## DYNAMICAL PROPERTIES OF DAVYDOV SOLITONS

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A brief review is given on the theory of Davydov solitons, some recent advances of the theory and its perspectives for the modern problems of physics and biophysics. In particular, the main properties of solitons and their dynamics in discrete macromolecular systems are analyzed. It is shown that the soliton model explains well some peculiarities of the experimental data on the saturation of charge carriers mobility with the intensity of the applied electric field in some low-dimensional conducting polymers. Charged solitons are proved to emit millimeter range electromagnetic radiation, via which intra- and inter-cellular signalling is possible. Such radiation is shown to result in the long-range interaction between electrosolitons, which leads to the synchronization of soliton dynamics. This can constitute one of the mechanisms of self-regulation in living systems. Study of the interaction between solitons shows that the Davydov model qualitatively describes the charge transport that accompanies oxidative-phosphoryllation redox processes. The input of soliton states into the stimulated luminescence is calculated and shown to describe qualitatively and quantitatively the main properties of the delayed luminescence from biological systems.

#### Introduction

It is thirty years since the first paper on Davydov's soliton [1] was published. The concept of molecular solitons [2] has found a wide area of applications in low-dimensional systems (LDSs) which include conducting polymers, macromolecular proteins, etc. Initially this concept has been suggested to explain the effective mechanism of the transfer of energy, that is released during the ATP hydrolysis processes in biological systems, on macroscopic distances in a cell. "Davydov soliton" (the very term has been suggested by Alwyn Scott [3]) constituted the main subject of the NATO ASI held in 1989 in Denmark, whose Proceedings were entitled "Davydov's Soliton Revisited" [4]. It is not the intention of the present paper to give a complete review

of the theory of molecular solitons; instead, some of the recent advances of this theory are briefly discussed below.

#### 1. Main Properties of Davydov Soliton

#### 1.1. General Description of Davydov's Model

A state of quasiparticles (electrons, holes, excitons),  $|\Psi(t)\rangle$ , in a molecular chain can be found from the Schrödinger equation with the Fröhlich Hamiltonian H, which, in the general case of an arbitrary number of quasiparticles and phonon modes, can be written as the sum of three terms

$$H = \sum_{k,\sigma} E(k) A_{k,\sigma}^{+} A_{k,\sigma} + \frac{1}{\sqrt{N}} \sum_{k,q,\sigma j} \chi_{j}(q) \times A_{k,\sigma}^{+} A_{k-q_{j},\sigma} (b_{q,j} + b_{-q,j}^{+}) + \sum_{q,j} \hbar \omega_{q,j} b_{q,j}^{+} b_{q,j}.$$
(1)

Here,  $A_{k,\sigma}^+$ ,  $A_{k,\sigma}$  are the creation and annihilation operators of a quasiparticle with the wave number k and spin projection  $\sigma$  in a conductive band with the dispersion law E(k),  $b_{q,j}^+$   $(b_{q,j})$  are the creation (annihilation) operators of phonons of the j-th branch with the wave number q and frequency  $\Omega_j(q)$ , and functions  $\chi_j(q)$  characterize the electron-phonon interaction.

Hamiltonian (1) conserves the number of quasiparticles and commutes with the operator of the total momentum of the system

$$P = \sum_{k,\sigma} \hbar k A_{k,\sigma}^{\dagger} A_{k,\sigma} + \sum_{q,j} \hbar q b_{q,j}^{\dagger} b_{q,j}$$
 (2)

which is connected with the translation operator  $T = \exp(iPx/\hbar)$ . The energy of a stationary state  $|\Psi(t)\rangle$ 

depends on the eigenvalue p of the operator P, and every value of p corresponds to the group velocity V = dE(p)/dp. In the coordinate system moving with this velocity, such stationary states satisfy the Schrödinger equation

$$(H - VP)|\psi\rangle = E|\psi\rangle, \quad |\psi(t)\rangle = \exp(iPVt/\hbar)|\Psi(t)\rangle.(3)$$

In the multiplicative adiabatic approximation under the unitary transformation [5]

$$A_{k,\sigma} = \sum_{\lambda} \Psi_{\lambda}(k) a_{\sigma,\lambda} \tag{4}$$

the part of Hamiltonian (1), which is quadratic with respect to the new operators, can be diagonalized. For this, the coefficients  $\Psi_{\lambda}(k)$  should satisfy the equations [5]:

$$[E(k) - \hbar V k] \Psi_{\lambda}(k) +$$

$$+\frac{1}{N}\sum_{q,j}\chi_{j}(q)(\beta_{q,j}+\beta_{-q,j}^{*})\Psi_{\lambda}(k-q_{j}) = E_{\lambda}\Psi_{\lambda}(k).$$
 (5)

As a result of (4), the Hamiltonian takes the form of the sum of two terms, one of which,  $H_0$ , is the operator which describes the adiabatic states of the electron-phonon system, and the second one,  $H_1$ , is the nonadiabaticity operator:

$$H_0 = W + \sum_{\lambda,\sigma} \left[ E_{\lambda} + \frac{1}{\sqrt{N}} \sum_{q,j} f_{\lambda\lambda}(q,j) (b_{q,j} + b_{-q,j}^+) \right] \times$$

$$\times a_{\sigma,\lambda}^{+} a_{\sigma,\lambda} + \frac{1}{\sqrt{N}} \sum_{q,j} \hbar(\omega_{q,j} - Vq) (\beta_{q,j} b_{q,j}^{+} + \beta_{q,j}^{*} b_{q,j}) +$$

$$+\sum_{q,j}\hbar(\omega_{q,j}-Vq)b_{q,j}^{+}b_{q,j},\tag{6}$$

$$H_{1} = \frac{1}{\sqrt{N}} \sum_{\lambda \neq \lambda', q, j} f_{\lambda \lambda'}(q, j) a_{\sigma, \lambda}^{+} a_{\sigma, \lambda'}(b_{q, j} + b_{-q, j}^{+}). \tag{7}$$

