Multiphonon states of a one-dimensional chain with anharmonicity

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The effect of anharmonicity on the spectrum of the vibrational excitations in a one-dimensional chain of interacting quantum anharmonic oscillators is investigated theoretically. The problem is reduced to that of determining the wave functions of a many-particle system of lattice phonons with point interaction As a result of solving the Schrödinger equation it is predicted that complexes of bound phonons are formed, and for these complexes the spatial width, exact dispersion law, and effective mass are determined. The question of the relation of the multiphonon complexes to the anharmonic solitons that arise in the given model in the classical limit is considered. It is demonstrated that the parameters of the solitons and the complexes coincide. The time after which the soliton is subjected to quantum-mechanical dispersion is determined. The results of the paper can be be used to describe interacting bosons in quasi-one-dimensional systems, both in continuous space and for a lattice.

The quantum theory of the elementary excitations of crystals is based historically on the concept of noninteracting quasiparticles. This has led to the appearance and formulation of the concepts of "electron in a crystal," "phonon," "exciton," and "magnon." These ideas have turned out to be very convenient in the analysis of the properties of solids, and time itself has proved their usefulness. However, the further development of the theory of solids has required that the interactions between quasiparticles be taken into account. Certain phenomena in solids can be explained only by invoking such concepts as "polaron," "polariton," "Cooper pair," "biexciton," and "biphonon." In the latter case we are concerned with a two-phonon bound state that arises as a result of the anharmonicity inherent in the vibrations of the crystal lattice. A detailed investigation of the properties of biphonons can be found in a review (Ref. 1). The biphonons predicted theoretically were later discovered in experiments in the study of the infrared spectra of molecular crystals and the spectra of the Raman scattering of light by polaritons. Allowance for the anharmonicity turned out to be important in the determination of the widths of the bands of two-phonon states, the magnitude of the dispersion, the presence of gaps in the polariton spectra, and also the contributions of the biphonons to the nonlinear susceptibilities of the crystals. With regard to the prospects for further investigations, the authors of Ref. 1 point to three-phonon and more-complicated phonon complexes, the study of which has already begun in Refs. 2 and 12. In the opinion of the authors of Ref. 1, the study of biphonons in one-dimensional and two-dimensional systems may be of great interest.

In the present paper we shall investigate the multiphonon states that arise in a one-dimensional chain of molecules. The study of this system also has a further aim—the quantization of solitons. In Ref. 4 it was shown that in a one-dimensional chain of interacting molecules, when the anharmonicity of the intramolecular vibrations is taken into account, solitary waves of vibrational excitations, i.e., wave packets that do not change their shape with time as they propagate along the chain, are formed. However, this phenomenon arises only in a classical description of the system, i.e., it is assumed that the number of vibrational quanta excited in the chain is sufficiently large. But what will happen in the chain if the number of vibrational quanta is small? In this case the classical description of the vibrational degrees of freedom of the molecules becomes incorrect and it is necessary to invoke the quantum formalism. To answer this question it is necessary to make use of the Hamiltonian of an anharmonic soliton chain and to quantize the variables appearing in this Hamiltonian. The resulting problem turns out to be equivalent to the problem of the multiphonon complexes in a one-dimensional system.

At the beginning of the paper we formulate the principal features of the model and the physical content of its parameters. The Schrödinger equation for the wavefunction of the multiphonon states is obtained, a method of approximate construction of all the wave functions of the system is indicated, and the energy states of the system are found. In Sec. 3 a discussion of the distinctive features of the resulting quasiparticle-dispersion laws, both in the discrete and in the continuum case, can be found. The last two sections are devoted to a comparison of the properties of solitons and multiphonon complexes, and to the related question of the correspondence of the quantum and classical properties of the chain.

1. DESCRIPTION OF THE MODEL

The physical system under investigation is a one-dimensional lattice with molecules firmly attached at the sites, each molecule having an internal vibrational degree of freedom. We assume that the vibrations of the molecules are sufficiently well described by the anharmonic-oscillator approximation, i.e., the dependence of the energy of a vibrational level on its number N is determined by the well known formula[5]

$$E_N = (\hbar\omega_0 + G/2)N - GN^2/2, \tag{1}$$

where $G = 2\hbar\omega_0 - E_2$ is the anharmonicity energy, and $\hbar\omega_0$ is the energy of the basic vibrational quantum. The Hamiltonian of such an oscillator in the second-quantization representation can be obtained from the expression (1) by replacing the level number N by the operator $\hat{N} = A^+A$ of the number of quanta:

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$$\hat{H}_0=(\hbar\omega_0+G/2)A^+A-0{,}5GA^+AA^+A. \qquad (2)$$

Between neighboring molecules there is an interaction which permits them to exchange molecular-vibration quanta. The role of this interaction can be played by the dipole-dipole interaction between the dipole moments induced in the molecules as a result of the vibrations. The operator of this interaction between the nth and $(n+1)$th molecules has the form

$$\hat{U}_{n,n+1}=Q(A_n^+A_{n+1}+A_nA_{n+1}^+), \qquad (3)$$

where Q is the matrix element corresponding to the transition of one quantum from one molecule to another. Finally, the model Hamiltonian takes the following form:

$$\hat{H}=\sum_{n=-\infty}^{\infty}\Big[\hbar\omega_0A_nA_n - \frac{1}{2}GA_n^+A_n^+A_nA_n-Q(A_n^+A_{n+1}+A_nA_{n+1}^+)\Big]. \qquad (4)$$

The dimensionless operators A_n^+ and A_n obey commutation relations of the Bose type.

