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Vibron Solitons and Coherent Polarization in an Exactly Tractable Oscillator-Lattice System

—— *Applications to Solitons in α Helical Proteins and Fröhlich's Idea of Biological Activity* ——

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An exactly tractable, nonlinearly coupled oscillator-lattice system is studied. This is a quasi one-dimensional (1d) model system in which each anharmonic oscillator in an oscillator system is coupled linearly with one another and nonlinearly with acoustic-type harmonic lattice vibrations. Such an oscillator system is shown to include, under certain circumstances, Frenkel excitons with exciton transfer by dipole-dipole interactions. When the on-site oscillator potential is of single-minimum type, the effect of oscillator-lattice interactions is mainly classified into two types: One is to modulate vibrons, which are elementary excitations in the lattice-free oscillator system, to yield vibron solitons governed by a discrete version of the 1d nonlinear Klein-Gordon equation, and the other is to produce coherent polarization and kinks that are stabilized by lattice deformation provided that the oscillator on-site potential contains positive quartic anharmonicity. The former is applied to solitons in α helical proteins to show that Davydov's idea can be formulated in a more physically reasonable and quantitatively correct form by the present model system. The latter is shown to be a working microscopic model to study Fröhlich's idea of biological activity due to the existence of coherent polarization field.

§ 1. Introduction

In spite of much current interest and speculations, little is known about physical mechanisms of biological activity in living organism. Fröhlich suggested for some time that biological activity and related phenomena may be due to coherent excitations of polar modes that are stabilized by nonlinear deformation of systems.[1] This idea was further developed by Bilz, Büttner and Fröhlich by studying a model dynamical system possessing metastable ferroelectric states with three types of nonlinear modes, elastic pulse solitons, ferroelectric kinks and periodic solitary waves.[2] A discussion was given on their possible relation to biological phenomena. A possible microscopic origin of these ideas, however, does not appear to have been elaborated. Davydov has shown that in α helical proteins solitons can be formed by coupling of propagation of amide-I vibrations with longitudinal phonons along spines and that such dynamical self-sufficient entities are responsible for mechanisms of energy transfer in biological systems.[3] In implementing this idea Davydov[3] and Scott[4] paid attention to the probability amplitude for the excitation of amide-I vibrations, treating solitons on the basis of quantum mechanics and using the exchange-type model Hamiltonian for excitation transfer originally employed for excitons in solid state physics. One of the drawbacks of such a theory is that due to normalization condition on the probability amplitude the soliton amplitude is automatically given. In a previous paper,[5] hereafter referred to as (I), a brief report of a theory of vibron solitons in 1d moleculor crystals was made to provide an alternative view on Davydov's idea. This is to formulate nonlinear coupling of molecular-vibration excitation waves (vibrons) with longitudinal phonons within the framework of lattice dynamics. It was pointed out that in such situations solitons are essentially classical, where displacement or polarization field is a relevant field variable, and the soliton amplitude is an arbitrary parameter. It was also shown that the difference of the properties of vibron solitons from those of Davydov solitons manifests itself in a most remarkable way in the soliton binding energy.

It is the purpose of this paper to present an exactly tractable model of an oscillator-lattice system which is capable of incorporating both of the pictures of Fröhlich and that of Davydov in a unified way and to make a more detailed study of vibron solitons by giving a significant improvement of the theory developed in (I). This is a quasi-one-dimensional system in which each anharmonic oscillator in an oscillator system is coupled linearly with one another and nonlinearly with acoustic-type harmonic lattice vibrations. Incidentally, this can be considered as an improved-version of an interacting-harmonic-oscillator model employed by Kemeny to discuss conformation changes in protein molecules.[6] The formulation of the problem is done with the observation that here both of anharmonicity and spatial discreteness are crucial. In contrast to the previous case (I), no continuum approximation is employed from the outset to treat equations of motion for the oscillator and lattice displacement fields. It is shown both analytically and numerically that vibron solitons provide us with a more adequate picture of solitons in α helical proteins and related organic solids as compared with Davydov solitons. It is also shown that the oscillator-lattice system adopted here can be considered as a working microscopic model to study the problem as suggested by Fröhlich.

This paper is organized as follows. In the next section we introduce an oscillator-lattice system as mentioned above. In §3 it is shown that the same oscillator model can be used for Frenkel excitons with exciton transfer by dipole-dipole interactions. In §4 we discuss an exactly tractable model to show that the oscillator-lattice interactions induce attractive on-site potentials and phonon-mediated vibration excitation transfer when viewed from the oscillator system. In §5 we study the properties of the on-site potential and its possible implication to Fröhlich's suggestion. In §6 we study the case of the harmonic vibration in the original oscillator system to make a detailed study of solitons and related problems in our model system. In §7 the result obtained in §6 is applied to the case of α helical proteins and compared with the Davydov theory. The last section is devoted to concluding remarks on the results contained in this paper.

§ 2. Model Hamiltonian for oscillator-lattice system

Let us consider a quasi one-dimensional (1d) oscillator system in which each oscillator is coupled linearly with neighbouring oscillators and nonlinearly with lattice vibrations. The Hamiltonian H_{osc} of the oscillator system is taken to be

$$H_{\mathrm{osc}}=\sum_n[(p_n{}^2/2\mu)+v(q_n)]-\sum_{nm}L(n,m)q_nq_m. \tag{2·1}$$

Here q_n and $p_n=\mu\dot{q}_n$ are the normal coordinate of the nth oscillator and its canonically conjugate momentum, respectively. The quantities μ, $v(q_n)$ and $L(n,m)$ $(=L(m,n)$, $L(n,n)\equiv 0)$ are an effective mass, the on-site potential for the nth oscillator and a force constant giving coupling between the nth and mth oscillators, respectively. The