Here.

$$W = \frac{1}{N} \sum_{q,j} \hbar(\omega_{q,j} - Vq) |\beta_{q,j}|^2, \tag{8}$$

$$f_{\lambda\lambda'}(q,j) = \chi_j(q) \sum_k \Psi_{\lambda}^*(k) \Psi_{\lambda'}(k-q). \tag{9}$$

In the zero adiabatic approximation, the stationary state  $\Psi$  of a quasiparticle in a potential well created by the deformation of a chain, accounting for the

interaction with the acoustic phonon branch only, is described by the system of equations which read in the continuum limit as:

$$i\hbar \frac{\partial \Psi(x,t)}{\partial t} + J \frac{\partial^2}{\partial x^2} \Psi(x,t) +$$

$$+a\chi \rho(x,t) \Psi(x,t) - \Lambda \Psi(x,t) = \varepsilon F(x,t)$$
(10)

$$\left(\frac{\partial^2}{\partial t^2} - V_a^2 \frac{\partial^2}{\partial x^2}\right) \rho(x,t) + \frac{\chi}{M} \frac{\partial^2}{\partial x^2} |\Psi(x,t)|^2 =$$

$$= \varepsilon f(x, t). \tag{11}$$

Here,  $\rho$  is a chain deformation, J is the exchange (resonance) interaction,  $\chi$  is the EPC constant, a is the lattice constant, M is a molecular mass,  $V_a$  is the sound velocity in a chain,  $V_a = a\sqrt{w/M}$ , w is the elasticity coefficient, and  $\Lambda = E_0 + W - 2J$ , where  $E_0$  is the quasiparticle on-site energy, and W is the phonon energy. Functions F(x,t), f(x,t) account for higher order derivatives, the influence of external fields, etc., that are assumed to be small, which is reflected by the presence of a small coefficient  $\varepsilon \ll 1$ .

The system of equations (10)—(11) in the absence of external fields within the accuracy of second space derivatives, i.e., at F=f=0, is called Davydov's system. For the running wave type functions, this system can be transformed to the Nonlinear Schrödinger equation (NLSE) whose normalized solution has the form of a soliton

$$\Psi_{\rm sol}(x,t) = \psi_{\rm sol}(x,t) e^{ikax - iEt/\hbar},$$

$$\psi_{\text{sol}}(x,t) = \frac{\sqrt{g}}{2\cosh\left[g(x - Vt/a)/2\right]},\tag{12}$$

with the parameters

$$g = \frac{\chi^2}{2Jw(1-s^2)}, \quad s^2 = \frac{V^2}{V_a^2},$$

$$k = \frac{mV}{\hbar}, \quad E = \frac{\hbar^2 k^2}{2ma^2} - \frac{Jg^2}{4}.$$
 (13)

The main characteristic of a moving soliton is the wave vector k which determines the soliton velocity, momentum, and energy (the latter includes the energy of deformation):

$$P_{\text{sol}}(k) = \hbar k + \frac{8a\chi^4 \tan(ka)}{3\hbar V_a^2 w^2 (1 - s^2)^3},$$
(14)

$$E_{\text{sol}}(k) = E_0 - 2J\cos(ka) - \frac{\chi^4(1 - 5s^2)}{3Jw^2(1 - s^2)^3\cos(ka)}, (15)$$

respectively. Such a soliton has the effective mass

$$m_s = m(1+\delta), \quad \delta = \frac{Jg_0^2}{3mV_a^2}, \quad m = \frac{\hbar^2}{2Ja^2},$$
 (16)

and can propagate along a chain with constant velocity  $V < V_a$  without changing its form and without losing its energy.

### 1.2. Conditions of Soliton Existence

Generally speaking, the ground states of a quasiparticle in a chain can be conventionally divided into three types which correspond to three different approximations in the Fröhlich Hamiltonian. Namely, these approximations are: (i) strong EPC, which corresponds to a small polaron; (ii) weak EPC, which corresponds to almost free quasiparticle; and (iii) adiabatic approximation, which is valid at intermediate values of EPC, and results in the formation of a soliton (large polaron) state. To show this explicitly and to get the estimate of adiabatic approximation validity, the variational method suggested in [6], turned out to be useful. In the case of one quasiparticle, the variational function in the site representation can be chosen in the form

$$|\Psi\rangle = \sqrt{a} \sum_{n} \Psi(n) e^{\sigma(n)} a_n^+ |0\rangle, \tag{17}$$

where

$$a_{\sigma n}^+ = \frac{1}{\sqrt{N}} \sum_k \exp(-ikna) a_{\sigma k}^+,$$

$$\sigma(n) = \frac{1}{\sqrt{N}} \sum_{q,j} \left[ f_{q,j}(n) b_{q,j}^{+} - f_{q,j}^{*}(n) b_{q,j} \right], \tag{18}$$

with the variational variables  $\Psi(n)$  and  $f_{q,j}(n)$  to be determined from the extremum condition for  $E=\langle\Psi|H|\Psi\rangle$  at the additional condition  $\langle\Psi|\Psi\rangle=1$ . This general form of a function, as it has been shown in [6], allows to describe all three approximations within the same variational scheme. Namely, it was shown that the wavefunction  $\Psi(n)$  satisfies Schrödinger equation in the deformational potential with the effectife exchange integral  $J^*=Je^{-G}$ , renormalized by the Franck—Condon factor G, which, in turn, depends on the wavefunction. Using the complete set of orthogonal eigenfunctions, that include ground state functions and functions of the continuum spectrum, and choosing the trial function of the ground state depending on the localization parameter,  $\kappa$ , the energy can be calculated

as a function of  $\kappa$ . This function depends on the EPC constants and nonadiabaticity parameters of the phonon branches as parameters.

