Anharmonicity and solitons in molecular chains

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A theoretical study is reported of a one-dimensional chain of dipole-interacting molecules. It is shown that the anharmonicity of molecular vibrations creates soliton waves. An analytic form and characteristics allowing for the discrete properties of the chain are obtained for solitons of width representing several periods of the one-dimensional lattice. We can describe the dynamics of solitons at low velocities using equations which are integrable by the method of the inverse scattering problem. An allowance is made for the influence of acoustic vibrations of the lattice on the properties of solitons. In this case a soliton is accompanied by a local deformation of the chain and can travel at a velocity higher than the velocity of sound. This model is used to describe vibrational excitation of α-helical protein molecules.

Mechanisms of energy transfer in long biological polymer molecules continue to attract major attention.[1–6] The knowledge of the nature of these mechanisms is important, particularly for the understanding of the processes occurring in DNA (Ref. 2).

According to the current ideas, the energy released by hydrolysis of adenosine triphosphate (ATP) is transported in a protein in the form of vibrational excitation quanta of $C=O$ bonds (amide-1 vibration) of peptide groups. The dipole-dipole interaction of quanta at neighboring peptide groups not only ensures excitation transfer, but also results in a dispersion manifested by a reduction in the amplitude and spatial broadening of initially localized wave packets of vibrational excitations. Estimates show that this dispersion makes the energy transport by amide-1 vibrations rather ineffective. Davydov[1] suggested a mechanism by means of which the energy of hydrolysis of ATP can be localized and transferred without losses by a soliton wave. The main condition for the appearance of such a wave is the interaction between vibrational excitations and displacements of peptide groups as a whole (phonons). This is manifested by the dependence of the energy of the amide-1 vibration on the length of the hydrogen bridge joining neighboring peptide groups and makes the vibrations nonlinear. It gives rise to soliton waves which are the result of mutual compensation of the dispersion and nonlinearity.[1]

Much work has been done on numerical modeling of the propagation of solitons in DNA (Ref. 3). In most cases the numerical solutions of model dynamic equations have been obtained without allowance for the noise, which corresponds to the motion of solitons at absolute zero. The results of these investigations confirm the theoretical conclusions of Davydov. On the other hand, Lomdahl and Kerr[4] studied numerically the dynamics of a chain at normal biological temperatures and found that thermal noise destroys Davydov solitons. These results make it necessary to seek an alternative to Davydov solitons.

Our aim will be to demonstrate another possibility of appearance of soliton waves in DNA. We shall show that amide-1 vibrations are localized to form a nonlinear soliton wave due to intrinsic anharmonicity. Such soliton waves are characterized by a high thermal stability since the energy of an amide-1 vibrational quantum is an order of magnitude higher than a thermal quantum at 300 K and the interaction with phonons does not play an important role in their formation, in contrast to Davydov solitons.[5]

1. MODEL SYSTEM OF EQUATIONS

We shall consider a one-dimensional chain consisting of molecules of identical type, each of which has an internal degree of freedom. The transfer of vibrational excitation from one molecule to another occurs as a result of the dipole-dipole interaction. Its potential depends linearly on the dipole moment of each of the interacting molecules and it decreases rapidly with distance, which will make it possible to use the nearest-neighbor approximation. Bearing in mind this point, we shall write down the Hamiltonian of an infinite chain of identical dipoles in the form

$$H=\sum_{n=-\infty}^{\infty}\left[\frac{p_n^2}{2m}+U(x_n)-Qx_nx_{n+1}\right]. \tag{1.1}$$

Here, x_n is the length of a dipole; m is the effective mass of the vibrational degree of freedom; Q is the dipole-dipole interaction constant, which is positive if the dipole moments are excited along the line joining them. In the case of negative values of Q all the results given below remain valid if we transform the variables as follows: $x_n\to(-1)^n x_n$.