Hamiltonian $H_{\rm latt}$ of the lattice-vibration system is chosen as

$$H_{\rm latt}=\sum_n[(P_n^2/2M)+(K/2)(u_{n+1}-u_n)^2], \qquad (2\cdot2)$$

where u_n and $P_n=M\dot{u}_n$ are the displacement of the nth molecule with molecular mass M from its equilibrium position and its canonically conjugate momentum, respectively. The quantity K is a force constant describing coupling between nearest-neighbour pairs of molecules. Oscillator-lattice interactions are due to fluctuations of the on-site potentials $v(q_n)$ and of the force constants $L(n, m)$ by lattice vibrations. We can then take the model Hamiltonian $H_{\rm int}$ of the oscillator-lattice interactions to be of the form

$$H_{\rm int}=\sum_n[V(q_n)(u_{n+1}-u_{n-1})-\lambda[\{(u_{n+1}-u_n)q_{n+1}+(u_n-u_{n-1})q_{n-1}\}q_n]. \qquad (2\cdot3)$$

Here $V(q_n)$ and λ are a function of q_n and a constant, respectively. Equation (2·3) may be understood by considering an example in which the on-site potentials and the force constants in the fluctuating oscillator system depend on the instantaneous position $x_n=na+u_n$ of the molecules in the lattice system through the form

$$v(q_n)\to v(q_n;x_n)=v_0(q_n)+\sum_m v_1(q_n;|x_m-x_n|), \qquad (2\cdot4)$$

$$L(n, m)\to L(|x_m-x_n|) \qquad (2\cdot5)$$

with

$$v(q_n)=v_0(q_n)+\sum_m v_1(q_n;|m-n|a), \quad L(m, n)=L(|m-n|a)\equiv L(|m-n|). \qquad (2\cdot6)$$

Here a is the lattice constant, and $v_0(q_n)$ and $v_1(q_n;|x_m-x_n|)$ are the on-site potential of the nth free oscillator and the energy shift term due to its interactions with neighbouring oscillators, respectively. Equation (2·3) is obtainable by expanding $v_1(q_n;|x_m-x_n|)$ and $L(|x_m-x_n|)$ to first order with respect to the u's and by assuming that the fluctuating part of $v(q;x_n)$ and $L(|x_m-x_n|)$ extends only over nearest neighbour pairs of oscillators. Explicit expressions for $V(q_n)$ and λ are then given by

$$V(q_n)=v_1'(q_n;|a|) \quad \text{and} \quad \lambda=L'(|a|), \qquad (2\cdot7)$$

where the prime on v_1 and L denotes differentiation with respect to the position of the molecules.

Since our model Hamiltonian (2·1), (2·2) and (2·3) is fairly general, it contains various physically interesting problems as specific cases. Two typical cases exist: (1) The on-site potential $v(q_n)$ is of single-minimum type and (2) it is of double minimum type or a sinusoidal function of q_n. In this paper we limit our discussion to the first case. Here simplest is the case of harmonic oscillators

$$v(q)=\mu\omega_0^2q^2/2\,, \qquad (2\cdot8)$$

where ω_0 is the eigenfrequency. Harmonic excitation waves propagating from one oscillator site to the next then exist in the lattice-free oscillator system (vibrons).[5] A typical example to which such a model system is applicable is the case of α helical proteins. Together with comparison with the Davydov theory, this will be discussed in detail in §7.

§ 3. An oscillator-lattice model for a Frenkel-exciton-lattice system

Essentially the same model Hamiltonian as that employed for the oscillator-lattice system can be used for Frenkel excitons in molecular crystals with exciton transfer by dipole-dipole coupling interacting with lattice vibrations. To illustrate this, we employ a two-level approximation for the electronic state of a given molecule to pick up only two states, the ground state and a relevant excited state among many molecular eigenstates. For the electronic part H_{el} of the Hamiltonian of the system, we can then associate a set of Pauli operators $\boldsymbol{\sigma}_n=(\sigma_n{}^x, \sigma_n{}^y, \sigma_n{}^z)$, where $\sigma_n{}^x$ and $\sigma_n{}^z$ are related to the transition dipole moment $2\boldsymbol{\mu}\sigma_n{}^x$ and the population difference between the ground state and the excited state, respectively, of the nth molecule. Here $\boldsymbol{\mu}$ is the matrix element of the dipole moment operator between these two states. We limit our discussion to the case of low exciton density to neglect dynamical exciton-exciton interactions. The quantity H_{el} is written in the form of the Ising model in a transverse field:[7]

$$H_{\mathrm{el}}=\sum_n \epsilon(x_n)\sigma_n{}^z-2\sum_{nm} J(|x_m-x_n|)\sigma_n{}^x\sigma_m{}^x, \quad \epsilon(x_n)=\epsilon_0+\sum_m D(|x_m-x_n|). \qquad (3\cdot 1)$$

Here ϵ_0 and x_n are the energy separation between the ground state and the excited state of the free molecule and the instantaneous position of the nth molecule, respectively. The quantities $D(|x_m-x_n|)$ and $J(|x_m-x_n|)$ are the shift of ϵ_0 due to the presence of other molecules and the dipole-dipole interaction energy, respectively.

