ELECTROMAGNETIC ABSORPTION BY MOLECULAR SOLITONS

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SUMMARY: The results on the investigation of the electrosoliton interaction with the external electromagnetic field are reported. It is shown that there are present two characteristic maximums in the absorption spectrum, one of which is connected with the dynamical generation of the sound wave in the chain, while the second one is connected with the soliton photodissociation (see also [5,6]).

INTRODUCTION

Many processes in living organisms are connected with the spatial propagation of energy and charges along protein molecules. In the 70-s Davydov proposed the soliton mechanism for energy and electron transport in biological macromolecules [1,2]. Solitons can be formed in soft one-dimensional molecular systems, such as the polypeptide chaines formed by hydrogen bonds along an alpha-helix protein molecule. The periodic potential of peptide dipole momentums in alpha-helix creates the conducting band for an extra electron, which interacts with the chain deformation and forms the so-called electrosoliton [3]. The internal and dynamical properties of electrosolitons can manifest themselves under the soliton interaction with the external electromagnetic field. dissociate at all.dissociate at all.dissociate at all. This problem we consider below. It is worth to mention that the results we obtain can be applied not only to the biological systems, but to various quasi-one-dimensional materials as well, e.g., electroconducting polymers, polydiacetylene and others, in which soliton states can exist.

1 Interaction with the external electromagnetic field

Let us consider only one isolated nondegenerate band of quasiparticle (either electron or intrapeptide vibration) states in a one-dimensional chain. With allowance for the interaction between quasiparticles and lattice vibrations the system is described by Fröhlich-type Hamiltonian

$$H = \sum_k E(k) B_k^+ B_k + \frac{1}{\sqrt{N}} \sum_{k,q} \chi(k,q) B_k^+ B_{k-q} (b_q + b_{-q}^+) + \sum_q \hbar\Omega_q b_q^+ b_q \qquad (1.1)$$

where $E(k)$ is the dispersion law of a qusiparticle band, Ω_q is the frequency of acoustic phonons corresponding to the displacements of peptide groups along hydrogen bond, and $\chi(k,q)$ is the coupling function. In the longwave approximation we can write

$$E(k) = E_0 + \frac{\hbar^2 k^2}{2m^*}, \quad \Omega_q = V_a|q|, \quad V_a = a\sqrt{\frac{w}{M}}, \qquad (1.2)$$

$$\chi(k,q) = \chi(q) = 2i\chi q \sqrt{\frac{\hbar}{2M\Omega_q}}. \qquad (1.3)$$

Here E_0 is the energy of the band bottom, m is quasiparticle effective mass, V_a is the sound velocity in the chain with the lattice constant a, unit cell mass M and elasticity coefficient w, χ is the coupling constant.

The one-particle ground state of Hamiltonian (2.1) corresponds to the soliton-like state and has been described by the wave function (see [2,4]):

$$|\Psi_s(t)> = |\Psi_e(t)> |\Psi_{ph}(t)>, \quad <\Psi_s(t)|\Psi_s(t)> = 1, \tag{1.4}$$

with

$$|\Psi_e(t)> = \sum_k \Psi_k(t) B_k^+ |0>_e, \quad \sum_k |\Psi_k(t)|^2 = 1, \tag{1.5}$$

$$|\Psi_{ph}(t) = e^{S(t)} |0>_{ph}, \quad S(t) = \frac{1}{\sqrt{N}} \sum_q [\beta_q(t) b_q^+ - \beta_q^* b_q]. \tag{1.6}$$

This paper deals with the investigation of the soliton interaction with an alternating electric field of the electromagnetic radiation,

$$\vec{\mathcal{E}}(t) = \frac{1}{2}[\vec{\mathcal{E}} e^{-i\omega t + i\vec{Q}\vec{R}} + c.c.] \tag{1.7}$$

The operator of electron interaction with the field can be written in the form

$$V(t) = -\frac{ie\hbar}{mc} \vec{A}(t)\vec{\nabla} = -\frac{1}{2} \sum_k e^{-i\omega t} \vec{\mathcal{E}}\vec{d}(k) B_k^+ B_k + h.c. \tag{1.8}$$

where e and m are electron charge and mass respectively, c is light velocity and $A(t)$ is vector-potential. In the site representation the interaction operator (1.8) can be written in the form where

$$\vec{d}(k) = \vec{j} \frac{ie\hbar\lambda}{m\omega a} \sin(ka) \approx jk \frac{ie\hbar\lambda}{m\omega}. \tag{1.9}$$

