fundamental
Sciences, Novi Sad(1) (b)

Abstract

A perturbation theory is developed for the kinetic coefficient of the electron transfer from donor molecules D_m *to accentor molecules* (A_l) *along a one dimensional molecular chain to which* D_m *and* A_l *are statistically joined. The influence of donors and acceptors to the soliton state is reflexed to the value of the corresponding kinetic coefficient.*

1. INTRODUCTION

In an earlier paper |1| an expression for the kinetic coefficient of the electron transfer from donor molecules (D_m) to the acceptor molecules (A_l) along a one-dimensional molecular chain is derived. The influence of Davydov solitons on the value of the kinetic coefficients was studied by the use of method of non-equlibrium statistical thermodinamics and a coherent state representation.

There has been assumed that the influence of donors and acceptors to the soliton state is small enough so that it can be neglected.

For this new paper, dealing with the irreversibility of the electron transfer, we suppose that donors and acceptors play the role of perturbation of the soliton state. Here we discuss the reflection of these perturbed soliton states on the exchange value of the kinetic coefficient.

The excitonic mechanisam of electron transfer (in the case when electron states in molecular cristal are characterized by the ecxiton like wave function |2|) have been studied paralelly to the solitonic one and the comparison of the values of kinetic coefficients in both cases is given.

(1) V. Vlahovića 3, 21000 Novi Sad, Yugoslavia

2. THE HAMILTONIAN OF THE SYSTEM

The dynamical system consists of the long one-dimensional molecular chain with a large number (N >> 1) identical molecules (molecular groups) with ν_D donors and ν_A acceptors statistically joined to the chain. The Hamiltonian of the dynamical system will be written in the following form:

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

In the above implicit expression we have:

1. The Hamiltonian of an extra electron in the chain of N >> 1 masive molecules (M) including the electron-phonon interaction and pure phonon Hamiltonian

$$H_0^{el-ph} = \Delta \sum_n B_n^+ B_n - \frac{L}{2} \sum_n B_n^+ (B_{n+1} + B_{n-1}) + \chi \sum_n B_n^+ B_n (U_{n+1} - U_{n-1})$$

$$+ \sum_n \frac{p_n^2}{2M} + \frac{K}{2} (U_n - U_{n-1})^2 , \tag{2.2}$$

where B_n^+ and B_n are Bose operators of the presence and absence of the electron at the siten of the molecular chain with the excitation energy Δ, L is the resonant interaction of dipol-dipol type enabling the transfer between neighbouring molecules, u_n and p_n are the diplacemant and conugated momentum of n-th molecule. Parameters k and χ respectively representes the elasticity constant and electron-phonon coupling constant.

2. The Hamiltonian of donors and acceptors

$$H(A,D) = \epsilon_A \sum_{l=1}^{\nu_A} A_l^+ A_l + \sum_{\sigma l} \hbar\omega_{\sigma l} a_{\sigma l}^+ a_{\sigma l} + \epsilon_D \sum_{m=1} D_m^+ D_m +$$

$$+ \sum_{\gamma, m} \hbar\omega_{\gamma m} d_{\gamma m}^+ d_{\gamma m} \tag{2.3}$$

where D_m^+, D_m and A_l^+, A_l are creation and annihilation Fermy operators of an electron in the donor (acceptor) ground state with energy ϵ_D (ϵ_A) · $d_{\gamma m}$ · $d_{\gamma m}$ and $a_{\sigma l}^+$ $a_{\sigma l}$ are Bose creation and annihilation operators of vibronic excitation (levels) of donor (acceptor) with energy $\hbar\omega_{\gamma m}$ $(\hbar\omega_{\sigma l})$.

3. The interaction between the donors (acceptors) and molecular chain:

$$H_{int} = \sum_{\sigma,l,n} (V_{nl}^{(\sigma)} \overset{+}{B}_n A_l a_{\sigma l} + h.c) + \sum_{\gamma,m,n} (W_{mn}^{(\gamma)} B_n \overset{+}{D}_m d_{\gamma m} + h.c)$$

Here $V_n^{(\sigma)}$ ($W_{nm}^{(\gamma)}$) is the matrix element of interaction an electron at the site n with the vibronic excitation $\sigma(\gamma)$ of the acceptor (donor) at the site l(m). These matrix element have their maximum value under the following conditions: $V_{nl}^{(\sigma)} = V_o^{(\sigma)} \delta_{nl}$, $W_{nm}^{(\gamma)} = W_o^{(\gamma)} \delta_{n,m}$.

3. THE GENERAL STATISTICAL METHODOLOGY

Here we briefly repeat the general statistical formalisam for the description of the solitonic mechanisam of the electron transfer along one-dimensional molecular chain which have been developed in our previous papers[1,3,4].