We shall assume that the amplitude of the molecular vibrations is low and expand the molecular potential $U(x)$ in powers of x. The simplest potential of this type allowing for the finite depth of the potential well is

$$U(x)=m\omega_0^2x_n^2/2-\alpha x_n^3-\beta x_n^4. \tag{1.2}$$

The term proportional to the third power of x describes the asymmetry of the potential well. It gives rise to a constant component of the vibrations and generation of the second harmonic, but it makes a small nonresonant contribution to the nonlinear frequency shifts (anharmonicity).[6] The role of anharmonicity is readily explained by assuming that $\alpha=0$ and avoiding difficulties of purely mathematical nature. Then, the potential of Eq. (1.2) becomes symmetric and has one stable equilibrium position at $x=0$ and two unstable positions at $|x|=r_{max}=(m\omega_0^2/4\beta)^{1/2}$, corresponding to decay of the bound state of the molecule.

The classical equations of motion for the Hamiltonian of Eqs. (1.1) and (1.2) are

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$$m d^2x_n/dt^2 + m\omega_0^2 x_n - 4\beta x_n^3 - Q(x_{n+1}+x_{n-1}) = 0. \qquad (1.3)$$

We shall find it convenient to use dimensionless quantities. We can obtain the relationship with the quantum characteristics of the system by employing the width of a wave packet of a harmonic oscillator in the ground state: $r_0 = (\hbar/m\omega_0)^{1/2}$ and by assuming that $x_n = r_0 b_n$, and $\tau = \omega_0 t$. Then, in terms of dimensionless variables, we obtain

$$d^2b_n/d\tau^2 + b_n - q(b_{n+1}+b_{n-1}) - 4gb_n^3/3 = 0, \qquad (1.4)$$

where

$$q = Q/m\omega_0^2, \quad g = 3\beta r_0^2/m\omega_0^2.$$

The constant g can be estimated from real spectra of isolated molecules since the frequencies of quantum transitions near the bottom of the well are given by the expression[7]

$$\Omega_{k,k-1} = (E_k - E_{k-1})/\hbar = \omega_0(1-gk). \qquad (1.5)$$

The continuum analog of Eq. (1.4) is what is known as the φ^4 equation

$$\partial^2\varphi/\partial\tau^2 - q\partial^2\varphi/\partial n^2 + (1-2q)\varphi - 4g\varphi^3/3 = 0. \qquad (1.6)$$

Pulses traveling at a constant velocity (solitary waves or kinks) and satisfying Eq. (1.6) are of the form

$$\varphi(n, \tau) = \pm(2/\varkappa)^{1/2}\,\mathrm{sech}\,[\theta(n - v\tau)] \qquad (1.7)$$

if

$$\varkappa = 4g/3\Omega_0^2, \quad \theta = \Omega_0(q - v^2), \quad \Omega_0^2 = 1 - 2q.$$

It is known that solutions of the (1.7) type are destroyed by collisions with one another and are unstable in the presence of small perturbations and, consequently, they are not solitons. Therefore, it is concluded in Ref. 8 that the φ^4 equation has no soliton solutions. However, we shall show below that Eq. (1.6) includes a class of solutions in the form of spatially modulated pulses (Fig. 1), the envelope of which can assume a stable soliton form.

2. EXCITONS AND SOLITONS

In the linear case (if $g = 0$) this system (1.4) is readily solved.[9] The general solution can be represented conveniently in the form of an expansion in normal vibration modes, which we can call single excitons. When a single exciton is excited, we have

$$b_n(\tau) = A_s \cos(k_s n - \Omega_{ex}\tau + \varphi_s), \qquad (2.1)$$

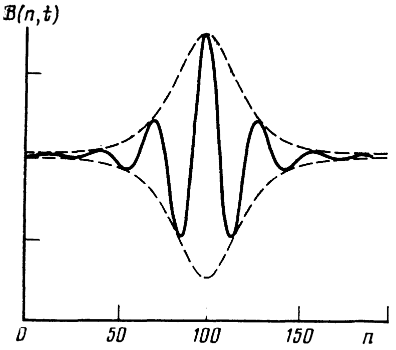

FIG. 1. Envelope soliton in a molecular chain.