Here $\vec{j}$ is a unit vector along the chain x-axis,

$$\lambda = 2a \int \varphi_e(x + \frac{a}{2}, y, z) \frac{\partial}{\partial x} \varphi_e(x - \frac{a}{2}, y, z)\, dx\, dy\, dz, \tag{1.10}$$

and φ_e is electron Wanier wavefunction. The case of Amid vibration was considered in [5,6] with the choice of the interaction operator in the dipole approximation:

$$V(t) = -\vec{E}(t)\, \vec{D}. \tag{1.11}$$

We assume that at the initial time moment the chain is in a soliton state (1.4). To investigate the influence of an external field on the soliton we shall use the perturbation theory. The wavefunction of the system satisfies the Schrödinger equation

$$i\hbar \frac{\partial |\Psi(t)>}{\partial t} = [H + V(t)] |\Psi(t)>, \tag{1.12}$$

the solution of which, according to the general perturbation theory [7] can be expanded over the complete set of stationary states of the Hamiltonian (1.1):

$$|\Psi(t)> = \sum_n a_n(t) |\Psi_n(t)>, \quad n = s, f \tag{1.13}$$

The perturbation $V(t)$ is assumed to be adiabatically included at the initial time moment $t = -\infty$ when $a_n = \delta_{n,s}$. The coefficients $a_f(t)$ determine the probability of quantum transition from the initial state $|\Psi_s>$ to the final one $|\Psi_f>$ and are expressed via the nondiagonal matrix elements of the perturbation,

$$a_f(t) = \frac{1}{i\hbar} \int_0^t <\Psi_s(t')|V(t')|\Psi_f(t')> dt'. \tag{1.14}$$

The diagonal elements can be taken into account by the renormalization of the amplitudes $a_n(t)$ [5] which does not affect the transition probability and can be included into the wavefunctions provided the following equation is fulfilled

$$< \Psi_s(t)| - i\hbar\frac{\partial}{\partial t} + H + V(t)|\Psi_s(t) > \; = \; 0 \tag{1.15}$$

In linear systems the diagonal elements lead to the energy levels shift, while its influence on the solitonic state is more complicated, as it will be shown below.

2 Diagonal perturbation of the soliton motion

Taking into account in Eq. (1.15) the explicit form of the soliton wavefunction (1.4), we obtain the following equations:

$$i\hbar \; \frac{\partial \Psi_k}{\partial t} \; - \; [\Lambda_1 + E(k) - V_k(t)]\Psi_k \; - \; \frac{1}{N}\sum_q \chi(q)(\beta_q + \beta^*_{-q})\Psi_{k-q} \; = \; 0, \tag{2.1}$$

$$- \; i\hbar \; \frac{\partial \beta_q}{\partial t} \; + \; \hbar\Omega_q\beta_q \; = \; - \; \chi^*(q)\sum_k \; \Psi^*_k\Psi_{s-q}, \tag{2.2}$$

where

$$\Lambda_1 \; = \; \frac{1}{N}\sum_q \left[\hbar\Omega_q|\beta_q|^2 - \frac{1}{2}\left(i\hbar\frac{\partial\beta_q}{\partial t}\beta^*_q + c.c\right)\right], \tag{2.3}$$

$$V_k(t) \; = \; \frac{1}{2}\left[(\vec{\mathcal{E}}\vec{d}_k)e^{-i\omega t} \; + \; c.c.\right] \tag{2.4}$$

Introducing the continuous variable x and functions $\psi(x,t)$ according to the transformation

$$\Psi_k(t) \; = \; \frac{1}{\sqrt{L}}\int_{-L/2}^{L/2} \; \psi(x,t)e^{-ikx}dx, \quad Ł = Na \; \to \; \infty, \tag{2.5}$$

we obtain from Eq.(2.1)

$$i\hbar \; \frac{\partial\psi}{\partial t} \; + \; \frac{\hbar^2}{2m^*}\frac{\partial^2\psi}{\partial x^2} \; - \; [\Lambda + U(x)]\psi \; - \; ig(t)\frac{\partial\psi}{\partial x} \; = \; 0, \tag{2.6}$$

where

$$\Lambda \; = \; E_0 \; + \; \Lambda_1, \tag{2.7}$$

$$g(t) \; = \; \mathcal{E}_l\frac{\hbar\lambda e}{m\omega} \; \sin(\omega t) \tag{2.8}$$

with $\mathcal{E}_l$ being the electric field amplitude projection on the chain axis, and $U(x)$ being the selfconsistent potential created by the lattice deformation:

$$U(x) \; = \; \frac{1}{N}\sum_q \chi(q)(\beta_q + \beta^*_{-q})e^{iqx} \; = \; 2\chi \; \frac{\partial u}{\partial x}. \tag{2.9}$$