Before determining the spectrum of the Hamiltonian (4), we shall consider particular cases in which the spectrum can be found easily. The one-dimensional crystal under investigation goes over into a set of unbound molecules in the limit $Q=0$. In this case the spectrum of the elementary excitations of the system consists of the set of quanta given by the expression (1). As the energy increases we get one-quantum and then two-quantum excitations concentrated on one molecule, two-quantum excitations on different molecules, three-quantum excitations on one molecule, and so on (Fig. 1). The levels form groups characterized by an equal number of excited quanta. Each level is multiply degenerate and, when the interaction is "switched on," undergoes splitting into a phonon band characterized, in addition, by a certain set of phonon wave numbers.

Another limiting case is the absence of anharmonicity. For $G=0$ the Hamiltonian becomes quadratic in the creation and annihilation operators of the vibrational quanta and is diagonalized by going over to creation operators of phonons with a certain value of the wave number:

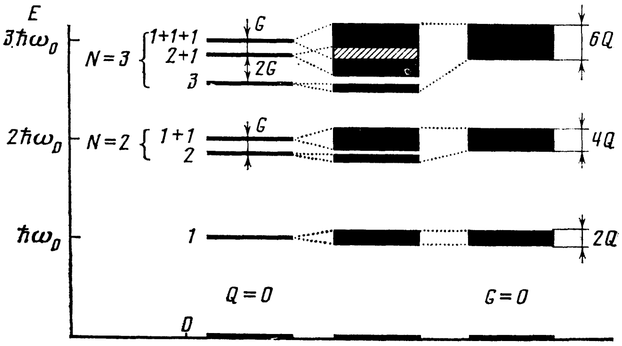

FIG. 1. Diagram of the energy levels of a chain of anharmonic oscillators. The limiting cases of unbound oscillators ($Q=0$) and chains of harmonic oscillators ($G=0$) are also illustrated.

$$A_n=(2\pi)^{-1/2}\int_{-\pi}^{\pi}B_ke^{ikn}\,dk,\qquad B_k=(2\pi)^{-1/2}\sum_{n=-\infty}^{\infty}A_ne^{-ikn}. \qquad (5)$$

The Hamiltonian in this case decomposes into a sum of Hamiltonians of the individual phonons:

$$\hat{H}_{G=0}=\int_{-\pi}^{\pi}(\hbar\omega_0-Q\cos k)B_k^+B_k\,dk. \qquad (6)$$

If in such a system several phonons are excited, the energy in the chain is equal to the sum of the energies of the individual phonons:

$$E_N(k_1,k_2,\ldots,k_N)=\sum_{s=1}^{N}(\hbar\omega_0-Q\cos k_s)=\sum_{s=1}^{N}E_1(k_s). \qquad (7)$$

The latter relation is a direct indication that for $G=0$ the quasiparticles (phonons) are noninteracting, and this property, like the relation (7), is violated when the anharmonicity is taken into account.

Turning to the determination of the spectrum of the Hamiltonian (4), we note that this Hamiltonian commutes with the operator of the total number of quanta

$$\hat{N}=\sum_{n=-\infty}^{\infty}A_n^+A_n. \qquad (8)$$

This implies that the wave functions of the stationary states of the Nth group of levels can be sought conveniently in the form of an expansion in functions with a definite number of vibrational quanta:

$$|N\rangle=\sum_{n_1,\ldots,n_N}\Phi_{n_1,\ldots,n_N}A_{n_1}^+A_{n_2}^+\ldots A_{n_N}^+|0\rangle, \qquad (9)$$

where $|0\rangle$ is the ground state of the chain.

We note that only those functions Φ that do not change on interchange of any pair of numbers have physical meaning, since the asymmetric part in the summation (9) drops out by virtue of the Bose commutation relations and does not make a contribution to the actual wavefunction. In this form we have here the principle of indistinguishability of phonons.

After substituting (9) into the time-independent Schrödinger equation we obtain

$$\Big[E_N-N\hbar\omega_0+G\sum_{r>s=1}^{N}\delta_{n_r,n_s}\Big]\Phi_{n_1\ldots n_N} + \frac{Q}{2}\sum_{s=1}^{N}[\Phi_{n_1\ldots n_s+1\ldots n_N}+\Phi_{n_1\ldots n_s-1\ldots n_N}]=0, \qquad (10)$$

where $\delta_{n,r}$ is the Kronecker δ-symbol. Our problem is to determine the spectrum of the eigenvalues and eigenfunctions for arbitrary Q and G.