Equation (3·1) is reducible to the exciton Hamiltonian H_{ex} plus the exciton-lattice interaction Hamiltonian $H_{\mathrm{int}}^{\mathrm{ex}}$, the former and the latter having the same form as Eqs. (2·1) and (2·3), respectively, provided that it can be treated classically and that the molecular excitation energy is much larger than the dipole-dipole interaction energy, i.e.,

$$\epsilon_0 \gg \sum_m J(|m-n|a)\equiv\sum_m J(n, m)\equiv J\,. \qquad (3\cdot 2)$$

This can be done by employing the following approximation procedure:

$$\sigma_n{}^z\cong-[(1/4)-(\sigma_n{}^x)^2]^{1/2}+(\sigma_n{}^y)^2=-[(1/4)-(\sigma_n{}^x)^2]^{1/2}+[(\dot{\sigma}_n{}^x)^2/\epsilon(x_n)^2] \qquad (3\cdot 3)$$

and by putting

$$\sigma_n{}^x=2^{-1/2}q_n\,. \qquad (3\cdot 4)$$

By the use of Eqs. (3·3) and (3·4), Eq. (3·1) is reduced to

$$H_{\mathrm{el}}=\sum_n[1/2\epsilon(x_n)]\dot{q}_n{}^2-(1/2)\sum_n\epsilon(x_n)(1-2q_n{}^2)^{1/2}-\sum_{nm}J(|x_m-x_n|)q_nq_m\,. \qquad (3\cdot 5)$$

Explicit expressions for H_{ex}, which corresponds to a non-fluctuating part of H_{el}, and $H_{\mathrm{int}}^{\mathrm{ex}}$ are obtained by expanding the quantities $D(|x_m-x_n|)$ and $J(|x_m-x_n|)$ in Eqs. (3·1) to first order with respect to the u's as in the case of Eqs. (2·4) and (2·5) and by assuming that the fluctuating part of the D's and the J's extend only over nearest neighbour pairs. Namely, putting

$$\epsilon(x_n)=\epsilon+D'(|a|)(u_{n+1}-u_{n-1}) \quad \text{with} \quad \epsilon=\epsilon_0+\sum_m D(|m-n|a), \qquad (3\cdot 6)$$

$$J(|x_m-x_n|)q_m\cong\sum_m J(n, m)q_m+J'(|a|)[(u_{n+1}-u_n)q_{n+1}+(u_n-u_{n-1})q_{n-1}], \qquad (3\cdot 7)$$

taking inequality (3·2) into account and using the procedure given in Appendix A, we get

$$H_{\rm ex}=H_{\rm osc} \quad \text{and} \quad H_{\rm int}^{\rm ex}=H_{\rm int} \tag{3·8}$$

with

$$\mu=1, \quad v(q)=-(\epsilon^2/2)(1-2q^2)^{1/2}, \quad L(n, m)=\epsilon J(n, m),$$
$$V(q)=-\epsilon D'(|a|)(1-2q^2)^{1/2}, \quad \lambda=\epsilon J'(|a|). \tag{3·9}$$

The total Hamiltonian of the exciton-lattice system under consideration can be obtained by adding the lattice Hamiltonian $H_{\rm latt}$ to $H_{\rm osc}+H_{\rm int}$. We take $H_{\rm latt}$ to be of the form (2·2). Under the condition (3·2) it is a very good approximation to put

$$v(q)=\text{const}+(\epsilon^2/2)q^2+O(q^4), \tag{3·10}$$

a situation quite analogous to the case of Eq. (2·8).

§ 4. Exactly tractable model

Equations of motion obeyed by q_n and u_n are obtained from Eqs. (2·1), (2·2) and (2·3) as follows:

$$\mu\ddot{q}_n+v'(q_n)-2\sum_m L(n, m)q_m+V'(q_n)(u_{n+1}-u_{n-1})$$
$$+2\lambda[(u_{n+1}-u_n)q_{n+1}+(u_n-u_{n-1})q_{n-1}]=0, \tag{4·1}$$

$$M\ddot{u}_n-K(u_{n+1}+u_{n-1}-2u_n)-[V(q_{n+1})-V(q_{n-1})]+2\lambda(q_{n+1}-q_{n-1})q_n=0. \tag{4·2}$$

Here the prime on $v(q_n)$ and $V(q_n)$ denotes differentiation with respect to the q's. We treat Eqs. (4·1) and (4·2) without resorting to the conventional continuum approximation with which severals of essential features of the problem inherent in spatially discrete systems are lost. We are particularly concerned here with the situation that a rigorous relationship between u_n and q_n is obtainable from Eq. (4·2) to reduce Eq. (4·1) to an exact nonlinear differential-difference equation written entirely in terms of the q_n's. This is realized in the case in which fluctuations of the inter-site potentials are much too small as compared with those of the on-site ones in the oscillator system and at the same time the velocity of excitations under consideration in the lattice system is much smaller than the velocity $c_s=(Ka^2/M)^{1/2}$ of long wavelength phonons. Equations (2·3), (4·1) and (4·2) are then reduced to

$$H_{\rm int}=\sum_n V(q_n)(u_{n+1}-u_{n-1}), \tag{4·3}$$

$$\mu\ddot{q}_n+v'(q_n)-2\sum_m L(n,m)q_m+V'(q_n)(u_{n+1}-u_{n-1})=0, \tag{4·4}$$

$$K(u_{n+1}+u_{n-1}-2u_n)+V(q_{n+1})-V(q_{n-1})=0. \tag{4·5}$$

Taking the 1d oscillator-lattice system in the direction of the x-axis, we rewrite Eq. (4·5) as

$$K\{\cosh[a(\partial/\partial x)]-1\}u+\sinh[a(\partial/\partial x)]V(q)=0. \tag{4·6}$$

By the use of the properties of the hyperbolic functions, Eq. (4·6) is integrated to give

$$u_{n+1}-u_n=-(1/K)[V(q_{n+1})+V(q_n)]+(u_0/2), \tag{4·7}$$

where u_0 is an integral constant. Inserting this back into Eq. (4·4), we get

$$\mu\ddot{q}_n+v'(q_n)+u_0V'(q_n)-2\sum_m L(n,m)q_m$$
$$-(1/K)V'(q_n)[2V(q_n)+V(q_{n+1})+V(q_{n-1})]=0. \tag{4·8}$$