It turns out that, in the case of one vibrational mode, optical [6] or acoustic [7], the self-trapped solitonlike states with finite nonzero value of the localization parameter correspond to the minimum of energy only within the finite interval of EPC values:

$$g_{j,c1} < g_j < g_{j,c2}, \quad j = \text{op, ac,}$$
 (19)

with the lower and upper critical values of EPC constants depending on the nonadiabaticity parameters,  $\gamma_i^*$ , respectively. Here,

$$g_{\rm ac} = \frac{\chi_{\rm ac}^2}{Jw}, \quad g_{\rm op} = \frac{|\chi_{\rm op}|^2}{2J\hbar\Omega_0},$$
  
$$\gamma_{\rm op}^* = \frac{\hbar\Omega_0}{J^*}, \quad \gamma_{\rm ac}^* = \frac{\hbar V_a}{2J^*a}.$$
 (20)

The ground state corresponds to an almost free quasiparticle, provided the EPC constant is less than the lower critical value,  $g_j < g_{j,c1}$ , and to a small polaron state, provided the EPC constant is bigger than the upper critical value, at  $g_j > g_{j,c2}$ . The analysis becomes more cumbersome in the case of several vibrational modes. It has been shown in [8] that, for a chain with two modes, the parametric region of soliton existence is much broader with respect to the EPC constant with one of the two phonon branches,  $g_i$ , as compared with the one-mode approximation, provided the EPC constant with the second mode,  $g_{j\neq i}$ , belongs to the domain where the one-mode adiabatic approximation is well valid.

In this respect, it is worth to mention here that, in the numerical analysis of soliton properties, the standard numerical values of the parameters that are characteristic of real polypeptides (see [3]), are usually used. For the overly simplified one-band single-chain model, these values give  $\gamma_{\rm ac}$  = 2.3,  $g_{\rm ac}$  = 0.9  $\div$ 3.9, at which, according to [7], the ground electron states do not correspond to a soliton. The single-chain model describes a real alpha-helix quite conventionally, both quantitatively and qualitatively. The account of the helical structure, resonance and elastic interactions between three peptide chains changes the effective band width and reduces the sound velocity in the helix as compared with a single chain. All this reduces the nonadiabaticity parameter,  $\gamma_{\rm ac} \approx 1$  [7]. But the most important is the presence of three bands in the  $\alpha$ helix, of which two, the lowest ones, are degenerate. Such a system can hardly be described adequately in all respects by a one-band model, in particular, a kind of Jahn—Teller effect can take place. Therefore, the numerical study of a model chain has to be carried with the numerical values of the parameters which are renormalized as compared with a real polypeptide.

This explains the very small values of the soliton life-time calculated by H. Bolterauer [4, p. 309] and J.V. Schweitzer and J.P. Cottingham, in [4, p. 285], as well as inconsistence of the conclusion about the thermal instability of solitons, obtained within the molecular dynamics model [9, 10] or using the perturbation theory [11]. Moreover, the problem of temperature influence on a mixed quantum-classical system requires a self-consistent quantum-mechanical consideration. According to the quantum-mechanical study [12], the temperature dependence of soliton parameters is nonmonotonous. There is some optimal value of temperature,  $T_0$ , at which a soliton has the lowest energy. Soliton stability increases with temperature increasing in the interval  $[0, T_0]$  due to the effective decrease of the electron band width,  $4J^*$ , and, respectively, the decrease of soliton dispersion. With the increase of temperature above  $T_0$ , the total soliton energy increases approaching the band bottom, which corresponds to the decrease of soliton thermal stability at  $T > T_0$ . There is some critical value of temperature,  $T_{\rm cr}$ , at which the kinetic energy of the lattice due to thermal vibrations overcomes the binding energy, and the soliton dissociates into a delocalized quasiparticle and a lattice deformation. These results agree with the results of computer simulations [13].

## 1.3. Soliton Dynamics in Discrete Molecular Chains and Electrosoliton Induced Electromagnetic Radiation

Numerical modelling of the soliton dynamics in a discrete molecular chain reveales some peculiarities as compared with analytical continuum models. Namely, it shows the presence of small oscillations of the soliton amplitude. The regular study of the dynamical dependence of soliton parameters has been done in [14—18]. Here, we report only that it turns out that a soliton in a chain moves along the periodical Peierls—Nabarro potential relief, whose height,  $U_p$ , depends on the width of a soliton and which has the period equal to the lattice spacing. Due to this, the dependences of the soliton velocity, momentum and energy on the quasimomentum differ from those predicted by the continuum models. Instead of a monotonic relation, they are oscillating functions of time. It has been shown in [17] that the instantaneous

soliton velocity is

$$V(t) \equiv \dot{r}(t) = V_0 dn(u, \kappa) =$$

$$= \overline{V} \left[ 1 + \sum_{n=1}^{\infty} \frac{4q^n \cos(n\omega t)}{1 + q^{2n}} \right], \tag{21}$$

where  $dn(u,\kappa)$  is the Jacobi elliptic function,  $u=\pi V_0 t/a$ , and  $\kappa^2=U_p/E_{\rm kin}$ , is the modulus of the elliptic integral. According to (21), the soliton moves with an average soliton velocity,  $\overline{V}=\pi V_0/2K(\kappa)$ , and has oscillating components with the main harmonic

$$\omega = \frac{\pi^2 V_0}{2aK(\kappa)}. (22)$$

and its overtones. Here,  $V_0$  is the initial soliton velocity due to the initial wavevector  $k_0$ ,  $K(\kappa)$  is the complete elliptic integral of the first kind, and  $q = \exp(-\pi K'/K)$ , where  $K' = K(\kappa')$ ,  $\kappa'^2 = 1 - \kappa^2$ . The amplitude of soliton oscillations in the barrier depends on the value of the carrying wave vector and on the strength of the electron-phonon coupling. The overcoming of the Peierls—Nabarro barrier has a threshold character not only with respect to the soliton kinetic energy, but also with respect to its binding energy, at a given value of k.