There the Zubarov's non-equlibrium statistical method[5] has been applied and the set of fundamental kinetic equations, that describes the time evolution of particle population, in the transition proces skeched as: $D^- + B \rightleftharpoons D + B^{(-)}$, $B^{(-)} + A \rightleftharpoons B + A^{(-)(*)}$, is derived. An ansatz introduced in ref. 3 yields to the following set of the kinetic equations for the donors and acceptors currents:

$$N(i) = L(N_i, N_j)\, \beta A_{iB} + L\,(N_j, N_i)\, \beta A_{jB} \qquad (i, j = A, D) \tag{3.1}$$

$$\beta = \frac{1}{k_B T}; \qquad A_{iB} = -(\mu_i - \mu_B)$$

Here one can easy recognize $L(N_i, N_j)$ as the Onsager's phenomenological coefficient (kinetic coefficient), and the chemical afinities A i B are corresponding thermodynamical forces[5,6].

Now we assert the simplified finall form of the $L(N_A, N_A)$ without, the detailed calculation which can be found elsewhen[1,3,4].

$$L(N_A,N_A) = \frac{i}{\hbar} \sum_{n,n',l,\sigma} \frac{V_{nl} V_{n'l}^{*(\sigma)}}{E} \int_{-\infty}^{0} e^{\epsilon t} \exp|-i\,(\frac{\epsilon_A}{h} + \omega_{\sigma l})\, t\, |\overline{N}_\rho(A)\, \overline{n}_{\sigma l}(a)$$

$$\ll B_n(0)|B_{n'}(t) \gg + c.\,c, \tag{3.2}$$

where $N_l(A) = [e^{(\epsilon_A - \mu_A)\beta} + 1]^{-1}$ and $n_{\sigma l}(a) = [e^{\hbar\omega_{\sigma l}\beta} - 1]^{-1}$

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

(*) Here A means acceptor, D-donor, B-molecular chain.

The solitonic contribution to the kinetic coefficient can be taken into account using the method that is based upon the fact that the correlators of the Green function, in the pure soliton state, can be expressed using the coherent state representation:

$$\ll B_n(0)\, B^+_{n'}(t) \gg = \frac{\theta(-t)}{ih}\, \beta_n(0)\beta^*_{n'}(t) \exp\left\{-\frac{\Delta-\mu_B}{kT}\right\} \tag{3.3}$$

4. THE INFLUENCE OF DONORS AND ACCEPTORS ON THE VALUES OF THE KINETIC COEFFICIENTS

The influence of donors and acceptors on the value of the kinetic coefficient is the consequence of the soliton shape modification in the vicinity of attached molecules. The description of the dynamical behaviour of the system can be reduced to the perturbed nonlinear Schrödinger equation (NSE). Following the standard Hamilton-equation method for the determination of time evolution of trial state vector[1,2,3] we got:

$$ih\beta(x,t)-(\Delta-L)\beta(x,t)+\frac{R^2_oL}{2}\,\beta_{xx}+G|\beta(x,t)|^2\beta(x,t) = \xi\frac{i}{h}F(x)\beta_o(x,t). \tag{4.1}$$

$0<\xi\ll 1$

Here $\beta_o(x, t)$ is the well knowah soliton solution of the unperturbed NSE[1] and $F(x)$ is

$$F(x) = \sum_{\sigma,l} R_o|V_o^{(\sigma)}|^2\, I_l^{\sigma}\,\delta(x-x_l)+\sum_{\gamma,m} R_o|W_o^{(\gamma)}|^2\, I_m^{\gamma}\delta(x-x_m) \tag{4.2}$$

$$I_i^j = \int_o^{\infty} d\tau\, \frac{\exp\{i|\omega_{sol}-\epsilon_i-\hbar\omega_{ij}|\,\tau\}}{\mathrm{ch}\,\frac{\mu V}{R_o}\,\tau}$$

$i = l, m;\quad j = \sigma, \gamma.$

The method of slowly varying coefficients enables us to derive the small corrections to the soliton envelope and phase. The perturbed NSE can be solved approximatively using the expansion of soliton phase and envelope up to the terms of the first order in ξ : $\theta = \theta_o + \xi\theta_1$ and $\phi = \phi_o + \xi\phi_1$.

The explicit form of this corrections on the unperturbed solution ($\beta_o = \phi_o \exp(i\theta_o)$) was found in ref. 3. A small exchange of the kinetic coefficient arrises as a result of the modification in a soliton shape. An addition term, caused by the shifts in the soliton shape, occures in the expression for the kinetic coefficient (3.3). Here we are interested in a perturbed value of coefficient ($L^{(1)}(N_A, N_A)$) only, because it describes the reflection of perturbed soliton state on the time evolution of the particle currents (3.1). The correction to the kinetic coefficient finally takes the form which is inversely proportional to the soliton velocity.