Here the function $u(x)$ and its space derivative

$$u(x) \; = \; \frac{1}{N}\sum_q \left(\frac{\hbar}{2M\Omega_q}\right)^{1/2}(\beta_q + \beta^*_{-q})e^{iqx}, \tag{2.10}$$

$$\rho(x,t) \; = \; \frac{\partial u(x,t)}{\partial x} \tag{2.11}$$

describe the meanvalue of molecule displacement and chain deformation, respectively. From eqs.(2.6), (2.2), we get the following system of equations:

$$i\hbar\,\frac{\partial\psi}{\partial t}\;+\;\frac{\hbar^2}{2m^*}\frac{\partial^2\psi}{\partial x^2}\;-\;[\Lambda+2\chi\rho]\psi\;=\;ig(t)\frac{\partial\psi}{\partial x}, \tag{2.12}$$

$$\frac{\partial^2\rho}{\partial t^2}\;-\;v_a^2\,\frac{\partial^2\rho}{\partial x^2}\;=\;\frac{2\chi a v_a^2}{w}\;\frac{\partial^2|\psi(x,t)|^2}{\partial x^2}.$$

In the absence of the perturbation when $g=0$, the system of equations (2.12) admits the soliton-like solution:

$$\rho_s(x,t)\;=\;-\;\frac{2\chi a}{w(1-s^2)}\;|\psi_s(x,t)|^2, \tag{2.13}$$

$$\psi_s(x,t)\;=\;\frac{\kappa\sqrt{1-s^2}}{\sqrt{G}}\;\frac{\exp\{i[k(x-\zeta(t))+\vartheta(t)]\}}{\cosh\kappa[x-\zeta(t)]}, \tag{2.14}$$

where

$$\zeta(t)\;=\;\zeta_0\;+\;\frac{\hbar k}{m^*}t,\quad \vartheta(t)\;=\;\frac{\hbar^2}{2m^*}(k^2+\kappa^2)t, \tag{2.15}$$

$$G\;=\;\frac{4ma\chi^2}{\hbar^2 w},\quad s\;=\;\frac{\hbar k}{m^*V_a}\quad \kappa\;=\frac{G}{2(1-s^2)}. \tag{2.16}$$

To investigate the weak influence of the electromagnetic field on the soliton, we shall use the adiabatic perturbation theory developed in [8,9]. We assume that for the weak perturbation characterized by the small parameter ε, the solution of Eqs. (2.12) is of the form

$$\rho(x,t)\;=\;-\;\frac{2\chi a}{w(1-s^2)}\;|\psi(x,t)|^2\;+\;\varepsilon r_1(x,t), \tag{2.17}$$

$$\psi(x,t)\;=\;\psi_s(x,t)\;+\;\varepsilon f_1(x,t). \tag{2.18}$$

Here $\psi_s(x,t)$ is the soliton state (2.14) with the time- dependent parameters obeying the following equations:

$$\dot\kappa\;=\;\varepsilon Q_1,\quad \dot k\;=\;\varepsilon Q_2,\quad \dot\zeta\;=\;\frac{\hbar k}{m^*}+\varepsilon Q_3,\quad \dot\vartheta\;=\;\frac{\hbar^2}{2m^*}(k^2+\kappa^2)+\varepsilon Q_4, \tag{2.19}$$

where $\dot\phi\;=\;d\phi/dt$.

Substituting the ansatz (2.17) into (2.12), we obtain the nonlinear Schrödinger equation with the perturbation in the right hand side

$$i\hbar\,\frac{\partial\psi}{\partial t}\;+\;\frac{\hbar^2}{2m^*}\frac{\partial^2\psi}{\partial x^2}\;+\frac{\hbar^2 G}{m^*(1-s^2)}|\psi|^2\psi\;=\;\varepsilon\left[ig\frac{\partial\psi}{\partial x}\;+\;2\chi r_1\psi\right]. \tag{2.20}$$