We observe that Eq. (4·8) is also derivable from the following effective oscillator Hamiltonian

$$H_{\mathrm{osc}}^{\mathrm{eff}}=\sum_n[(p_n{}^2/2\mu)+U(q_n)]-\sum_{nm}L(n,m)q_nq_m+\sum_n W(q_n,q_{n+1}), \tag{4·9}$$

where

$$U(q_n)=v(q_n)+u_0V(q_n)-(2/K)V(q_n)^2, \tag{4·10}$$

$$W(q_n,q_{n+1})=-(1/K)V(q_n)[V(q_{n+1})-V(q_n)]. \tag{4·11}$$

Several remarks are in order on the result obtained above by comparing Eq. (4·9) with Eq. (2·1): (1) The effect of the oscillator-lattice interactions on the oscillator system amounts here to modifying the original on-site potential $v(q_n)$ as $U(q_n)$: The factor $-(2/K)V(q_n)^2$ acts as an attractive potential, while $u_0V(q_n)$ arises when a static deformation exists in the lattice system. When $v(q_n)$ is harmonic, the first factor may give rise to dynamical trapping of vibrons under certain circumstances, a situation somewhat analogous to polarons in electron-phonon systems. Such dynamical entities, which are more stable than vibrons themselves, are called here vibron solitons.[5] It will be shown at later stage that for long wavelength excitations the vibron solitons have the form of envelope solitons similar to those described by the nonlinear Schrödinger (NLS) equation. (2) The oscillator-lattice interactions induce phonon-mediated transfer of excitations from one oscillator site to the next described by the factor $W(q_n, q_{n+1})$. This is effective for short wavelength excitations. (3) When envelope solitons exist in the oscillator system, the phonon field takes the form of kink-like excitations. This is due to the fact that for long wavelength excitations Eq. (4·7) is reduced to $u_{n+1}-u_{n-1}=-(4/K)V(q_n)+u_0$ and that $V(q_n)$ represents a measure of energy. (4) The effect of finite velocity of excitations in the lattice system can be approximately taken into account by taking u_n in Eq. (4·2), with the last term omitted, to be of the form

$$u_n=u(na-vt)\equiv u(\xi) \tag{4·12}$$

and by approximating the equation as

$$K[1-(v^2/c_s{}^2)]\{\cosh(a(d/d\xi)]-1\}u+\sinh[a(d/d\xi)]V(q)=0. \tag{4·13}$$

Here v is the velocity of excitations. This approximation procedure gives the renormalization of K in Eqs. (4·7), (4·8), (4·10) and (4·11):

$$K\to K[1-(v^2/c_s{}^2)]=K^*. \tag{4·14}$$

In Appendix B we employ another approximation procedure to reduce Eq. (4·2) to a form somewhat similar to Eq. (4·8) by introducing a renormalized form of $V(q_n)$.

§ 5. On-site potential and implication to Fröhlich's model of biological activity

We specify here the form of the on-site potentials $v(q)$ and $V(q)$ to see how the quantities modified on-site potential $U(q)$ looks like. Confining ourselves to the case in which $v(q)$ is of single minimum type, we take these two quantities to be of the forms

$$v(q)=(\mu\omega_0^2/2)q^2+(b/4)q^4\,, \quad b>0 \tag{5·1}$$

$$V(q)=(A/2)q^2+(B/4)q^4\,, \quad A>0, \quad B>0\,. \tag{5·2}$$

Equation (5·1) is a generalization of Eq. (2·8), and the quantities b, A and B are constants. Inserting Eqs. (5·1) and (5·2) into Eq. (4·10), we get an explicit expression for $U(q)$. Here we are primarily concerned with situations that essential features of $U(q)$ can be gained by discarding sixth- and eighth-order anharmonic terms to get

$$U(q)=(\mu\omega_0^2+u_0A)(q^2/2)+[b+u_0B-(2A^2/K)](q^4/4) \tag{5·3}$$

on the assumption that $A\gg B$. Three cases of physical interest exist:

$$U(q)=\begin{cases} (\mu\omega_0'^2/2)q^2-(b_1/4)q^4\,, & b_1>0\,, \quad \text{(case (1))} \qquad (5·4)\\ (\mu\omega_0'^2/2)q^2+(b_2/4)q^4, & b_2>0, \quad \text{(case (2))} \qquad (5·5)\\ -(\alpha/2)q^2+(\beta/4)q^4, & \alpha,\beta>0, \quad \text{(case (3))} \qquad (5·6)\end{cases}$$

where

$$\omega_0'^2=\omega_0^2+(u_0A/\mu)>0, \quad \alpha=-(\mu\omega_0^2+u_0A)>0\,,$$
$$b_1=(2A^2/K)-b-u_0B>0\,, \quad b_2=b+u_0B-(2A^2/K)>0\,,$$
$$\beta=b_2\,. \tag{5·7}$$

Of these three cases, case (3), which is only realizable for $u_0\neq0$ with the condition $u_0A<0$ and $|u_0A|>\mu\omega_0^2$, is most remarkable in the sense that the modified on-site potential $U(q)$ is entirely different in character from the original one $v(q)$. Namely, here the oscillator-lattice interactions modify the original single minimum potential to a double minimum one. In cases (1) and (2) vibrons experience negative and positive dynamic or anharmonic potentials, respectively. In these two cases shift of vibron frequency takes place for $u_0\neq0$.