2. DERIVATION OF THE WAVE FUNCTIONS

We shall elucidate the physical content of Eq. (10). The coupling Q of the oscillators leads to the appearance of a term in the form of a second-order difference derivative with respect to the coordinate n_s. If we consider functions Φ that are slowly varying with the number n_s, this term can be replaced by the second partial derivative with respect to the coordinate n_s; consequently, this operator is analogous to the operator of the momentum squared. The term associated with the anharmonicity has the form of an interaction potential that is nonzero only when the coordinates of the particles coincide. This implies that the general equation (10) describes a gas of N bosons with a point interaction potential, with the coordinates of the particles taking a discrete series of values.

Turning to the determination of the solutions of Eq. (10), we make use of the fact that the interaction potential is equal to zero when the particle coordinates do not coincide. At points where this is the case, the equation has the form of the Schrödinger equation for free particles, and its solution will be a set of plane waves. One of these regions will be $n_1 > n_2 > ... > n_N$, and in this region we choose a solution in the form of one wave, characterized by a set of wave numbers k_1, k_2,..., k_N:

$$\Phi_{n_1>n_2>\ldots>n_N}=\exp\left[i(k_1n_1+k_2n_2+\ldots+k_Nn_N)\right]. \qquad (11)$$

The wave function (11) corresponds to the energy

$$E_N=N\hbar\omega_0-Q\sum_{s=1}^{N}\cos k_s. \qquad (12)$$

We shall find the conditions for joining of the wave function with the solutions in other regions. The latter solutions should correspond to the same energy eigenvalue E_N. Therefore, the plane waves that appear in the solution can differ from (11) only in the ways in which the set of wave numbers $(k_1, k_2,..., k_N)$ is arranged in their products with the coordinates $n_1, n_2,..., n_N$. The number of possible combinations is reduced considerably if we take account of the continuity condition, which consists in the fact that the expressions obtained for the wave function in, e.g., the regions $n_1 > n_2 > ... > n_N$ and $n_2 > n_1 > ... > n_N$ should give the same result for $n_1 = n_2$. Thus, for (11) in the region $n_2 > n_1 > ... > n_N$ the solution will contain only two plane waves, differing in the arrangement of the quasimomenta k_1 and k_2:

$$\Phi_{n_2>n_1>\ldots>n_N}=A\exp\left[i(k_1n_1+k_2n_2+\ldots+k_Nn_N)\right]$$
$$+B\exp\left[i(k_2n_1+k_1n_2+\ldots+k_Nn_N)\right], \qquad (13)$$

where $A + B = 1$. The second equation for the coefficients A and B can be obtained from Eq. (10) itself, considered for the case $n_1 = n_2$. The coefficients A and B turn out to depend only on the momenta k_1 and k_2:

$$A(k_1, k_2)=1-B(k_1, k_2)=1+i\varepsilon/(\sin k_2-\sin k_1); \qquad (14)$$

here $\varepsilon = Q/G$ is the relative anharmonicity.

The joining coefficients obtained make it possible to determine the wave function in all regions.

However, the wave function obtained will be approximate, since it does not satisfy Eq. (10) on lines on which the coordinates of three or more particles coincide. Nevertheless, this approximation leads to qualitatively correct, physically noncontradictory, and quantitatively reliable results. It is straightforward to show that in this approximation the wave function has the form of the Bethe ansatz,[6] as for exactly integrable many-particle problems. In the weak-anharmonicity case of interest to us ($\varepsilon \ll 1$), the model under investigation is close to being exactly integrable, and this makes it possible to select this approximation.

The wave function (11) describes a bound state of all N particles, with complex quasimomenta, and is already symmetric by construction. In order that the energy remain real for complex $k_s = k_s' + ik_s''$, it is necessary that the orthogonality condition

$$\sum_{s=1}^{N}\sin k_s'\,\mathrm{sh}\,k_s''=0 \qquad (15)$$

be fulfilled. Then the energy is calculated from the formula

$$E_N=N\hbar\omega_0-Q\sum_{s=1}^{N}\cos k_s'\,\mathrm{ch}\,k_s''. \qquad (16)$$

For complex quasimomenta the wave function should remain finite. In the region $n_1 > n_2 > ... > n_N$ the coordinates n_1 and n_2 can increase without limit while leaving $n_1 > n_2$. In order that the wave function not increase when this happens, the conditions $\mathrm{Im}(k_1) > 0$ and $\mathrm{Im}(k_1) > \mathrm{Im}(k_2)$ must be fulfilled. Taking these relations into account in the region $n_2 > n_1 > ... > n_N$ and requiring that the wave function be finite when $n_2 \to \infty$, we obtain the condition $A(k_1, k_2) = 0$ Using analogous arguments for the transition into each region $n_{s+1} > n_s$, we arrive at the system of equations $A(k_s, k_{s+1}) = 0$, or

$$\sin k_s-\sin k_{s+1}=i\varepsilon, \qquad s=1, 2, \ldots, N-1, \qquad (17)$$

which determines the energy of the bound state of all N particles.

From the form of the system (17) we readily note that the quantities $\sin k_s$ form an arithmetic progression with step $i\varepsilon$. It is not difficult to express these quantities in terms of the first term $\sin k_1$ of the progression.