Because of these oscillations, electrosolitons can emit electromagnetic waves [18, 19]. In the general case, the scalar and vector potentials of the electromagnetic field created by the charge and current distributions are determined by the Maxwell equations [20]:

$$\varphi(\lbrace x_{\alpha}\rbrace, t) = \frac{1}{4\pi\varepsilon_0} \int \frac{[\rho_e(\lbrace x_{\alpha}'\rbrace)]}{r(x_{\alpha}, x_{\alpha}')} dv',$$

$$\vec{A}(\{x_{\alpha}\},t) = \frac{\mu_0}{4\pi} \int \frac{[\vec{j}(\{x'_{\alpha}\})]}{r(x_{\alpha},x'_{\alpha})} dv'.$$
 (23)

Here,  $x_{\alpha}$ ,  $\alpha=1,2,3$ , is the  $\alpha$ -coordinate of the radius-vector,  $\varphi(\{x_{\alpha}\},t)$  and  $\vec{A}(\{x_{\alpha}\},t)$  are the scalar and vector potentials of the field. The rectangular brackets in (23) mean that the corresponding variables are determined with account of the retardation effects, i.e., are taken at the time moment  $t'(x_{\alpha}, x'_{\alpha}) = t - r(x_{\alpha}, x'_{\alpha})/c$ , where  $r(x_{\alpha}, x'_{\alpha})$  is the distance between  $x_{\alpha}$  and  $x'_{\alpha}$ . Finally, the charge and current distributions are determined by the electron wave function  $\psi_n(t)$ :

$$\rho_e(t) = e \sum_n \frac{|\psi_n(t)|^2}{\pi r_0^2 a},$$

$$\vec{j}(t) = -\frac{ieJ}{\hbar} \sum_{n} \left( \psi_n^* \psi_{n+1} - \psi_{n+1}^* \psi_n \right) \frac{\vec{l}}{\pi r_0^2 a}, \tag{24}$$

respectively. Here, e is the electron charge, and  $\vec{l}$  is a unit vector along the chain axis with the characteristic transverse size parameter  $r_0$ . Within the continuum approximation for the soliton envelope (12), the expression for current (24) takes the form  $\vec{j}(t) \approx e\vec{V}(t)\rho_e(t)$ . When calculating the EMF potentials from Eqs. (23), the terms of two types appear, which decrease in space as  $1/r^2$  or as 1/r. It is known that the latter ones describe the radiation fields. Substituting the time derivative of the soliton velocity from (21), we get for these terms in the wave zone (i.e., where the inequalities  $r \gg r_0$ ,  $r \gg 1/\mu$  are valid):

$$\vec{E}_{\rm rad}(\vec{r}) = -\frac{eV_0^2}{2a\varepsilon_0c^2r^3} \times$$

$$\times \sum_{n=1}^{\infty} \frac{4nq^n}{1+q^{2n}} \sin(n\omega t) \vec{r} \times \left( \vec{r} \times (\vec{l}) \right), \tag{25}$$

$$\vec{B}_{\rm rad}(\vec{r}) = -\frac{eV_0^2}{2a\varepsilon_0 c^2 r^2} \sum_{m=1}^{\infty} \frac{4mq^m}{1 + q^{2m}} \sin(m\omega t) \vec{l} \times \vec{r}. \quad (26)$$

Thus, electrosolitons that propagate along a discrete chain emit EMR which, according to (25), (26), contains characteristic harmonics with frequencies  $n\omega, n =$ 1, 2, .... The value of the main harmonic frequency  $\omega$  (22) of electrosoliton radiation depends on soliton velocity. In the case of electrosolitons that participate in charge transfer processes in biological systems, this velocity is determined by the metabolic activity. For an approximate estimate, we can use the value of soliton velocity from numerical simulations [21],  $V_0 \approx$  $1.5 \cdot 10^3$  m/s. Together with the characteristic value of polypeptide chain spacing  $a = 4.5 \cdot 10^{-10}$  m, this gives  $\nu \approx 10^{12} \ s^{-1}$ , which allows us to conclude that the soliton-induced EMR can be relevant for the highfrequency EMF which exists around biological cells and is registered by the microdielectrophoresis and other methods [22, 23].

### 1.4. Solitons in the Presence of External Fields

The dynamical properties of solitons are manifested in external fields. Moreover, one can expect to prove the existence of Davydov solitons by their input into the scattering spectra of external radiation. In particular, this has been calculated in [24—26] for the scattering spectra of slow neutrons and of X-ray in [27]. In [28], the possibility of the experimental observing of a soliton mode by neutron scattering was analyzed using the data on the experiments with [(CH<sub>3</sub>)<sub>4</sub>N] [NiCl<sub>3</sub>].

It has been shown in [29] that, in the external constant magnetic field oriented parallel to chain axes, an electrosoliton moves along the helical trajectory with the wave function that describes the superposition of the soliton propagations along the chain and along the closed orbits in the perpendicular direction with the quantized energy. In the case of the magnetic field oriented perpendicular to the chain axis, the soliton velocity is the oscillating function of time:

$$V(t) = V_0 \cos(\omega t), \quad \omega = \frac{\omega_B}{m_{B,s}c}.$$
 (27)

Here,  $\omega_B = |Be|/m_Bc$  and  $m_B = \sqrt{m_y m_z}$  are the cyclotron frequency and free cyclotron mass, respectively, with  $m_y, m_z$  being the transverse components of the effective mass of a quasiparticle. The effective cyclotron mass in (27) is determined as

$$m_{B,s} = \sqrt{(1+\delta)m_x m_y} = \sqrt{m_s m_y},\tag{28}$$

i.e., it exceeds the cyclotron mass of a band electron due to the phonon "dressing" of a soliton. Therefore, the cyclotron frequency of a soliton is less than that of a free electron.