Since cases (1) and (2) are studied in detail in §6, the remaining part of this section is devoted to case (3). Here the oscillator-lattice interactions induce a shift of equilibrium position of oscillators from $q=0$ to $q=\pm(\alpha/\beta)^{1/2}$ and a lowering of the potential energy minimum from zero to $-(\alpha^2/4\beta)$. And the lowering of energy in the oscillator system is compensated by an increase in the potential energy of the lattice system due to the appearance of the strain energy. This is a kind of displacive phase transition or the appearance of coherent states both in the oscillator system and the lattice system which are stabilized by deformation of the lattice system. The effective oscillator Hamiltonian $H_{\rm osc}^{\rm eff}$ takes the form of standard φ^4 lattice model Hamiltonian except the W-term in Eq. (4·9):

$$H_{\rm osc}^{\rm eff}=\sum_n[(p_n^2/2\mu)+U^*(q)]+(1/2)\sum_{nm}L(n,m)(q_m-q_n)^2+\sum_n W(q_n,q_{n+1}), \tag{5·8}$$

where

$$U^*(q)=-(\alpha^*/2)q^2+(\beta/4)q^4 \quad \text{with} \quad \alpha^*=\alpha-\sum_m L(n,m). \tag{5·9}$$

An explicit expression for $W(q_n, q_{n+1})$ is omitted. If each oscillator has a non-vanishing dipole moment, the oscillator system becomes polarized by its nonlinear coupling with the lattice system. It is shown that the ground state of case (3) is a metastable state. For this purpose, let us define the total energy H_{tot} of the oscillator-lattice system as a whole by the equation

$$H_{\text{tot}}=H_{\text{osc}}^{\text{eff}}+H_{\text{latt}}[\{p_n\},\ \{u_n(q)\}]. \tag{5·10}$$

Here the second term is the value of H_{latt} in which all the P_n's are set equal to zero (cf., Eq. (4·5)) and at the same time the factor $u_{n+1}-u_n$ is written in terms of the q_n's by using Eq. (4·7). A straightforward calculation gives

$$H_{\text{tot}}=H_{\text{osc}}+\sum(Ku_0^2/8). \tag{5·11}$$

It is understood here that the solution to Eq. (4·8) should be inserted in H_{osc} in Eq. (5·11). It is seen that the ground state energy of the oscillator-lattice system in case (3) is larger than that in cases (1) and (2) by the factor given by the second term in Eq. (5·11). Thus, case (3) is characterized by the existence of a metastable state in which the mean displacement or polarization does not vanish as is the case for a ferroelectric system in its ground state. Excitations around the ground state of physical interest here are kinks or topological solitons, which, for long wavelength excitations, take the form

$$q_n \to q(x,t)=\pm q_0 \tanh[(x-vt)/l_0]. \tag{5·12}$$

Here

$$l_0=[\mu(c_1^2-v^2)/\alpha^*]^{1/2} \quad \text{and} \quad c_1=(2/\mu)\sum_l L(l)l^2a^2 \tag{5·13}$$

are the kink width and the velocity of vibrons in the long wavelength limit, respectively. The quantity v is the kink velocity.

A situation here is reminiscent of the idea put forward by Fröhlich as mentioned in §1.[1] Setting up on phenomenological level equations of motion for a polarization field and a longitudinal elastic field, he and his coworkers[2] showed specifically that the nonlinear coupling of these two fields leads to an excited metastable state with nonvanishing mean polarization field. Assuming that the employed model may be applicable to proteins and in particular to enzymes, he speculated that these molecules possess a metastable excited state with high dipole moment which under the influence of an electric field may become the ground state.[1] This implies that if the rate of chemical activity of an enzyme in the metastable, polarized, state is much higher than it is in the ground state, then it could be switched on by the electric field due to adsorbed ions or due to dipole groups in an attached substrate. In the latter case after completion of the chemical reaction the polarized state becomes metastable, again, the required energy having been supplied by the chemical reaction. Subsequently, Bilz, Büttner and Fröhlich suggested that several essential features of the behaviour of biological systems such as membranes and enzymes may be described by a microscopic model originally proposed for the ferroelectric phase transition in perovskites.[2] The basic reasoning employed by these workers still appears to remain on phenomenological level. The present oscillator-lattice model in case (3) may be the first implementation of Fröhlich's idea on microscopic level, as far as the present author is aware of. Much remains to be done, however, to see whether the result obtained in this section or the argument of similar nature may be applicable to real situations in the problem of biological activity.

§ 6. Vibron solitons and exciton solitons

In what follows we shall dwell upon cases (1) and (2) considered in §5. In doing this we confine ourselves to the case $u_0=0$ and $A\gg B$ for the sake of simplicity. Inserting Eqs. (5·4) and (5·5) into (4·8), we then obtain

$$\ddot{q}_n+\omega_0{}^2q_n-(2/\mu)\sum_m L(n,m)q_m-(-1)^{\eta-1}(b_\eta/\mu)q_n{}^3$$
$$-(A^2/2K\mu)q_n(q_{n+1}^2+q_{n-1}^2-2q_n{}^2)=0\,,$$
$$\eta=1 \text{ for case (1)} \quad\text{and}\quad \eta=2 \text{ for case (2).} \tag{6·1}$$

Equation (6·1) is an equation of motion for vibrons, Frenkel excitons or optical mode phonons, which are often called quasi-particles hereafter, with the dispersion relation

$$\omega^{(0)}(k)=[\omega_0{}^2-(2/\mu)\sum_m L(n,m)\exp[ik(m-n)a]^{1/2} \tag{6·2}$$

nonlinearly modulated by acoustic phonons. The bottom and the top of the frequency band $\omega^{(0)}(k)$ are given by

$$\omega^{(0)}(k_1)\equiv\omega_1=[\omega_0{}^2-(2/\mu)\sum_m L(n,m)]^{1/2}\,,\qquad k_1=0\,, \tag{6·3}$$

and

$$\omega^{(0)}(k_2)\equiv\omega_2=[\omega_0{}^2+(2/\mu)\sum_m(-1)^{|m-n|-1}L(n,m)]^{1/2}\,,\qquad k_2=\pi/a\,, \tag{6·4}$$

respectively.