To determine this term it is necessary to make use of the orthogonality condition (15), which can be satisfied by selecting the wave numbers in a symmetric manner: $k_s^* = k_{N+1s}$. The solution of the system in this case depends on just one real parameter $k = \mathrm{Re}(k_1)$. Going over to real quantities, we obtain the solution of the system (15), (17) in the form

$$\cos k_s'\,\mathrm{sh}\,k_s''=\varepsilon(N+1-2s)/2=\varepsilon_s, \qquad (18a)$$

$$\sin k_s'\,\mathrm{ch}\,k_s''=\sin k_1'\,\mathrm{ch}k_1''=R(k), \qquad s=1, 2, \ldots, N/2. \qquad (18b)$$

From the latter expressions, by eliminating, e.g., k_s'', it is not difficult to obtain the quantities determining the energy (16):

$$\cos^2 k_s'=0{,}5[1-R^2-\varepsilon_s^2+[(1+R^2+\varepsilon_s^2)^2-4R^2]^{1/2}], \qquad (19a)$$

$$\mathrm{ch}^2 k_s''=2R/[1+R^2+\varepsilon_s^2-[(1+R^2+\varepsilon_s^2)^2-4R^2]^{1/2}]. \qquad (19b)$$

The analytical expressions obtained for the energy of the bound state of N quasiparticles describe, in fact, the entire spectrum of the system. States in which groups of N_s particles are bound can be constructed analogously, and for each group of particle quasimomenta a system of equations of the form (15), (17) arises. Therefore, the general expression for the energy bands of the system has the form

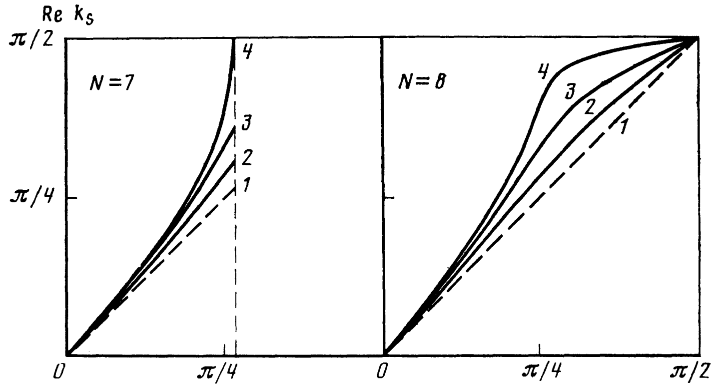

FIG. 2. Dependence of the real parts of intermediate wave numbers of a complex on its momentum $k = \mathrm{Re}k_s$ for an even ($N = 8$) and an odd ($N = 7$) complex for $\varepsilon = 0.2$. The numbers label curves corresponding to intermediate wave numbers k_s with different labels $s = 1, 2, 3, 4$.

$$E_N(k_1, N_1; k_2, N_2; \ldots; k_L, N_L) = \sum_{s=1}^{L} E_{N_s}(k_s), \qquad \sum_{s=1}^{L} N_s = N \tag{20}$$

and expresses the absence of residual interaction between complexes of bound particles.

3. BAND STRUCTURE IN THE CONTINUUM AND LATTICE MODELS

We shall ascertain the values of the wave number k for which a bound state can be formed. For a chain, k varies in the range from π to π, but we shall consider only positive values, since the spectrum is symmetric because of the equivalence of the two directions along the chain. By assumption, $\mathrm{Im}(k_1) > 0$. From (18a) for $s \neq 1$ it follows that this is possible in the region $|k| < \pi/2$ if $\varepsilon > 0$, and in the region $\pi/2 < |k| < \pi$ if $\varepsilon < 0$, which coincides with the conditions for the appearance of solitons.[4] The coupling constant Q appears in all the equations in the combination $Q \cos k$, and the coupling changes its character in accordance with whether the vibrations of neighboring molecules are in phase or π out of phase. Therefore, in the discrete case, in contrast to the continuum case, bound states arise for all signs of the constants Q and G. Below we confine ourselves to considering the case when $Q > 0$ and $G > 0$.

The calculations show that in the case of an even number of particles the system (18) has solutions for all values of the parameter k in the interval from $\pi/2$ to $\pi/2$, while for odd N there exists a certain value $k_{\max}$ above which the system is incompatible (Fig. 2). For $k > k_{\max}$ it is not possible to satisfy the equation for the intermediate quasimomentum with number $(N + 1)/2$. The value of k at which this happens can be found easily from the system (18) if we take into account that $k'_{(N+1)/2} = 0$ and $k''_{(N+1)/2} = \pi/2$:

$$\sin^2 k_{max} = 1 + \varepsilon^2 p^2/2 - \varepsilon p[\varepsilon^2 p^2/4 + 1]^{1/2}, \qquad N = 2p + 1. \tag{21}$$

With increase of N and ε the region of admissible values of k for the odd complexes becomes narrower. It is evident that a pair potential cannot always bind an odd number of particles.