The study of soliton properties in the external electromagnetic field (EMF) has been carried in [30—33]. In this case, the total Hamiltonian of the system can be written in the form  $H(t) = H_0 + V(t)$ , where  $H_0$  is given in (6) and V(t) is the operator of the quasiparticle interaction with EMF. The wavefunction of the system,  $|\Psi(t)\rangle$ , satisfies the Schrödinger equation with the Hamiltonian  $H(t) = H_0 + V(t)$  and can be expanded over the complete set of the stationary states  $|\Psi_{\lambda}(t)\rangle$  of the Hamiltonian  $H_0$ . This set includes a soliton state and delocalized electron states in the band. The account of the corresponding diagonal and nondiagonal matrix elements of the perturbation results in two qualitatively different effects of EMR on solitons.

The nondiagonal matrix elements of the perturbation V(t) determine the probability of a quantum transition from the initial soliton state  $|\Psi_s\rangle$  into the delocalized band states  $|\Psi_j\rangle$ . As calculated in [30, 32], the total probability of soliton dissociation per unit time has resonant dependence on the frequency with the resonance frequency  $\omega_{\rm diss}$  which depends on the value of the electron-phonon coupling, g. With the increase of g,  $\omega_{\rm diss}$  tends to the value corresponding to the most probable soliton transition into the delocalized band state with zero wavenumber k=0:  $\omega_{\rm diss}\approx\omega_{k=0}=\chi^4/(\hbar Jw^2)$ . At small values of g,  $\omega_{\rm diss}$  is displaced to the higher frequency value due to the input of the soliton transitions into the band states with  $k\neq 0$  [32]. For the

parameters characteristic of the amide-I vibration in an  $\alpha$ -helix [3],  $\omega_{\rm diss} \approx 34 \div 65$  GHz [30]. This qualitatively corresponds to the experimentally observed nonthermal millimeter electromagnetic wave bioeffects [33, 34].

The diagonal elements lead not only to a shift of the energy levels, as is usual for linear systems, but also to the nontrivial change of the dynamics of solitons. This is governed by the system of equations (10)—(11), in which

$$F(x,t) = iA \frac{\partial \psi}{\partial x} \cos(\omega t), \quad f(x,t) = B \frac{\partial^2 |\psi(x,t)|^2}{\partial x^2},$$
 (29)

where A, B are some real constants, and  $\omega$  is the frequency of EMF, respectively. This system of equations was solved in [31, 32] analytically for the case of an electromagnetic field of small amplitudes within the Mitropolsky—Bogolyubov—Krylov perturbation theory and numerically. In the presence of a weak periodic perturbation in the zero adiabatic order, the soliton wavefunction (12) is unchanged except for the slow time dependence of its c.m.c.,  $\zeta(t)$ , and phase,  $\vartheta(t)$ . For the steady-state motion of the driven soliton with account of the retardation effects in the deformation accompanying soliton, the equation can be obtained as

$$\ddot{\zeta}(t) = \frac{F_0}{m_d(\omega)} \cos\left[\omega t - \phi(\omega)\right]. \tag{30}$$

Here,  $m_d(\omega)$ , the dynamical mass of the soliton in the field, and  $\phi$ , the phase shift due to the soliton acceleration under the external force, are functions of the EMF frequency. The corresponding analysis shows that  $\phi \to 0$  at low and high frequencies, while the frequency dependence of  $m_d(\omega)$  is qualitatively different for low and high frequencies as compared with the characteristic constant  $\omega_0$ :

$$\omega_0 \equiv \frac{2\kappa V_a}{\pi}.\tag{31}$$

Namely, at  $\omega \ll \omega_0$ , a soliton propagates as a classical Newtonian particle in a slowly oscillating external field with a dynamical mass equal to the effective mass of the soliton in the absence of the field,  $m_d \approx m_s$ . At high frequencies  $\omega \gg \omega_0$ , the deformation cannot follow the comparatively fast electron motion, and the dynamical mass approaches the mass of a free band quasiparticle,  $m_d \approx m$ . Due to oscillations, solitons emit sound waves in the backward and forward directions. This process occurs with the absorption of energy by solitons from the external field and is also frequency-dependent. The energy absorption per field oscillation period,  $T=2\pi/\omega$ , is proportional to the EMF frequency at low frequencies and decreases exponentially at high

frequencies attaining the maximum at the dynamical resonant frequency  $\omega_{\rm dyn}=1.3\omega_0$ . The numerical calculations have confirmed these results and proved the applicability of the perturbative analysis and the stability of solitons in rather strong EMFs apart from the resonant frequency. In the very strong EMFs when the adiabatic approximation breaks down, the amplitude of the soliton decreases significantly with the increase of the amplitude of oscillating tails and with the appearance of some stochasticity features in the system behavior.

#### 1.5. Few-soliton States

The interaction between Davydov solitons is much more complicated than the interaction between solitons in completely integrable systems, where it is reduced to the phase and c.m.c. shift. Of course, the interaction between Davydov solitons depends on the statistics the quasiparticles obey. Namely, two electrosolitons with opposite spins form a bisoliton state, as was shown first in [35, 36] and later in [37—43]. In particular, two extra electrons in a chain satisfy the stationary two-component nonlinear Schrödinger equations [44, 45]

$$\begin{split} \frac{d^2\Psi_i}{dx^2} &= \mu_i^2 \Psi_i - 2g(\Psi_1^2 + \Psi_2^2) \Psi_i, \\ E_i &= -\frac{\hbar^2 \mu_i^2}{2ma^2}, \quad i = 1, 2. \end{split} \tag{32}$$

Here, the parameter g is determined in Eq.(13). The system of Eqs. (32) admits the solution  $\Psi_1 = \Psi_2$  which corresponds to the lowest energy  $E_{bs} = -\frac{2}{3}Jg^2$ ,  $\mu = g$  and describes a bisoliton [35, 36]. For fermions, this solution has the sense only in the case of opposite spins of electrons in the initial state, i.e., when  $\sigma \neq \sigma'$ . System (32) can be solved using the inverse scattering transformation [44] for a two-soliton state, as was done in [36], or, since it belongs to the Liouville-type class, using the method of quadratures, as it was done in [5], using the method of quadratures. A normalized solution of Eq. (32) has the form:

$$\Psi_{1,2} = \frac{\mu}{\sqrt{2g\cosh(2\mu\lambda)}} \times \left[ \frac{e^{\mp\mu\lambda}}{\cosh\left[\mu(x-R)\right]} \pm \frac{e^{\pm\mu\lambda}}{\cosh\left[\mu(x+R)\right]} \right]. \tag{33}$$