We are concerned with nonlinearity-induced localized modes or solitons of the quasi-particles stationary ones of which appear below the bottom or above the top of the frequency band $\omega^{(0)}(k)$ for cases (1) and (2), respectively. We divide q_n into negative and positive frequency parts:

$$q_n=Q_n+Q_n{}^*\equiv\bar{Q}_n\exp(-i\omega_\eta t)+\bar{Q}_n{}^*\exp(i\omega_\eta t). \tag{6·5}$$

We insert this into Eq. (6·1) and employ a rotating-wave approximation to retain only terms with their main time-dependence given by $\exp(-i\omega_\eta)$ and their complex conjugate. We then obtain

$$\ddot{Q}_n+\omega_0{}^2Q_n-(2/\mu)\sum_m L(n,m)Q_m-(-1)^{\eta-1}(3b_\eta/\mu)|Q_n|^2Q_n$$
$$-(A^2/2K\mu)[2Q_n(|Q_{n+1}|^2+|Q_{n-1}|^2)+Q_n{}^*(Q_{n+1}^2+Q_{n-1}^2)-6|Q_n|^2Q_n]=0\,,\quad \eta=1,2, \tag{6·6}$$

and c.c. In studying the problem we neglect the effect of phonon-mediated transfer of quasi-particles to omit the second line in Eq. (6·6). We seek the solutions in the form

$$Q_n=\phi_n\exp[-i(\omega t-\bar{k}na)] \quad \text{with} \quad \bar{k}=\begin{cases} k & \text{for } \eta=1\,, \\ k_2-k & \text{for } \eta=2\,. \end{cases} \tag{6·7}$$

Here ω and k are real constants identified as the eigenfrequency and momentum of solitons, respectively, while ϕ_n is a (real) envelope function depending on site index and time variable t. Putting Eq. (6·7) into Eq. (6·6), we get

$$\begin{aligned}&\ddot{\phi}_n+[\omega^{(0)}(k_\eta-k)^2-\omega^2]\phi_n\\ &\quad -(-1)^{\eta-1}(2/\mu)\sum_{l=1}^{\infty}\mathcal{L}(l)\cos(kla)(\phi_{n+l}+\phi_{n-l}-2\phi_n)-(-1)^{\eta-1}(3b_\eta/\mu)\phi_n{}^3=0\,,\end{aligned} \tag{6·8a}$$

$$2\omega\dot{\phi}_n+(2/\mu)\sum_{n=1}^{\infty}\mathcal{L}(l)\sin(kla)(\phi_{n+l}-\phi_{n-l})=0\,, \tag{6·8b}$$

where

$$\mathcal{L}(l)=L(l) \text{ for case (1)} \quad \text{and} \quad (-1)^{l-1}L(l) \text{ for case (2)}. \tag{6·9}$$

Here we have used Eqs. (6·2), (6·3), (6·4) and the relation $\omega^{(0)}(-k)=\omega^{(0)}(k)$. A physical insight into the appearance of solitons can be gained by rewriting Eq. (6·8a) as

$$\sum_{l=1}^{\infty}L_\eta(l)\cos(kla)(\phi_{n+l}+\phi_{n-l}-2\phi_n)-[(-1)^{\eta-1}/\omega_{L\eta}^2]\ddot{\phi}_n=-\mathcal{V}_\eta'(\phi_n;k), \tag{6·10}$$

where

$$L_\eta(l)=(2/\mu)\mathcal{L}(l)/\omega_{L\eta}^2 \quad \text{with} \quad \omega_{L\eta}^2=(2/\mu)\sum_{l=1}^{\infty}\mathcal{L}(l), \tag{6·11}$$

$$\mathcal{V}_1(\phi;k)=-\frac{\omega^{(0)}(k)^2-\omega^2}{\omega_{L1}^2}\frac{\phi^2}{2}+\frac{3b_1}{\mu\omega_{L1}^2}\frac{\phi^4}{4}\,, \tag{6·12a}$$

$$\mathcal{V}_2(\phi;k)=-\frac{\omega^2-\omega^{(0)}(k_2-k)^2}{\omega_{L2}^2}\frac{\phi^2}{2}+\frac{3b_2}{\mu\omega_{L2}^2}\frac{\phi^4}{4}\,. \tag{6·12b}$$

It is seen that the potential functions $\mathcal{V}_1(\phi_n;k)$ and $\mathcal{V}_2(\phi_n;k)$ so introduced are of double-minimum-type for $\omega^{(0)}(k)>\omega$ and $\omega^{(0)}(k_2-k)<\omega$ for cases (1) and (2), respectively, otherwise they are of single-minimum-type. It is only in such cases that localized modes or solitons can exist.

To illustrate this in the simplest way, let us first pay attention to stationary localized modes or stationary or non-propagating solitons for which $k=0$ and ϕ_n is time-independent at the same time. Equation (6·10) is reduced to

$$\sum_{l=1}^{\infty}L_\eta(l)(\phi_{n+l}+\phi_{n-l}-2\phi_n)=-\mathcal{V}_\eta'(\phi_n;0), \tag{6·13}$$

while Eq. (6·8b) is automatically satisfied. Equation (6·13) can be regarded as a discrete-time version of the equation of motion for a Newtonian particle with mass $\sum_{l=1}^{\infty}l^2L_\eta(l)a^2$ under the potential field $\mathcal{V}_\eta(\phi_n;0)$ in a one-dimensional space ϕ_n with na playing the role of time. Obviously, the localized modes are only realizable for $\omega<\omega_1$ for case (1) and $\omega>\omega_2$ for case (2). Equation (6·13) is integrable only in the continuum limit, taking the form

$$(d^2\phi/dx^2)-(-1)^{\eta-1}[(\omega_\eta{}^2-\omega^2)/c_\eta{}^2]\phi+(3b_\eta/\mu c_\eta{}^2)\phi^3=0 \tag{6·14}$$

with

$$x=na \quad \text{and} \quad c_\eta{}^2=(2/\mu)\sum_{l=1}^{\infty}\mathcal{L}(l)l^2a^2. \tag{6·15}$$