In Fig. 3 one can trace the characteristic changes that occur in the dispersion law of even and odd complexes with increase of the relative anharmonicity $\varepsilon = G/Q$. For even complexes the dispersion law has a mildly sloping part adjacent to the value $k = \pi/2$, the width of which grows with increase of ε. We note that this part corresponds to the excitation of heavy quasiparticles of low mobility. For odd complexes the mildly sloping part is absent because of the cutoff of the spectrum at $k > k_{\max}$. In both cases the width of the band of bound states decreases, albeit differently, with increase of the anharmonicity. The width of an odd band never becomes smaller than the half-width of the one-particle band, while the even bands narrow to zero (Fig. 4).

Of special interest is the continuum approximation, for which various authors[7] have already obtained, for the analogous problem, a solution with which our result can be com-

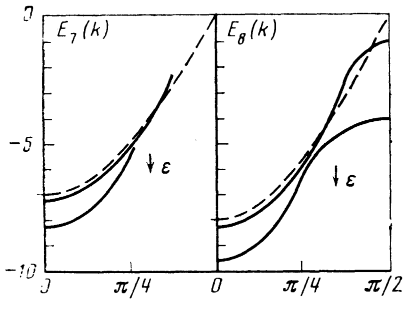

FIG. 3. Variation of the dispersion laws of an even ($N = 8$) and an odd ($N = 7$) complex with increase of the relative anharmonicity ($\varepsilon = 0$; 0.05; 0.02). The energy values are reckoned from the quantity $N\hbar\omega_0$, and Q is taken as the unit of energy. The arrow indicates the order of the curves with increase of ε.

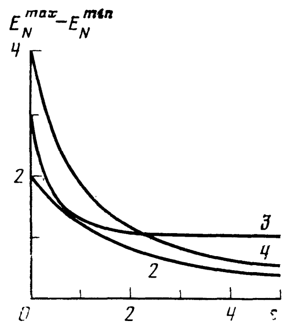

FIG. 4. Decrease of the bandwidth of a complex with increase of the relative anharmonicity. The half-width Q of the one-particle band is taken as the unit of width of the band. The numbers label curves corresponding to different $N = 2, 3, 4$.

pared. This comparison illustrates that our chosen approximation for the wave function is more accurate the smaller ε.

In order to convince ourselves that the problem under investigation is one for which the continuum limit can be taken, we shall consider wave functions that vary slowly with change of the discrete coordinates n_s. This is possible if all the wave numbers are small in magnitude: $|k_s| \ll 1$, which gives the following conditions for the transition to the continuum:

$$|k| \ll 1, \quad \varepsilon N \ll 1. \tag{22}$$

When the conditions (22) are fulfilled, in the system (15), (17) we can replace all the trigonometric and hyperbolic functions by their arguments, and in this case we obtain for the wave numbers the formulas of the continuum theory:

$$k_s'=k, \quad k_s''=\varepsilon(N+1-2s)/2, \quad s=1, 2, \ldots, N, \tag{23}$$

and for the dispersion law the expression

$$E_N(k)=N\hbar\omega_0+NQk^2/2-NG^2(N^2-1)/24Q. \tag{24}$$

The dependence of the energy on the wave number has the form of the dispersion law of the free particle, and this particle is the complex of bound phonons.

The last term in (24) is the binding energy of the particles in the complex, and has a cubic dependence on the number of particles. An analogous result was obtained in Ref. 7. In the discrete model the binding energy of the particles in the case of strong anharmonicity, as follows from (16) and (19) for $\varepsilon \gg 1$, is proportional to the square of the number of particles:

$$E_N(0)=N\hbar\omega_0 - Q\sum_{s=1}^{N}[1+\varepsilon^2(N+1-2s)^2/4]^{1/2} \approx N\hbar\omega_0-GN^2/4. \tag{25}$$

This result agrees with the unbound-oscillator limit (1), but the correction for the anharmonicity is smaller by a factor of 2. Thus, in this, worst case, our approximation gives a qualitatatively correct result.

To conclude this section we shall consider the mutual disposition of the bands of free and bound states. If the anharmonicity is set equal to zero, the imaginary parts of the wave numbers (23) will vanish and the real parts will be equal. Then the bound-state wave function (11) goes over into a wave function of free particles with equal momenta. Therefore, when the anharmonicity is "switched on" the bound states split off from the band of free states along the line in momentum space on which the momenta of the quasiparticles are equal (Fig. 5). From the physical point of view, this is obvious: Particles moving with different velocities interact for a limited time and therefore cannot form a complex.

The continuum and lattice models have many differences in the structure of the bound states. The most important and decisive difference is the restriction on the range of variation of the wave number for the chain, a consequence of which is the sharply expressed band structure of the spectrum. The restrictions (22) are the conditions for applicability of the continuum model to the description of a discrete chain, but not of the continuum model itself. In the latter the wave number is unrestricted, and therefore the width of each band is infinite (see (24)). The main property unifying the two models is the fact of the appearance of bound states of particles; in the lattice model, unlike the continuum model, bound states arise for all signs of the constants Q and G.