where the frequency is described by $\Omega_{ex}^2 = 1 - 2q\cos k_s$ and the wave number is $k_s = 2\pi s/N$; $s = 0, 1, \ldots, N-1$ assumes exactly N values. All the molecules in the chain vibrate at the same amplitude. Exciton wave packets represent excitations which involve a finite number of molecules. Such excitations expand during propagation in a chain of harmonic oscillators and their amplitude decreases because of dispersion the faster and narrower are these excitations.

The situation is different in a chain of anharmonic oscillators. In an analysis of a nonlinear chain we shall use the fact that in the case of a weak nonlinearity and dispersion ($gb_n^2 \ll 1$, $q \ll 1$) the molecular vibrations are almost harmonic and we can introduce a complex vibration amplitude $a_n(\tau)$:

$$b_n(\tau) = 0.5[a_n(\tau)e^{-i\Omega\tau} + \text{c.c.}]. \qquad (2.2)$$

Substituting Eq. (2.2) into Eq. (1.4) and ignoring nonresonance terms, we obtain the following equation:

$$\frac{d^2a_n}{d\tau^2} - 2ia_n + (1-\Omega^2)a_n - q(a_{n+1}+a_{n-1}) - g|a_n|^2a_n = 0. \qquad (2.3)$$

In this section we shall be interested in fairly smooth excitations, covering several neighboring molecules, and we shall therefore use the continuum approximation in the form

$$a_{n\pm1} \approx \exp[ik(n\pm1)]\left(A \pm \frac{\partial A}{\partial n} + 0.5\frac{\partial^2 A}{\partial n^2}\right). \qquad (2.4)$$

Here, $A(n,\tau)$ is a real function which varies slowly with the number n and which depends in fact on one self-similar variable $\xi = n - n_0 - v\tau$. We then obtain from Eq. (2.3)

$$v = q\Omega^{-1}\sin k, \qquad (2.5a)$$

$$(q\cos k - v^2)\frac{d^2A}{d\xi^2} + (\Omega^2 - 1 + 2q\cos k - gA^2)A = 0. \qquad (2.5b)$$

We can regard the quantities ξ and A as time and the coordinate of an imaginary material point with a mass $m^* = q\cos k - v^2$. In this sense Eq. (2.5b) describes the path of such a point in a field of forces characterized by the potential

$$U(A) = gA^4/4 - (1 - 2q\cos k - \Omega^2)A^2/2. \qquad (2.6)$$

The solution satisfying the condition $A(\xi)\to 0$ in the limit $|\xi|\to\infty$ exists only for $\Omega^2 < 1 - 2q\cos k$, when the potential well described by Eq. (2.6) has two stable equilibrium positions separated by a maximum (Fig. 2). Such a path (separatrix) corresponds to the energy at the maximum of the potential and is described analytically by the law

$$A = A_0\,\mathrm{sech}\,\theta\xi. \qquad (2.7)$$

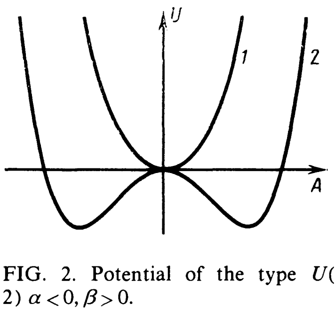

FIG. 2. Potential of the type $U(A) = \alpha A^2 + \beta A^4$: 1) $\alpha > 0, \beta > 0$; 2) $\alpha < 0, \beta > 0$.