Solutions to Eqs. (6·14) with the boundary condition $\phi(\pm\infty)=0$ and $|d\phi/dx|_{x=\pm\infty}=0$ are given by

$$\phi=\alpha\mathrm{sech}[\alpha(3b_\eta/2\mu c_\eta{}^2)^{1/2}x] \quad \text{with} \quad \omega^2=\omega_\eta{}^2-(-1)^{\eta-1}(3b_\eta/2\mu)\alpha^2\,, \tag{6·16}$$

where α is an arbitrary parameter identified as the amplitude of the stationary solitons. With the above preliminary discussion on the case of continuum limit in mind, we study Eq. (6·13) which is generally non-integrable. Without loss of the essential feature of the problem, we confine ourselves to the case in which the $L(n, m)$'s extend only nearest neighbour pairs. Then, it is reduced to

$$\phi_{n+1}+\phi_{n-1}-2\phi_n=-\mathcal{V}_\eta{}'(\phi_n;0). \tag{6·13'}$$

Here the lattice discreteness in the oscillator system is regarded as a perturbation to the integrable system governed by Eq. (6·14). The spatial discreteness effect can then be deduced from the well-known KAM theorem.[8] Let us consider solutions plotted in (ϕ_n, $\phi_{n+1}-\phi_n$)-space, for which three characteristic features exist, fixed points, invariant trajectories and chaotic phases. Qualitative features of the solutions are as follows: For small anharmonicity all trajectories which exist in the integral system persist albeit deformed. As anharmonicity increases, fewer and fewer of the KAM trajectories remain, and their disappearance is connected with the appearance of chaotic phases (see Fig. 1). Here the region in the vicinity of the hyperbolic point O corresponding to the energy maximum point or unstable point in $\mathcal{V}_\mu(\phi_n;0)$ and that in the close vicinity of the separatrix corresponding to the soliton solution (6·16) are most sensitive to the perturbation. The appearance of chaotic phases in the vicinity of the unstable point and the smearing of the separatrix imply random spatial arrangement of stationary solitons which are slightly deformed from those in the continuum limit.

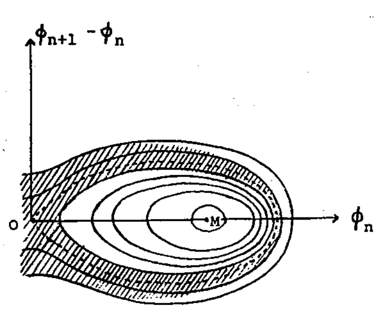

Fig. 1. Schematic feature of solutions to Eq. (6·13′). The points O and M are a hyperbolic point and an elliptic point, respectively, of $\mathcal{V}_\eta(\phi_n, 0)$. A dotted trajectory is a separatrix corresponding to solitons in the continuum limit. The shaded region represents chaotic phases.

We go back to the more general case of moving solitons which are governed by Eqs. (6·10) and (6·8b), the former and the latter being considered to determine the eigenfrequency ω and the envelope function ϕ_n and the soliton momentum k, respectively. Since Eqs. (6·8b) and (6·10) are much more difficult to treat as compared with Eq. (6·13) or (6·13′), we first assess the properties of moving solitons by considering again the continuum limit. To understand physical situations, we go back one step further to equations obeyed by the Q_n's. Equation (6·6) with or without the second line then reduce to one and the same equation

$$\frac{\partial^2 Q}{\partial x^2}-\frac{1}{c_1^2}\frac{\partial^2 Q}{\partial t^2}-m_1^2c_1^2Q+2m_1g_1|Q|^2Q=0 \qquad \text{for case (1),} \tag{6·17a}$$

$$\frac{\partial^2 Q'}{\partial x^2}+\frac{1}{c_2^2}\frac{\partial^2 Q'}{\partial t^2}+m_2^2c_2^2Q'+2m_2g_2|Q'|^2Q'=0 \qquad \text{for case (2)} \tag{6·17b}$$

with

$$Q_n=Q_n'\exp(ik_2na), \quad Q_n'\to Q'(x,t)\equiv Q'. \tag{6·18}$$

Here

$$m_\eta=\omega_\eta/c_\eta^2 \quad \text{and} \quad g_\eta=3b_\eta/2\mu\omega_\eta \tag{6·19}$$

are the mass of the quasi-particles and coupling constants characterizing the oscillator-lattice interactions. The use of the continuum approximation corresponds to expanding the frequency band $\omega^{(0)}(k)$ in the vicinity of the bottom or the top of it (cf., Eq. (6·7)):

$$\omega^{(0)}(\bar{k})\cong[\omega_\eta^2+(-1)^{\eta-1}c_\eta^2k^2]^{1/2}\cong\omega_\eta+(-1)^{\eta-1}(k^2/2m_\eta) \tag{6·20}$$

and taking the middle of the above equation. Similarly, a continuum-version of Eqs. (6·8a) or (6·10) and (6·8b) is given by

$$\frac{\partial^2\phi}{\partial x^2}-(-1)^{\eta-1}\frac{1}{c_\eta^2}\frac{\partial^2\phi}{\partial t^2}+\frac{(-1)^{\eta-1}(\omega^2-\omega_\eta^2)-c_\eta^2k^2}{c_\eta^2}\phi+2m_\eta g_\eta\phi^3=0\,, \tag{6·21a}$$

$$k\frac{\partial\phi}{\partial x}+\frac{\omega}{c_\eta^2}\frac{\partial\phi}{\partial t}=0\,. \tag{6·21b}$$