The corresponding density of charge distribution has two localized peaks with the distance between the peaks

$$R = \frac{1}{2\mu} \ln \frac{2\mu \cosh(2\mu\lambda)}{\Delta} \to \infty \quad \text{at} \quad \Delta \to 0.$$
 (34)

The integration constant  $\lambda$  determines the level of electron corelation: at  $\lambda=0$ , the electron state is absolutely collectivized and both electrons participate in the formation of the collective state with equal probabilities, while the symmetry is brokenat  $\lambda \neq 0$  and, at a large enough value of  $\lambda$ , the functions  $\Psi_1$  and  $\Psi_2$  describe individual solitons, respectively. The value of  $\mu$  determined from the normalization condition equals  $\mu=g/2$ , and two electrons have the energy

$$E_{\rm tr,0} = -\frac{1}{6}Jg^2 + 2Jg^2 \cosh^2(g\lambda) \exp(-2gR), \tag{35}$$

which yields that there is the repulsion between solitons caused by the exponentially decreasing force  $F=\partial E/\partial R \propto \exp{(-2gR)}$ . The integration constant  $\lambda$  characterizes the level of hybridization of electrons in the bound state. These results are confirmed by the numerical calculations of (33). At  $|\lambda| \geq 5$ , the electrons with parallel spins form the unbound state, and their wavefunctions can be described as independent free solitons.

One can show that the case where there are four extra electrons in a chain, can be reduced formally to the case of two electrons with the substitution  $g \to G = 2g$ . This means that, in the zero adiabatic approximation, there is the repulsion between two bisolitons, which exponentially decreases with distance, due to which the bisolitons are separated by the distance as maximum as possible for the given chain length.

It has been shown in [5] that the account of the nonadiabatic term  $H_1$  (7) of the Hamiltonian results in the additional direct interaction between two solitons (or, similarly, two bisolitons) via the phonon field which stabilizes the two-soliton solution. Considering the nonadiabatic term of the Hamiltonian  $H_1$  as a perturbation, one can calculate the first order energy correction accounting for the complete set of states of the two-component NLSE (32) including the bound states  $\lambda = 1, 2$ , as determined in (33), and the continuous spectrum. This gives the energy correction

$$\Delta E \approx -J \frac{\gamma g^3}{2^2 \pi^5} -$$

$$-\frac{3Jg\gamma}{4\pi^2\cosh\left(\lambda q\right)}\frac{1}{R^2}\left(1-\frac{1}{3}\cos\frac{2gR}{\pi}\right). \tag{36}$$

Here,  $\gamma$  is the nonadiabaticity parameter (20). Therefore, the lowest state of two extra electrons in a chain corresponds to a singlet bisoliton. In the triplet state, there is the repulsion between two electrons as well as between two bisolitons. This situation is opposite

to what happens with two small bipolarons which form a bipolaron drop. The repulsion between two (bi)solitons is partly compensated by the interaction between electrosolitons via the phonon field accounted by the nonadiabatic terms of the Hamiltonian.

The equilibrium distance between the c.m. coordinates of solitons in the triplet state can be determined from the minimization condition of the total energy within the accuracy of the first nonadiabatic order  $E_{\text{tot}} = E_{\text{tr,0}} + \Delta E$ , where the terms are given in (35) and (36), respectively. As a result, in the presence of  $N_e$  extra electrons in a chain, the periodic lattice of bisolitons is formed in it in the form of a cnoidal wave with the distribution period [46, 47]  $l = N/N_{bs}$ ,  $N_{bs} = N_e/2 = 1/\delta$ , that corresponds to a many-electron solution of the Peierls—Fröhlich problem at zero temperature [47]. Here,  $\delta$  is the concentration of bisolitons. The envelope of a cnoidal wave is described by the periodic Jacobi function [46]

$$\Psi_{\rm cn}(x,t) = \sqrt{\frac{g}{2}} E^{-1}(k) dn \left( \frac{g(x - Vt/a)}{E(k)}, k \right) \times \exp\left[i \left(qx - \Phi_{\rm cn}(t)\right)\right]. \tag{37}$$

Here, E(k) is a complete elliptic integral of the second kind, the modulus of which, k, is determined by the space period of the function, and, hence, b they bisoliton concentration  $\delta = 1/l$  according to the relation

$$gl = 2E(k)K(k) \tag{38}$$

with K(k) being a complete elliptic integral of the first kind. The energy of the cnoidal wave per period, i.e., the energy per bisoliton in a coherent superlattice, is a function of the concentration of bisolitons

$$E_{\rm cn} = -\frac{2}{3} J g_0^2 \left[ E(k)(2 - k^2) + K(k)(1 - k^2) \right] E^{-3}(k).$$
(39)

The analysis of expression (39) shows that the inequality takes place  $l > l_{\rm cr} = \pi^2/2g$ . This means, there is some critical value of bisoliton concentration

$$\delta_{\rm cr} = \frac{2g_0}{\pi^2},\tag{40}$$

above which, at  $\delta > \delta_{\rm cr}$ , the cnoidal wave is not stable because of the too strong repulsion between the electrons. It follows also from Eq. (39) that the energy gap that separates a localized electron level from delocalized states in the conduction band vanishes when  $\delta$  tends to  $\delta_{\rm cr}$  [48].