The relationship of the frequency Ω and the reciprocal width θ of a soliton to its amplitude and wave number k follows from Eq. (2.5b):

$$\Omega^2=1-2q\cos k-gA_0^2/2, \tag{2.8a}$$

$$\theta^2=gA_0^2/2(q\cos k-v^2). \tag{2.8b}$$

In the case of complex amplitudes of the vibrations of molecules, we obtain the expression

$$a_n(\tau)=A_0\exp[ikn+i\delta]\operatorname{sech}[(n-n_0+v\tau)\theta], \tag{2.9}$$

where n_0 and δ are the arbitrary initial position and phase of a soliton.

We shall analyze the expressions obtained in the case of a discrete chain. The wave number k for this chain assumes the values between 0 and 2π, whereas k and $2\pi-k$ represent the waves traveling in opposite directions; consequently, it is sufficient to consider the range $0\leqslant k<\pi$. The reciprocal width θ can have real values in the range $0\leqslant k<\pi/2$. This is due to the fact that if $\pi/2<k<\pi$, the linear dispersion $D=0.5d^2\Omega_{ex}/dk^2\approx q\cos k$ becomes negative and the nonlinearity simply enhances its effect. In the remaining range of wave numbers the solution (2.9) is valid for the values of k which are not too close to $\pi/2$. This last requirement is the condition of validity of the continuum approximation: $\theta<1$.

The frequency of Eq. (2.8a) has real values for amplitudes less than the critical one $A_{max}\propto g^{-0.5}$. When the amplitude is $A_0\sim A_{max}$, the nonresonance terms dropped from Eq. (2.3) become important. The existence of the boundary amplitude is related to the possibility of decay of the bound state of molecules.

The constant quantity

$$N_0=0.5\sum_n|a_n|^2\approx\int_{-\infty}^{\infty}0{,}5|a_n|^2\,dn \tag{2.10}$$

represents the total number of vibration quanta $\hbar\omega_0$ excited in a chain and it assumes values each of which is a positive integer. The normalization condition of Eq. (2.10) yields a relationship between the width and amplitude of solitons:

$$A_0^2=N_0\theta. \tag{2.11}$$

For a given value of N_0 a soliton can be described by a single parameter which is the wave number k. An increase in k reduces the soliton width but increases the amplitude and velocity.

The soliton frequency is described by the approximate expression (valid if $N_0g<q\cos k\ll1$):

$$\Omega=1-q\cos k-g^2N_0^2/8q\cos k. \tag{2.12}$$

The exciton and soliton spectra are plotted in Fig. 3 for different values of N_0. For all possible numbers of the wave number k they are separated by an energy gap and the appearance of solitons in the investigated chain is favored by energy considerations.

We shall now consider the effects associated with a strong anharmonicity. If the number of excited vibrational quanta is large, the anharmonicity of molecular vibrations predominates over the dipole-dipole interaction of neighboring molecules and is the main process controlling the dynamics of vibrational excitations. At low values of the coupling constant q and anharmonicity g there is a range of amplitudes x in which the expansion of the potential (1.2) is still valid, but the continuum approximation can no longer be used, as the reciprocal soliton width (2.8b) becomes greater than unity. In this case practically the whole excitation is concentrated at one molecule and although it is comparable with a soliton in respect of its stability, the mobility of such an excitation is low. The low mobility of a localized excitation is due to the anharmonicity of the vibrations. In view of the large difference between the amplitudes of the vibrations of neighbors, the nonlinear frequencies of their vibrations differ strongly and, consequently, the dipole-dipole interaction becomes nonresonant and does not ensure excitation transfer. When the amplitude is even larger, the expansion (1.2) assumed for the potential is no longer valid, but in this case the dipole-dipole interaction becomes completely unimportant and the vibrations of a molecule can be regarded as free.