The modulation of the soliton parameters can be found from the condition that the leading secularities are absent in the first order correction. This leads to the following expressions in the 'nonrelativistic' limit when the soliton velocity is far less than that of the sound:

$$Q_1\;=\;0,\quad Q_2\;=\;-\;\frac{2\chi G}{\hbar}\;\int_{-\infty}^{\infty}r_1(x,t)\tanh\left[\kappa(x-\zeta)\right]|\psi_s|^2dx,$$

$$Q_3\;=\;-\;\frac{1}{\hbar}g(t),\quad Q_4\;=\;-\;\frac{2\chi G}{\hbar\kappa}\int_{-\infty}^{\infty}r_1\{1-\kappa(x-\zeta)\tanh[\kappa(x-\zeta)]\}|\psi_s|^2dx. \tag{2.21}$$

The first order correction in the adiabatic approximation obeys the equation

$$\frac{\partial^2 r_1}{\partial t^2}\;-\;V_a^2\frac{\partial^2 r_1}{\partial x^2}\;=\;-\;\frac{2\chi a}{w}\;\ddot\zeta\;\frac{\partial|\psi_s|^2}{\partial x} \tag{2.22}$$

with the initial condition $r_1(t \to -\infty) = 0$, and, hence, reads as

$$r_1 \;=\; -\;\frac{\chi a}{\pi w V_a}\;\int_{-\infty}^{t} dt'\;\ddot{\zeta}(t')\;\int_{-\infty}^{\infty} dq\;\frac{\sin\left[V_a q(t-t')\right]}{q}\int_{-\infty}^{\infty} dx'\;e^{iq(x-x')}\frac{\partial|\psi_s(x',t')|^2}{\partial x'}. \qquad (2.23)$$

According to (2.19), Q_1 determines the modulation of the soliton width, which as it follows from (2.21), is not changed with the electromagnetic field switching:

$$\kappa \;=\; \frac{1}{2}\;G \qquad (2.24)$$

Substituting now (2.23) into equations (2.21), we obtain the equation for the soliton center of mass motion in the presence of the external force

$$m^*\ddot{\zeta}(t)\;+\;\int_0^{\infty}\ddot{\zeta}(t-\tau)K(\tau)\;d\tau\;=\;F_0\cos(\omega t), \qquad (2.25)$$

where

$$F_0\;=\;-\;e\mathcal{E}_l\lambda\frac{m^*}{m}, \qquad (2.26)$$

and the kernel

$$K(\tau)\;=\;-\;\frac{4\chi^2 a\kappa}{\mu V_a^2}\;\frac{d}{d\tau}\;\frac{\kappa V_a\tau\cosh(\kappa V_a\tau)\;-\;\sinh(\kappa V_a\tau)}{\sinh^3(\kappa V_a\tau)} \qquad (2.27)$$

describes the retardation effects in the deformation accompanying the soliton.

The solution of Eq.(2.25) is

$$\ddot{\zeta}(t)\;=\;\frac{F_0}{m_d(\omega)}\;\cos\left[\omega t-\phi(\omega)\right], \qquad (2.28)$$

where the values

$$m_d(\omega)\;=\;\sqrt{[m^*+\mu_1(\omega)]^2\;+\;\mu_2^2(\omega)},\quad \phi\;=\;\arcsin\frac{\mu_2(\omega)}{m_d(\omega)}. \qquad (2.29)$$

can be treated as the dynamical soliton mass and the phase shift of the soliton acceleration relative to the external force, respectively. Here

$$\mu_1(\omega)\;=\;\frac{\pi}{2\kappa V_a}\int_0^{\infty}\frac{x^4\;dx}{\left[x^2-\left(\frac{\pi\omega}{2\kappa V_a}\right)^2\right]\sinh^2 x},$$

$$\mu_2(\omega)\;=\;\frac{4\chi^2 a\kappa}{\pi w V_a^2}\left(\frac{\pi\omega}{2\kappa V_a}\right)^2\;\sinh^{-2}\frac{\pi\omega}{2\kappa V_a}. \qquad (2.30)$$

In the low frequency limit when the inequality is fulfilled

$$\omega\;\ll\;\omega_0\;\equiv\;\frac{2\kappa V_a}{\pi} \qquad (2.31)$$

the phase shift φ tends to zero, and the soliton behaves as the classical Newtonian particle in the slowly oscillating external field with the dynamical mass equal to the free soliton mass,

$$m_d\;\approx\;m^*\;+\;\frac{8m^*\chi^4 a^2}{3\hbar^2 w V_a^2}. \qquad (2.32)$$

At high frequencies of the external field when $\omega\;\gg\;\omega_0$, the phase shift also tends to zero, but now the deformation can not follow comparatively fast electron motion, and the dynamical mass approaches to the mass of the free undressed quasiparticle,

$$m_d\;\approx\;m^*. \qquad (2.33)$$

The deformational system is described by the first-order correction (2.23) which can be rewritten in the form of the two terms