#### 1.6. Solitons in Two-dimensional Lattices

Unlike 1DSs which have been systematically studied, 2D electron-phonon systems have been studied mainly numerically [49-52]. First of all, there was much scepsis about the soliton stability in 2DSs, because the simplest reduction in 2DSs leads to the 2DNLSE, whose solitons are unstable with respect to a shrinking or, in the limit, to a collapse [53]. At the same time, even the earliest numerical studies of 2Dsoliton states [50-52] have shown that a discrete 2Dlattice supports solitonic-like solutions for appropriate values of the coupling constants. These 2D solitons are very robust objects that propagate without energy loss, and their collisions with boundaries are almost elastic. The stabilization of solitons is a result of an interplay between discreteness, dispersion, and nonlinear interactions. The lattice discreteness turns out to be very important at soliton shrinking, and the lowest order continuum approximation becomes not valid, and higher order terms have to be taken into account. It has been shown in [52] that this leads to the modified 2D NLSE with extra terms that stabilize the localized solutions:

$$i\frac{d\varphi}{d\tau} + \nabla\varphi + 2g\left(|\varphi|^2 + \frac{1}{12}\nabla|\varphi|^2\right)\varphi = 0. \tag{41}$$

It is well known that the 2D NLSE has a stationary solution at a fixed value of the nonlinearity parameter, (g=5.85 at the normalization to one) only, and corresponds to zero value of the total energy and arbitrary values of the localization parameter and binding energy. The solution of 2D NLSE is marginally stable in the linear approximation [54] and is unstable with respect to perturbations of finite amplitude [53]. In (41), there is an extra term, coming from the account of lattice discreteness, which stabilizes the solutions. Indeed, differentiating the square of the localization radius

$$R^2 = \int |\vec{r}|^2 |\varphi|^2 dx dy \tag{42}$$

with respect to  $\tau$  gives [52, 53, 55–57]

$$\frac{d^2R^2}{d\tau^2} = 8(\mathcal{E} + \delta), \quad \delta = \frac{1}{12}g \int (\Delta|\varphi|^2)^2 dxdy. \tag{43}$$

It follows from (43) that initial configurations with negative energy  $\mathcal{E}$  will start shrinking unless the extra term  $\delta$ , which is positive, can compensate  $\mathcal{E}$ . As the result of such a shrinking,  $\delta$  increases until the r.h.s. of (43) becomes negative. Then the wave function starts to expand untill  $\delta$  becomes small enough to make the

soliton start to shrink again. This process continues, and, as a result, a soliton oscillates in size. Numerical results support these analytical conclusions: a 2D lattice with electron-phonon interaction admits solitonic solutions when the coupling constant g is larger than its lower critical value,  $g_{c1} \approx 5.8$ , and less than its upper critical value,  $g_{c2} \approx 8$ . In this interval a solitonic solution is stable with respect to finite and not too large perturbations. At g > 8 the self-trapping changes into the regime of strong localization. The more detailed analysis of solitons in 2D lattices can be found in [58, 59].

# 1.7. Soliton Input into the Delayed Luminescence of Biosystems

One of the applications of the theory of Davydov solitons is connected with the explanation of the delayed luminescence (DL) of biosystems [60, 61]. The phenomenon of the DL consists of photoinduced light emission long time (seconds and more) after illumination. Experimentally observed correlation between the DL and chloroplast organization [62] and analogies in certain features of DL spectra from biological and some solid state systems [63] indicate that this phenomenon in biosystems can be connected with the collective electron states. In the meantime, in view of long duration of DL and high physiological temperatures, it can hardly be connected with delocalized states, such as conventional band electrons or excitons. Another possibility is connected with Davydov solitons, which are much more stable than electron delocalized states and can be created by the pre-illumination of a sample. Indeed, it has been shown in [60, 61] that the soliton mechanism explains qualitatively and quantitatively all the main features of the DL from simple biosystems.

The general scheme of the DL in the soliton model is the following one. Electrons released in the ionized centers of luminescence (the charge separation complexes) in systems which produce photosynthesis, or released in the redox processes, are self-trapped with a certain probability in the macromolecules as, for instance, alpha-helical polypeptide proteins, actin filaments, etc. The luminescence arises from the decay of these localized states into the conductive electron band with the following fast transition into recombination centers. Two possible situations can occur: weak or strong electron correlations. In the first case (at very small concentrations, in not long enough macromolecules, etc.), electrons localize in independent (bi)soliton states, and the probability

of electron localization does not depend on soliton concentration (so-called non-correlated model [60]). In the opposite case of large concentration of (bi)solitons, the correlation between solitons is strong and bisolitons form a periodical cnoidal wave in a chain (37). In this case, the number of available localized states is determined by the critical concentration (40),  $\nu_0 = 2\delta_{\rm cr}$ . Analysis of both models shows that the kinetics of the DL depends on two basic parameters: (i) on kinetics rate  $\gamma_{\rm lum}$ , determined as the ratio of the characteristic rates of the localization and recombination processes, and (ii) the level of excitation which is the ratio of the number of initial excited states to their total available number:  $x_0 = n_0/\nu_0$ .

According to these models, the initial intensity  $I_0 = I(\tau = 0)$  is, in the general case, a non-linear function of the level of excitation  $x_0$ ,

$$I_{\text{nc},0} = \frac{x_0^2}{x_0 + \gamma_{\text{lum}} (1 - x_0)},$$

$$I_{\text{corr},0} = \frac{x_0^2}{x_0 + \gamma_{\text{lum}} (1 - x_0)^2},$$
 (44)

which become linear in the limit of zero values of  $\gamma_{\text{lum}}$ , only. Indeed, the experimental study of the DL of biosystems reveals the nonlinear dependence of  $I_0$  on the intensity of the stimulating light [62—64]. At small values of the kinetics rates  $\gamma \ll 1$ , both models predict a similar behaviour of  $I_0(x_0)$ . Increasing the value of  $\gamma$  even at  $\gamma < 1$ , the deviation between the two models increases.