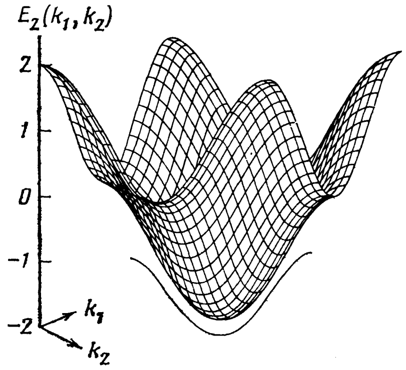

FIG. 5. The arrangement of the band of biphonons with respect to the band of free phonons in configurational momentum space is shown for the example of a band of two-particle states. The units of measurement of the energy correspond to those in Fig. 3.

4. SOLITONS AND MULTIPHONON COMPLEXES

Our solution of the quantum problem of multiphonon complexes makes it possible to compare their characteristics with the parameters of solitons. For this we shall need certain characteristics of anharmonic solitons, the detailed derivation of which can be found in Ref. 4.

In the classical description of a chain of oscillators the quantity A_n is a dimensionless complex number, the modulus of which is equal to the amplitude of the vibrations of the nth molecule, divided by the amplitude of the zero-point quantum fluctuations. In this case, from the Hamiltonian (4) we obtain the equations of motion of the vibrational excitations in the form

$$i\hbar dA_n/dt=\partial H/\partial A_n^* \rightarrow i\dot{A}_n-A_n+0{,}5q(A_{n+1}+A_{n-1}) +g|A_n|^2A_n=0. \tag{26}$$

Here we have introduced the dimensionless time $\tau=\omega_0 t$, dimensionless coupling $q=Q/\hbar\omega_0$, and dimensionless anharmonicity $g=G/\hbar\omega_0$.

Equation (26) is the difference analog of the well known nonlinear Schrodinger equation (NSE), and was the second equation to be integrated by means of the method of the inverse scattering problem (ISP).[8] Despite the outward simplicity of Eq. (26) and its similarity to the NSE, to our knowledge nobody has yet obtained its exact one-soliton solution. Therefore, to determine approximate solutions we shall make use of the continuum approximation in a form that takes maximum account of the discrete properties of the chain:

$$A_{n+s}(\tau)=\exp[ik(n+s)](1+s\partial_n+{}^1/_2 s^2\partial_n^2)A(n, \tau), \quad s=0, \pm 1. \tag{27}$$

The difference equation (26) is replaced by a partial differential equation, the one-soliton solution of which will have the form

$$A(n, \tau)=A_0 \exp(-i\Omega\tau) \operatorname{sech} [\theta(n-n_0-v\tau)]. \qquad (28)$$

The soliton velocity v, amplitude A_0, and frequency Ω are related to the basic parameters (the wave number k and inverse half-width θ) by

$$\Omega=1-(1+\theta^2/2) q \cos k, \quad v=q \sin k, \quad A_0^2=\theta^2 q \cos k/g. \qquad (29)$$

The energy stored in the chain when one soliton is excited in it can be calculated by substituting the solution (28) into the expression for the Hamiltonian:

$$E=\hbar\omega_0 \int_{-\infty}^{\infty} [(1-q \cos k) |A|^2-0,5g|A|^4+0,5q \cos k |\partial_n A|^2] dn$$
$$= 2A_0\theta^{-1}[\hbar\omega_0-(1+\theta^2/6) Q \cos k]. \qquad (30)$$

In the classical case the soliton amplitude A_0 and, with it, the energy E take a continuous series of values. In accordance with the rules of quasiclassical quantization we shall require that the number of quanta bound in the soliton take integer values. This requirement leads to a further relation:

$$N=\int_{-\infty}^{\infty} |A(n, \tau)|^2 dn=2A_0\theta^{-1}. \qquad (31)$$

If for the basic parameters of the soliton we take the number of quanta N and the wave number k, the parameters we need (the energy and inverse half-width) will be expressed as

$$\theta=GN/2Q \cos k, \qquad (32a)$$

$$E_N=N\hbar\omega_0-NQ \cos k-N^3G^2/24Q \cos k. \qquad (32b)$$

In order to compare the energy and width of the soliton with those of the complex, in the system (17) determining the dispersion law of the complex it is necessary to make use of a suitable continuum approximation. The first step will be to assume that the real parts of all the intermediate quasimomenta are the same and equal to k. Then for the dispersion law and the imaginary parts of the wave numbers we obtain

$$\operatorname{sh} k_s''=G(N+1-2s)/2Q \cos k, \quad s=1, \ldots, N, \qquad (33a)$$

$$E_N=N\hbar\omega_0-\sum_{s=1}^{N} [Q^2 \cos^2 k+G^2(N+1-2s)^2/4]^{1/2}. \qquad (33b)$$

These expressions, as calculations have shown, approximate the dispersion law rather well, and are therefore useful for various applications. To obtain the continuum approximation that we need, in the formula (33b) we must expand the square root, assuming $\cos k$ to be larger than the second term under the root:

$$E_N=N\hbar\omega_0-NQ \cos k-N(N^2-1) G^2/24Q \cos k. \qquad (34)$$

For large N the expression obtained for the energy differs insignificantly from the quasiclassical formula (32b).