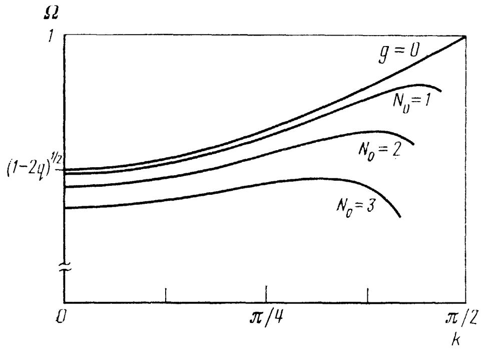

FIG. 3. Exciton (uppermost curve) and soliton spectra corresponding to $g=0.005$, $q=0.01$, and different numbers of excited quanta $N_0=1$, 2, and 3.

3. SOLITONS AT LOW VELOCITIES

In the preceding section we derived the nonlinear dispersion law for solitons and identified the ranges of the wave numbers k in which solitons can exist in a discrete chain. In practice, the majority of the initial perturbations are sufficiently smooth to correspond to low values of k. We shall analyze this case to a greater depth and compare the results with those obtained for thoroughly investigated systems. We shall show that at low values of the wave numbers and amplitudes of the molecular vibrations we can reduce Eq. (1.4) to the nonlinear Schrödinger equation.

We shall associate real quantities $b_n(\tau)$ with complex amplitudes $a_n(\tau)$ in accordance with the relationships

$$b_n=0.5(a_n+a_n^*),\qquad db_n/d\tau=-0.5i(a_n-a_n^*), \tag{3.1}$$

imposing on a_n an additional condition

$$da_n/d\tau+da_n^*/d\tau=-i(a_n-a_n^*). \tag{3.2}$$

Substitution of Eq. (3.1) into Eq. (1.4) subject to Eq. (3.2) gives

$$ida_n/d\tau-a_n+0{,}5q(a_{n+1}+a_{n-1}+\text{c.c.})$$
$$+{}^1/_6g(a_n^3+3|a_n|^2a_n+\text{c.c.})=0 \tag{3.3}$$

If $q=g=0$, the function $a_n(\tau)=a_n(0)\exp(-i\tau)$ is rapidly oscillating. Therefore, if $q\ll1$ and $g|a_n|^2\ll1$, we can separate[10] slow and fast motion, and adopt reduced equations

$$2(ida_n/d\tau-a_n)+q(a_{n+1}+a_{n-1})+g|a_n|^2a_n=0. \qquad (3.4)$$

At low soliton velocities corresponding to $k \ll 1$ the amplitude a_n varies slowly from molecule to molecule. In this case we can assume that

$$a_{n\pm1}\approx a_n\pm\partial a_n/\partial n+0{,}5\partial^2a_n/\partial n^2, \qquad (3.5)$$

so that after the substitution

$$a_n(\tau)=\exp[-i(1-q)\tau]\,\Psi(n,\ \tau) \qquad (3.6)$$

we can reduce Eq. (3.5) to the familiar nolinear Schrödinger equation:

$$2i\partial\Psi/\partial\tau+q\partial^2\Psi/\partial n^2+g|\Psi|^2\Psi=0. \qquad (3.7)$$

The soliton solution of the nonlinear Schrödinger equation is given by (2.9) if $v = qk$ and

$$2q\theta^2=gA_0^2, \quad \Omega=1-q+qk^2/2-gA_0^2/4. \qquad (3.8)$$

The same expressions can be obtained from Eq. (2.8) subject to the above approximations.

The relationships of Eq. (3.1) make it possible to determine the initial conditions for Eq. (3.7) and to investigate the dynamics of vibrational excitations in a chain of molecules allowing for the anharmonicity if the condition $k < 1$ is satisfied. The nonlinear Schrödinger equation is one of the classical equations for soliton physics.[11] Under given initial conditions its solution is found by the method of the inverse scattering problem. Any sufficiently strong excitation gradually decays into solitary waves, i.e., solitons (in particular, one soliton may form), which then propagate without a change in the velocity or shape and acquire only phase shifts as a result of collisions.