Two mechanisms of the DL, correlated and non-correlated, can complement each other. Realization of one or another depends on the biological system and the corresponding conditions. One of the reasons of the correlated behaviour of solitons can be connected with the length of polypeptide macromolecules, in which solitons can be formed. Another reason can be due to the state of metabolic activity of a system that determines the number of (bi)solitons and the level of their coherence.

# 2. Experimental Evidences of Soliton Existence

A wide class of organic and inorganic materials was recently synthesized. Some of them possess strongly anisotropic physical characteristics and reveal many unusual properties, due to which some of these compounds find numerous applications in modern technologies and attract an ever increasing scientific interest. Some of these characteristic features arise from the electron-phonon coupling. Many applications in nanotechnologies, including quantum computation, information processing, sensing, etc., are based on the discoveries of large polarons, charge and spin density waves. The high-temperature superconductivity in perovskites, superconductivity in LD organic and inorganic materials, including the recently discovered superconductivity in magnesium diboride, MgB<sub>2</sub>, [65] and in organic polymer films [66] also reveal the important role of electron-phonon interaction.

There is the ample experimental evidence for large polaron-type states in 1D molecular structures [67— 71], although the term "large polaron" or "soliton" is far not always used (other call this "composite polaron", "complex polaron", "solitary polaron", etc.). In particular, polarons and bipolarons are considered to be the reason of the high conductivity of conducting polymers. For example, the so-called acoustic solitarypolaron model [71, 72] describes reasonably well the carriers mobility in polydiacetylene, both in weak and moderate electric fields. However, this model failed in strong electric fields as it predicts that a saturation of the carriers drift velocity should occur at the sound velocity whereas experimentally this is observed to take place at remarkably lower values. This problem has been solved in [17] as arising from the violation of applicability in strong fields when solitons attain large values of quasimomentum, and the lattice discreteness needs to be accounted properly. In a discrete lattice at large values of quasimomentum, a soliton velocity attains saturation, whose value  $V_{0,\text{max}}$  and the value of k for which this saturation occurs depend on the values of the parameters of the chain (see [17]). For the polydiacetylene parameters,  $V_{0,\text{max}}$  is  $\approx 2V_a/3$ , which is obviously less than the value predicted by the continuum model and very close to the experimentally observed value  $\sim 0.7 V_a$ ) [68]. Moreover, the increase of the soliton velocity results in a perturbation of the soliton, that is, its envelope changes, oscillating tails appear, and their amplitude and energy increase with k. At the same time, the total current in the system first increases with k and, for large values of k, it reaches a plateau. A further increase of the carrying wave vector k results in a decrease of the current due to the more intensive emission of phonons and radiation from the soliton. This corresponds to the region of negative resistance that is observed experimentally at large fields in some conducting polymers.

The soliton model of the DL provides a qualitative

and quantitative explanation of the main characteristic features of the DL spectra from yeast and alga A.a [60, 61]. These include the kinetics of time decay, the nonlinear dependence on the intensity of the stimulating light and the same time trend for all the emission spectral components. Unicellular alga A.a, seems to be a system admitting the existence of correlated self-trapped electron states. In particular, in A.a, there are very long macromolecules, like actin filaments and microtubules which form the cytoskeleton of cells and are responsible for the motility of organelles and the streaming of cytoplasma on the whole. These microfilaments have largely variable length from 10-20 to few hundreds of subunits, they have a double-chain helical structure and, in the presence of the fibrin protein, they are bundled together into parallel arrays. These macromolecules are good candidates for a system, in which a large number of correlated electrosolitons can be excited under certain conditions. Indeed, it turns out that the correlated soliton model gives a higher precision of the theoretical fit of experimental data for A.a. in the wide interval of intensities of the stimulating light and in the whole time interval of experimental measurements, as compared with the non-correlated model [61].

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# ДИНАМІЧНІ ВЛАСТИВОСТІ ДАВИДОВСЬКИХ СОЛІТОНІВ

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Резюме

Зроблено короткий огляд сучасного стану теорії давидовських солітонів, започаткованої 30 років тому, а також перспектив її застосування до сучасних проблем фізики та біофізики. Проаналізовано основні властивості солітонів та їх динаміки в макромолекулярних системах. Показано, що солітонна модель правильно пояснює експериментально спостережуване насичення дрейфової швидкості носіїв заряду в сильних електричних полях для ряду полімерів. Доведено, що електросолітони випромінюють електромагнітні хвилі, за рахунок чого відбувається синхронізація їхнього руху, що може забезпечувати внутрішньоклітинний та міжклітинний обмін інформацією. Вивчення взаємодії між давидовськими солітонами показує, що солітонна модель якісно правильно пояснює основні характеристики транспорту зарядів в окислювально-відновлювальних процесах. Показано також, що солітонні стани дають внесок у затриману люмінесценцію біологічних систем. Така модель не лише якісно, але й кількісно пояснює експериментальні дані для простих (одноклітинних) біологічних систем.

# ДИНАМИЧЕСКИЕ СВОЙСТВА ДАВЫДОВСКИХ СОЛИТОНОВ

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Резюме

Сделан краткий обзор современного состояния теории давыдовских солитонов, основы которой заложены 30 лет тому назад, а также перспектив ее применения к современным проблемам физики и биофизики. Проанализированы основные свойства солитонов и их динамики в макромолекулярных системах. Показано, что солитонная модель правильно объясняет наблюдаемое экспериментально насыщение дрейфовой скорости носителей заряда в сильных электрических полях для ряда полимеров. Доказано, что электросолитоны излучают электромагнитные волны, за счет чего происходит синхронизация их

движения, что может обеспечивать внутриклеточный и междуклеточный обмен информацией. Изучение взаимодействия между давыдовскими солитонами показывает, что солитонная модель правильно объясняет основные характеристики транспорта зарядов в окислительно-восстановительных процессах на

качественном уровне. Показано также, что солитонные состояния дают вклад в задержанную люминесценцию биологических систем. Такая модель не только качественно, но и количественно объясняет экспериментальные данные для простых (одноклеточных) биологических систем.