$$L_{sol}^{(1)}(N_A, N_A) = \sum_{\sigma, l} \frac{\bar{N}_l(A)\bar{n}_\sigma(a)|V_o^{(\sigma)}|^2 R_o}{\hbar^2 v} \times \tag{4.3.a}$$

$$\times \frac{\left[1+2\mathrm{th}\frac{\mu}{R_o}(x_l - x_o)\right] R(o)}{\mathrm{ch}^2 \frac{\mu}{R_o}(X_l - X_o)\,\mathrm{ch}\frac{\pi R_o \Omega_{\sigma l}}{2\mu v}} \exp\left\{-\frac{\Delta - \mu_B}{kT}\right\}$$

$$R(o) = \frac{\mu}{\hbar L}\left[\sum_{\sigma, l} \frac{\mathrm{Im}(I_l^\sigma)|V_o^{(\sigma)}|^2}{f(\tau_l(o))} + \sum_{\gamma, m} \frac{\mathrm{Im}(I_m^\gamma)|W_o^{(\sigma)}|^2}{f(\tau_m(o))}\right] \tag{4.3.b}$$

$$f(\tau_i) = 1 + \frac{35}{2}\mathrm{th}\frac{\mu}{R_o}(x_j - x_o - vt) - 34\mathrm{th}^2\frac{\mu}{R_o}(x_j - x_o - vt) \tag{4.3.c}$$

$i = l, m$

We expect that the kinetic coefficient of the standing soliton is of the special interest because of the inversional proportionality of $L_{sol}^{(1)}(N_A, N_A)$ to the soliton velocity. We have the following expression for the kinetic coefficient in that case:

$$L_{sol}^{(1)}(N_A, N_A) = \mu \sum_{\sigma, l} \frac{W_{sol}^{(\sigma)}\bar{N}_l(A)\bar{n}_{\sigma l}(a)}{\beta(\Delta - \hbar\omega_{sol}(o) - \mu_B + \mu_A)} \times$$

$$\times \frac{1 + \mathrm{th}\frac{\mu}{R_o}(x_l - x_o)}{\mathrm{ch}^2\frac{\mu}{R_o}(x_l - x_o)} R(v = o)\, e^{-\frac{\Delta - \mu_B}{kT}} \tag{4.4.a}$$

with

$$R(v = o) = \frac{\mu}{L}\left\{\sum_{\sigma', l'} \frac{|V_o^{(\sigma)}|^2}{(\omega_{sol}(o) - \frac{\epsilon_A}{\hbar} - \omega_{\sigma' l'}) f(\tau_l)} + \sum_{\gamma, m} \frac{|W_o^{(\gamma)}|^2}{(\omega_{sol}(o) - \frac{\epsilon_D}{\hbar} - \omega_{\gamma m}) f(\tau_m)}\right. \tag{4.4.b}$$

$$W_{sol}^{(\sigma)} = \frac{2\pi}{\hbar^2}|V_o^{(\sigma)}|^2 \delta\left(\omega_{sol} - \frac{\epsilon_A}{\hbar} - \omega_{\sigma l}\right) \tag{4.4.c}$$

The influence of donors and acceptors to the excitonic mechanisam of electron transfer causes the occurance of an extra term in the expression for the excitonic kinetic coefficient

$$L_{ex}^{(1)}(N_A, N_A) = \frac{1}{N} \sum_{k, \sigma, l} \frac{W_{k\sigma l}^{ex}\bar{N}_l(A)\bar{n}_{\sigma l}(a)}{\beta(\Delta - \hbar\omega_k^{(o)} - \mu_B + \mu_A)} \hbar\omega_k^{(1)}, \tag{4.5.a}$$

where

$$W^{ex}_{k\sigma l} = \frac{2\pi}{\hbar^2} | V_o^{(\sigma)}|^2 \, \delta \, (\hbar\omega_k^{(o)} - \epsilon_A - \hbar\omega_{\sigma l} + \hbar\omega_k^{(1)}) \qquad (4.5.b)$$

and $\hbar\omega_k = \hbar\omega_k^{(o)} + \hbar\omega_k^{(1)}$ is the total exciton energy defined through the energy parameters of system[3].

5. DISCUSSION AND CONCLUSIONS

The soliton formed as a local deformation of the molecular chain accompanied by the motion of an extra electron is perturbed by the influence of donors and acceptors attached to the chain. Therefore the shape of the soliton is altered in the vicinity of the attached molecules. We obtained the wave function of the perturbed soliton by the use of the „slow varying coefficients" method. An expression for the kinetic coefficient which comprises the perturbative term was obtained. The perturbed value of the kinetic coefficient $(L^{(1)}_{sol} \; (N_A, N_A))$ has the dependence of perturbing potentials in the form $\dfrac{|V_o^{(j)}|^4}{\mathrm{ch}\, \dfrac{2\mu}{R_o} (x_l - x_o)}$ $(j = \sigma, \gamma)$ so the correction, just as the unperturbed value, have strongly localized caracter. The value of kinetic coefficients decreases with the increasing of the soliton velocity.

In the case when the electron transfer is achieved in terms of the excitonic mechanism we have an increase of the value of perturbed coefficient in the comparison with that of the solitonic one. For the ratio of solitonic and excitonic correction term we have approximatively

$$\frac{N(A)^{sol}}{N(A)^{ex}} \approx \frac{\mu^2 \exp \left(- \dfrac{\Delta - \mu_B}{kT}\right.}{\rho\nu_A |\bar{n}_{\sigma l} \, (a) \, (1 - 2\bar{N}_l \, (A)) + 1 - \bar{N}_l \, (A))|}$$

$$\rho = \frac{\nu_A}{N}$$

The role of the solitonic mechanisam decreases with the increasing of the concentration of acceptors.

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