The nonlinear Schrodinger equation for the investigated system describes well the vibration at the fundamental frequency close to 1 (in dimensionless units) when the value of k is small. The exact solution of Eq. (1.4) includes vibrations of all the frequencies which are multiples of the fundamental frequency. However, the existence of overtones does not destroy a soliton. This is illustrated clearly by the analogy developed below with the sine-Gordon equation:

$$\partial^2u/\partial t^2-\partial^2u/\partial x^2+\sin u=0, \qquad (3.9)$$

which has been investigated in the theory of spin waves and in other field theories.[8]

The scaling transformation of the variables

$$t=\Omega_0\tau, \quad x=nq^{1/2}/\Omega_0, \quad B=\Omega_0(8g)^{-1/2}u$$

reduces Eq. (1.6) to the equation

$$\partial^2u/\partial t^2-\partial^2u/\partial x^2+u-u^3/6=0, \qquad (3.10)$$

which was obtained from Eq. (3.9) for low values of u. The properties of the solutions of Eqs. (3.9) and (3.10) are similar in the range $u \ll 1$.

One of the exact solutions of the sine-Gordon equation is a "breather" or a 0π pulse[11]:

$$u(x,\ t)=4\,\mathrm{arctg}\{A\cos(kx-\Omega t+\delta)/4\,\mathrm{ch}[\theta(x-x_0-vt)]\}, \qquad (3.11)$$

which describes a bound state of kinks (2π pulses) and has all the properties of a soliton. The exact dispersion relationships for a breather which follow from Eq. (3.9) are

$$\Omega^2=k^2+(1+A^2/16)^{-1}, \quad v=k/\Omega, \quad \theta=A\Omega/4. \qquad (3.12)$$

We can readily show that the parameters of a breather described by Eq. (3.12) reduce, like the solution (3.11), to the corresponding parameters of anharmonic solitons and solitons obtained as a result of solution of the nonlinear Schrödinger equation of Eq. (3.8) if A and k are small and scaling transformations are applied. The solution (3.11) contains all the overtones and is nevertheless a sign-Gordon soliton. A similar situation occurs also in the case of Eq. (1.4), because the sine-Gordon equation tends to Eq. (1.4) if $|u(x,t)| \ll 1$.

Therefore, the properties of a chain of anharmonic oscillators can be analyzed on the basis of two mutually complementary models. The information accumulated on the properties of physical systems described by the non-linear Schrödinger and sine-Gordon equations can, subject to certain restrictions, be used also to describe the influence of the anharmonicity on the propagation of vibrational excitations in long molecules.

4. SOLITONS AND PHONONS

In the above discussion the motion of molecules as a whole near their equilibrium positions in a chain ignored. In the α-helix model of a protein molecule the displacements of peptide groups alter the length of the hydrogen bond and this in turn affects the energy of the amide-1 vibration (modulation of the frequency ω_0) and the energy of the dipole-dipole interaction (modulation of Q). In the Davydov theory an allowance for these factors is of fundamental importance because it is the dipole-dipole interaction which is responsible for the stability of solitons. In our case the stability is ensured by the anharmonicity, but the coupling to phonons (although it does not play a decisive role) is responsible for a number of important differences which will be investigated below.

If we allow for the exciton-phonon interaction and anharmonicity, the Hamiltonian of a chain becomes

$$H=H_{ex}+H_{ph}+H_{int}, \qquad (4.1)$$

where

$$H_{ex}=0.5\sum_n[m(dx_n/dt)^2+m\omega_0^2x_n^2-2\beta x_n^4-2Qx_nx_{n+1}], \qquad (4.2a)$$

$$H_{ph}=0.5\sum_n[M(du_n/dt)^2+\varkappa(u_n-u_{n+1})^2], \qquad (4.2b)$$

$$H_{int}=\sum_n[f_1x_n^2(u_{n+1}-u_{n-1})+f_2x_nx_{n+1}(u_{n+1}-u_n)]. \qquad (4.2c)$$

Here, u_n is the displacement of the nth molecule, M is the mass of this molecule, $\varkappa$ is the rigidity of the chain and f_1 and f_2 are the exciton-phonon interaction constants (for a protein the value of f_2 is 68 times less than for f_1).