The multiphonon complexes, like the solitons, have a characteristic size, which is determined by the rate with which the wave function falls off with increase of the coordinates of the quasiparticles. It is obvious that this rate is determined by the imaginary part k_1'' of the wave number multiplying the largest of the coordinates in the expression (11) for the bound-state wavefunction. For this quantity we obtain from (33a) for $s = 1$ an expression close to (32a) for small k_s'' (only for small k_s'' is the continuum approximation that we used above valid).

The above-demonstrated coincidence of the parameters of the solitons and the multiphonon complexes, which proves that they have the same origins, has a deep mathematical nature. By means of the ISP method one can show that the soliton variables diagonalize the Hamiltonian and are therefore normal coordinates of the action-angle type for the corresponding nonlinear wave equations. In view of this the result that is obtained upon quantization of the original variables (as has been done in the present paper) should not differ substantially from the result of quasiclassical quantization of the soliton variables. In Ref. 9 this conclusion was confirmed, but the spatial widths of the soliton and complex were not compared. The classical equations (26) of the dynamics of the chain have not yet been integrated by the ISP method. In the present paper it is shown that the wave function of the corresponding quantum problem differs from the general (for exactly integrable problems) form of the Bethe ansatz. This tells us that the anharmonic chain is not a completely integrable system, but, as shown above, soliton behavior of the waves in this system is possible for weak anharmonicity.

5. THE CORRESPONDENCE PRINCIPLE IN THE THEORY OF SOLITONS

The question of the correspondence of the classical and quantum-mechanical descriptions in the theory of solitons is far from exhausted by the coincidence of the parameters of the solitons and the complexes. In this approach the dynamical properties of the solitons, which alone make the soliton a soliton, remain outside the framework of the discussion. In fact, according to the generally accepted definition,[10] a soliton is a nonlinear wave that does not change its shape with time or during propagation, and, after collision with other solitons, experiences only phase shifts. According to this definition, a soliton is a purely dynamical phenomenon, and, therefore, a complete resolution of the correspondence principle must be sought in an analysis of the classical and quantum dynamics of the propagation of vibrational excitations along the chain. Without claiming an exhaustive investigation of this question, we shall give an account of the general conclusions that follow from the theory developed above.

We begin the study of the dynamical properties of the chain with an analysis of the linear systems. Complete and exhaustive information on the dynamics of the linear (with $G = 0$) equation (26) is contained in its Green function, in terms of which the solution is expressed as

$$A_n(\tau)=\sum_{n_0} G(n, \tau | n^0, 0) A_{n^0}(0). \qquad (35)$$

It is obvious that the Green function is the solution of the linear equation with an initial condition of the type $A_n(0) = \delta_{n,n^0}$, i.e., describes the spreading of a localized excitation.

The general expression for the Green function in terms of the set of normalized eigenfunctions of the equation is known to have the form

$$G(n, \tau | n^0, 0)=\int \chi_n^k \chi_{n^0}^{k*} \exp(-i\Omega_k\tau) dk, \qquad (36)$$

where Ω_k is the frequency (energy) eigenvalue and k is the set of eigenvalues characterizing the eigenfunction χ_n^k. For Eq. (26) with $G = 0$ the set of eigenfunctions has the form

$$\chi_n^k=(2\pi)^{-1/2}\exp(ikn), \quad \Omega_k=1-q\cos k, \quad -\pi<k<\pi. \tag{37}$$

Taking these expressions into account we obtain for the Green function an integral expressed in terms of Bessel functions[11]:

$$G(n,\tau|n^0,0)=(2\pi)^{-1}\int_{-\pi}^{\pi}\exp[ik(n-n^0)-i\tau(1-q\cos k)]dk$$
$$=\exp(-i\tau)\,i^{n-n^0}J_{n-n^0}(q\tau). \tag{38}$$

Analysis of this expression shows that the width of the region encompassed by the excitation increases smoothly in accordance with the law $l = \tau q$ (lattice sites). Then the amplitude of the excitation as a whole decreases in proportion to $\tau^{-1/2}$. In the linear theory of waves this phenomenon is called dispersion.

A remarkable property of linear systems is the fact that the quantum dynamics does not differ from the classical dynamics. For example, the time-dependent Schrödinger equation (10) for one-phonon excitations takes the form

$$i\hbar d\Phi_n/dt=\hbar\omega_0\Phi_n-Q(\Phi_{n+1}+\Phi_{n-1}). \tag{39}$$

It describes the spatial spreading of a quantum-mechanical packet for one quasiparticle and coincides in form with the classical equation. From this we can conclude that the dispersion of a classical wave containing an enormous number of particles is equivalent in nature to the quantum-mechanical dispersion of the wave packet for one particle. An increase of the number of particles in the linear system does not lead to substantial changes of the dynamics.