$$r_1 \;=\; -\;\frac{\chi a}{wV_a}\;\int_0^\infty \ddot{\zeta}(t-\tau)\{|\psi_s(\xi_+)|^2 - |\psi_s(\xi_-)|^2\}\;d\tau, \tag{2.34}$$

where

$$\xi_\pm \;= x - \zeta(t) \pm V_a\tau\left(1 \pm \frac{\bar{v}(\tau)}{V_a}\right) \;\approx\; x - \zeta(t) \pm V_a\tau,$$
$$\bar{v}(\tau) \;=\; \frac{\zeta(t) - \zeta(t-\tau)}{\tau}, \quad \frac{\bar{v}(\tau)}{V_a} \;\ll\; 1. \tag{2.35}$$

Equation (2.34) asymptotically describes two sound waves generated by by the oscillating soliton motion and moving in the opposite directions:

$$r_1(x,t) \;=\; -\;\frac{e\mathcal{E}\lambda\chi a\pi\omega}{2m_d w V_a^3\kappa}\;\sinh^{-1}\frac{\pi\omega}{2\kappa V_a} \times \left\{ \begin{array}{c} \cos\left[\omega(t - \frac{x-z}{V_a}) - \phi\right],\; x - z \to \infty, \\ -\;\cos\left[\omega(t + \frac{x-z}{V_a}) - \phi\right],\; x - z \to -\infty \end{array} \right. \tag{2.36}$$

The energy flow absorbed from the electromagnetic field by the sound waves per field oscillation period $T = 2\pi/\omega$ is equal to the following value:

$$\epsilon_1 \;=\; \frac{d\bar{E}}{dt} \;=\; -\;V_a^3\omega^3\;\frac{(e\mathcal{E}\lambda)^2}{2\pi m_d^2(\omega)}\;\left(\frac{\pi\chi a}{2w\kappa V_a^3}\right)^2\sinh^{-2}\frac{\pi\omega}{2\kappa V_a}. \tag{2.37}$$

where the dynamical mass is determined in (2.29). Substituting its asymptotics at low and high frequencies (2.32), (2.33) into (2.37), we find that this flow is proportional to the frequency at low frequencies, and exponentially decreases at high frequencies:

$$\epsilon_1 \;\propto \left\{ \begin{array}{cc} \omega, & \omega \;\ll\; \omega_0, \\ \omega^3\;\exp(-\gamma\omega), & \omega \;\gg\; \omega_0 \end{array} \right. \tag{2.38}$$

with the maximum absolute value at $\omega \;\approx\; \omega_0$ (see (2.31)).

3 Nondiagonal matrix elements

As it was indicated in section 1, the nondiagonal matrix elements of the perturbation (1.14) determine the probability of quantum transition of the system under the influence of the perturbation:

$$P_s \;=\; \frac{2}{\hbar^2}\Re\;\int_{-\infty}^{t} dt' < \psi_s(t)|V^+(t)e^{-i\frac{H}{\hbar}(t-t')}V(t')|\psi_s(t') >, \tag{3.1}$$

and, as it is shown in [5], describes the photodissociation of the bound soliton state of of the electron and chain deformation into the free elevtron state with omitted phonons. The energy absorption which is proportional to the transition probability, is described by the Gaussian function:

$$E \;\propto\; P_s \;=\; \frac{\sqrt{2\pi}}{\hbar B}\;\sum_q |\vec{\mathcal{E}} \times \vec{D}_{sq}|^2\;\exp\left\{-\;\frac{(\omega - \Omega_q)^2}{2B^2}\right\}, \tag{3.2}$$

where

$$\vec{D}_{sq} \;=\; \frac{\vec{j}}{\sqrt{N}}\;\frac{ie\hbar\lambda}{2m_e\omega a}\;\frac{\pi(qa + i\kappa)}{\sqrt{2\kappa}\cosh\frac{\pi q a}{2\kappa}}, \tag{3.3}$$

$$\Omega_q \;=\; \frac{\chi^4}{Jw^2} \;+\; \frac{1}{2}\Delta m V^2 \;+\; \frac{\hbar^2 q^2}{2m^*}, \quad B^2 \;=\; \frac{12.6\chi^2 V_a\kappa^2}{\pi^3\hbar w a}. \tag{3.4}$$

The energy of soliton photodissociation can be determined as the maximal losses of energy which take place at the frequency $\omega \;=\; \Omega_{q=0} \;=\; \chi^4/(Jw^2)$.

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