The Hamiltonians for the equation of motion considered in the approximation of slow amplitudes of Eq. (3.1) in terms of dimensionless variables yield

$$\hbar\omega_0(ida_n/d\tau-a_n)+J(a_{n+1}+a_{n-1})$$
$$+0,5\hbar\omega_0 g|a_n|^2a_n=\chi_1a_n(u_{n+1}-u_n)$$
$$+\chi_2[a_{n+1}(u_{n+1}-u_n)+a_{n-1}(u_n-u_{n-1})], \qquad (4.3a)$$
$$M\omega_0{}^2d^2u_n/d\tau^2-\varkappa(u_{n+1}-2u_n+u_{n-1})$$
$$=0.5\chi_1(|a_{n+1}|^2-|a_{n-1}|^2)+0.5\chi_2\,\mathrm{Re}[a_n{}^*(a_{n-1}-a_{n+1})]. \qquad (4.3b)$$

Here,

$$\chi_1=f_1r_0{}^2, \qquad \chi_2=f_2r_0{}^2/2, \qquad J=0,5r_0{}^2Q=q\hbar\omega_0/2.$$

If the soliton width is sufficiently large, its characteristics can be found in the continuum approximation:

$$a_{n\pm1}\approx\exp[ik(n\pm1)-i\Omega\tau](A\pm\partial A/\partial n+0,5\partial^2A/\partial n^2), \qquad (4.4a)$$
$$u_{n\pm1}\approx U\pm\partial U/\partial n+0,5\partial^2U/dn^2. \qquad (4.4b)$$

Assuming that $A(n,\tau)$ is a real function and that each mth derivative is a quantity of the mth order of smallness, we obtain—to within the second order of magnitude—the system

$$\hbar\omega_0\left(\frac{\partial A}{\partial\tau}+q\frac{\partial A}{\partial n}\sin k\right)=-\chi_2\sin k\left(\rho\frac{\partial A}{\partial n}+0.5A\frac{\partial\rho}{\partial n}\right), \qquad (4.5a)$$

$$2[\Omega-1+q\cos k+0,5gA^2+2(\chi_1+\chi_2\cos k)\rho/\hbar\omega_0]A$$
$$+q(\partial^2A/\partial n^2)\cos k=0, \qquad (4.5b)$$
$$\varkappa\partial^2\rho/\partial n^2-M\omega_0{}^2\partial^2\rho/\partial\tau^2=(\chi_1+\chi_2\cos k)\partial^2A^2/\partial n^2, \qquad (4.5c)$$

where $\rho = -\partial U(n,\tau)/\partial n$ is function representing the relative reduction in the distance.

If $\chi_2\neq0$, the system (4.5) does not have solutions of the solitary wave type

$$A(n,\tau)=A(\xi), \qquad \rho(n,\tau)=\rho(\xi), \qquad \xi=n-n_0-v\tau. \qquad (4.6)$$

The results of a numerical analysis[3] of the system (4.3) in the case when $g=0$ and the parameters are those of real proteins show that the influence of χ_2 on the properties of solitons is slight. This result follows from the system (4.5) if the number of excited quanta is sufficiently small, so that the right-hand side of Eq. (4.5a) can be ignored compared with the left-hand side. In this case, Eq. (4.5) admits an exact solution of the (4.6) type if $v = q\sin k$ and

$$\rho(\xi)=[(\chi_1+\chi_2\cos k)/\varkappa(1-s^2)]A^2. \qquad (4.7)$$

Here, $s=v/v_s$ and $v_s=(\varkappa/M\omega_0^2)^{1/2}$ is the dimensionless velocity of sound.