Because the Schrödinger equation is linear in the wave function it is possible to describe the quantum dynamics of vibrational excitations in terms of the Green functions even when anharmonicity is taken into account. The dynamics is described by Eq. (10), in which it is necessary to replace the energy eigenvalue E_N by the operator $i\hbar d/dt$ of differentiation with respect to time. The wave functions and energy eigenvalues of this equation were found in Sec. 2. In the general case there is an entire spectrum of states, differing in the numbers of bound and free particles, the total number of which is equal to N. Each such state is characterized by its set of eigenvalues and makes its contribution to the total Green function, the calculation of which is difficult. Therefore, we shall concentrate on the contribution from the states in which all N particles are bound and are characterized by the same wave number. It is possible to obtain an analytical result only in the continuum limit, when the real parts of the wave numbers appearing in the expression (11) for the wave function are equal to k, while the imaginary parts do not depend on k [see (23)]. For the energy we make use of the formula (24) and obtain for the Green function, to within an oscillatory factor, the following result:

$$G(n_1>\ldots>n_N,\tau|n_1^0>\ldots>n_N^0,0)$$
$$\approx\exp[-k_1''(n_1+n_1^0)-\ldots-k_N''(n_N+n_N^0)]$$
$$\times(2\pi)^{-1}\int_{-\infty}^{\infty}\exp[ik(n_1-n_1^0+\ldots+n_N-n_N^0)-i\tau Nqk^2/2]dk$$
$$=\exp[-k_1''(n_1+n_1^0)-\ldots-k_N''(n_N+n_N^0)]$$
$$\times\frac{\exp[i(X-X^0)^2/\tau qN^{-1}]}{(2\pi iqN\tau)^{1/2}}, \tag{40}$$

where $X = (n_1 + n_2 + \ldots + n_N)/N$ is the coordinate of the center of mass of the complex and qN^{-1} is the rate of dispersion of the wave packet of such excitations. The phenomenon of the N-fold slowing of the rate of dispersion, while appearing to be not very important for small numbers of particles, becomes decisive for classical nonlinear waves, in which an enormous number of particles are excited. It is this which leads to the appearance, in the solutions of classical nonlinear wave equations, of the nondispersive wave packets that have been given the name "solitons."

It is well known that the dispersion is induced by the existence of an effective mass of the quasiparticle and occurs more slowly the larger the mass of the particle. The effective mass is inversely proportional to the second derivative of the energy with respect to the quasimomentum, which, in the case of a complex of N particles with equal momenta k, is equal to $K = Nk$. Then for the effective mass we obtain from (33b) the expression

$$\frac{m_1}{m_N}=\frac{1}{\hbar\omega_0}\frac{\partial^2E_N(k)}{\partial(Nk)^2}=\frac{1}{N^2}\sum_{s=1}^{N}\left[1+\frac{\varepsilon^2(N+1-2s)^2}{4}\right]^{-1/2}. \tag{41}$$

It is obvious that the effective mass of a complex of N particles is N times greater than the mass m_1 of one particle. Thus, allowance for the anharmonicity leads in the quantum picture to the appearance of an entire spectrum of elementary excitations, having ever increasing effective masses. A wave packet describing the propagation of N bound quasiparticles disperses N times more slowly than for free particles.

In view of this the question of the applicability of the classical equation (26) for the description of anharmonic solitons arises. It follows from what has been said above that the classical soliton solution will correctly reflect the quantum dynamics of the vibrational excitations until quantum-mechanical dispersion begins to have an effect. If N quanta of the vibrations of the chain are bound in the soliton, this will occur after a time

$$t_{\rm cl}=N/q\omega_0. \tag{42}$$

Within such time intervals the classical theory of anharmonic solitons is valid for quantum systems as well. For classical chains of oscillators the constant q amounts to 0.1–0.001, while $N\sim10^{30}$. The classicality time (42) is enormous, and certainly exceeds the response time of the dissipative processes that are always present in real systems.

CONCLUSION

The use in the present paper of the Bethe-ansatz approximation for the wave function has turned out to be effective and can be useful for other many-particle problems with interaction. However, in selecting such a formulation it is possible to omit certain states from the analysis. Thus, in our model, states of the "excited triphonon" type do not appear.[12]

At present the question of how bound multiphonon states can be reliably detected is not completely clear. The presence of such states can be ascertained from analysis of the infrared spectra of crystals or in the spectra of inelastically scattered neutrons. The existence of three- or four-phonon complexes can evidently be confirmed with the aid of spectra of the Raman scattering of light by polaritons, such spectra having proved of excellent value in the analysis of biphonons. In any case, all these methods deserve attention and can be the subject of a separate investigation.

The influence of the anharmonicity on the phonons reduces to the formation of phonon complexes. These can be crystal phonons that, for whatever reasons, can be regarded as one-dimensional, vibrational excitations of long linear molecules, or phonons in polymers. In the latter case an object of great interest is the DNA molecule. In this molecule are vibrational excitations with energy 0.24 eV (the so-called amide-1 vibration). In the opinion of most investigators, it is these vibrations which play the principal role in the transfer of the characteristic energy portion equal to 0.5 eV along the DNA chain. The multiphonon complexes studied in the present paper can play the role of a carrier of this energy over large distances along the DNA and are, in this role, an alternative to Davydov solitons.[3]

The model considered is not restricted, however, to phonons in polymers. Generally speaking, the role of the phonons can be taken by any particles that are bosons. The anharmonic chain (4) is a general model for quasi-one-dimensional chains of nonlinear oscillators with linear interaction of nearest neighbors in the limit of small amplitude of the vibrations, and, therefore, the lowest few bands of elementary excitations of such systems have the general structure described in the present paper.

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