The amplitude $A(\xi)$ satisfies the ordinary differential equation

$$q(d^2A/d\xi^2)\cos k+[2(\Omega-1+q\cos k)+GA^2]A=0, \qquad (4.8)$$

which was investigated in Sec. 2. The previous results are valid also in this case when the anharmonicity g is replaced with a nonlinearity dependent on the soliton velocity and is described by

$$G=g+4(\chi_1+\chi_2\cos k)^2/\hbar\omega_0\varkappa(1-s^2). \qquad (4.9)$$

Using the parameters of the DNA molecule[3] $M=114m_p$, $\hbar\omega_0=0.205$ eV, $\varkappa=19\ N/m$, $\chi_1=34\times10^{-12}\ N$, $J=7.2$ cm^{-1} and $\chi_2=1\times10^{-12}\ N$, we find the second term in Eq. (4.9) is equal to 0.0072. The anharmonicity of the CO molecules is $g=0.006$, so that the two effects are of the same order of magnitude.

In this case solitons appear at such velocities that the nonlinearity described by Eq. (4.9) remains positive. In particular, if the exciton velocity $v_0=q$ is greater than the velocity of sound v_s, then a soliton can travel at a supersonic velocity ($s>1$). In this case it follows from Eq. (4.7) that local compression changes to dilatation.

In the case of Davydov and other types of solitons formed as a result of interaction of two extended vibrational subsystems this result is impossible. Therefore, for such systems the soliton velocity does not exceed the smaller of the two velocities v_s and v_0, since at high velocities the interaction destroys a soliton. It follows from Eq. (4.9) and the results of Sec. 2 that the anharmonicity of molecular vibrations imparts to a soliton an additional stability margin in the case of the interaction with phonons and conserves the properties of this soliton when this interaction is no longer active.

In the α-helix model of the DNA the velocity of sound is twice as high as the exciton velocity and this effect is not manifested, but supersonic solitons are possible in other quasi-one-dimensional systems.

CONCLUSIONS

We investigated a one-dimensional chain of anharmonic oscillators. We found that soliton waves of a vibrational excitation appear in such a chain and we determined the parameters of these waves. We studied the relationship between the investigated chain system and completely integrable models based on the nonlinear Schrödinger and sine-Gordon equations. In our opinion this problem is interesting because many quasione-dimensional systems of different physical nature, exhibiting nonlinearity and dispersion within some framework, can be described by equations of the type (2.3) or (4.3). Therefore, the model of a chain of anharmonic oscillators is fairly general and deserves study.

By way of example, we investigated amide-1 vibrations in an α-helical protein molecule, which is a system of considerable theoretical importance. The absence of accurate data on the anharmonicity of these vibrations did not allow us to find the actual values of the parameters of soliton waves in a protein, but we derived formulas which can be used to do this. Rough estimates made in Sec. 4 indicate that the anharmonicity of such systems has to be allowed for together with the exciton-phonon interactions, and that allowance for the anharmonicity gives rise to new effects, such as, for example, supersonic propagation of soliton waves.

Our aim was to stimulate interest of experimentalists in the effects of a weak anharmonicity in quasi-one-dimensional systems. A direct experimental confirmation of the existence of soliton waves in long linear molecules may be provided by a study of the vibrational spectra of such systems. This is supported by experiments on acetanilide[12] but the anharmonicity was not allowed for in these experiments.

A study of the vibrational spectra may require investigation of the corresponding quantum-mechanical models. It should be pointed out that excitations which are called excitons in the present study describe one of the optical branches of phonons in real polymers. A self-consistent quantum-mechanical description of the anharmonicity of molecular vibrations[13] shows that the formation of bound states of two phonons (biphonons) and larger phonon complexes is possible and the existence of the latter has been confirmed experimentally. It is shown above that in the classical context they represent soliton waves.

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