The envelope function $\phi=\phi(x,t)$, eigenfrequency ω and momentum k are therefore obtained as follows:

$$\phi(x,t)=\alpha\,\mathrm{sech}[\alpha(3b_\eta/2\mu c_\eta^2)^{1/2}\gamma_\eta(x-vt)], \quad \gamma_\eta=[1-(-1)^{\eta-1}(v^2/c_\eta^2)]^{-1/2} \tag{6·22}$$

with $v\ll c_s$

$$\omega=[\omega_\eta^2+(-1)^{\eta-1}(c_\eta^2k^2-\omega_\eta g_\eta\alpha^2)]^{1/2}\equiv\omega_\eta(k), \tag{6·23}$$

$$k=\gamma_\eta m_\eta^* v \quad \text{and} \quad m^*=\omega_\eta(0)/c^2\,. \tag{6·24}$$

In this dynamical case v and α are arbitrary parameters identified as the velocity and amplitude of solitons, respectively. The solutions obtained above represent envelope solitons which behave like relativistic particles. As in the case of stationary solitons, the soliton frequency decreases or increases as their amplitude increases for cases (1) and (2), respectively. In the non-relativistic limit the above solutions are reduced to (see also Eq. (6·20))

$$\gamma_\eta=1, \qquad k=m_\eta v\,, \tag{6·25}$$

$$\omega=\omega_\eta+(-1)^{\eta-1}[(k^2/2m_\eta)-(g_\eta^2/2)\alpha^2]\equiv\omega_\eta(k). \tag{6·26}$$

It is worth noticing that Eqs. (6·22) with Eqs. (6·25) and (6·26) are one-soliton solutions to the 1d NLS equation

$$i(-1)^{\eta-1}\frac{\partial\psi}{\partial t}+\frac{1}{2m_\eta}\frac{\partial^2\psi}{\partial x^2}-(-1)^{\eta-1}\omega_\eta\psi+g_\eta|\psi|^2\psi=0\,. \tag{6·27}$$

This is also a non-relativistic form of Eqs. (6·17a) ($Q=\exp(-i\omega_1 t)\psi$) and (6·17b) ($Q'=\exp(-i\omega_2 t)\psi$) for $\eta=1$ and $\eta=-1$, respectively. Such a non-relativistic approximation can be used for

$$\omega_\eta \gg g_\eta a^2 . \tag{6·28}$$

By the use of the second of Eqs. (6·19), (6·28) is rewritten as

$$(\mu/2)\omega_\eta{}^2 a^2 \gg (3/4) b_\eta a^4 . \tag{6·29}$$

Inequality (6·29) means that the soliton amplitude a should satisfy the condition that the corresponding harmonic energy is much larger than the corresponding anharmonic energy multiplied by three. The solution in the non-relativistic limit for case (1) was obtained in (I).

We now go back to the original discrete oscillator model by giving a brief discussion on solutions to Eqs. (6·8b) and (6·10). As in the case of Eq. (6·13′), we assume nearest neighbour interaction for the $L(n, m)$'s to obtain

$$\phi_{n+1}+\phi_{n-1}-2\phi_n-[(-1)^{\eta-1}/\omega_{L\eta}^2(k)]\ddot{\phi}_n=-\mathcal{V}_\eta{}'(\phi_n; k), \tag{6·30a}$$

$$2\omega\dot{\phi}_n+\omega_{L\eta}^2\sin(ka)(\phi_{n+1}-\phi_{n-1})=0 , \tag{6·30b}$$

where

$$\omega_{L\eta}(k)^2=\omega_{L\eta}^2\cos(ka) \text{ and } \omega_{L\eta}^2\to\omega_{L\eta}^2(k) \text{ in } \mathcal{V}_\eta(\phi_n; k). \tag{6·31}$$

The second of (6·31) means that the quantity $\omega_{L\eta}^2$ in $\mathcal{V}_\eta(\phi_n; k)$ should be replaced by $\omega_{L\eta}^2(k)$. Equations (6·30) are a generalization of Eq. (6·13′) to the case of moving solitons. Since the former is much more difficult to treat numerically as compared with the latter, here we content ourselves to making the following approximation procedure, reserving its detailed analysis for another occasion. As in the case of Eqs. (4·12) and (4·13), we take ϕ_n to be of the form $\phi_n=\phi_n(na-vt)\equiv\phi(\xi)$ and approximate $(v^2/\omega_{L\eta}^2(k))(d^2/d\xi^2)$ by $[v^2/a^2\omega_{L\eta}^2(k)]2[\cosh\{a(d/d\xi)-1\}]$. In terms of

$$s=\xi/[a-v(t/s)], \tag{6·32}$$

Eq. (6·30a) is then rewritten as

$$\phi_{s+1}+\phi_{s-1}-2\phi_s=-\gamma_\eta(k)\mathcal{V}_\eta{}'(\phi_s; k), \tag{6·33}$$

where

$$\gamma_\eta(k)=[1-(v^2/c_\eta(k)^2)]^{-1/2} \quad \text{with} \quad c_\eta(k)=a\omega_{L\eta}(k). \tag{6·34}$$

Such an approximation may be used for $v\ll c_\eta(k)$, where $c_\eta(k)$ is an extrapolation of c_η to the case of discrete oscillator system. Since this is entirely identical in form to Eq. (6·13′), the result obtained there can be used here. We observe first of all that Eqs. (6·22) and (6·23) obtained for moving solitons by the use of the continuum approximation can be extrapolated by comparing Eqs. (6·30) with Eqs. (6·12) and (6·16),

$$\phi_n=a\ \mathrm{sech}[a(3b_\eta/2\mu c_\eta(k)^2)^{1/2}\gamma_\eta(k)(na-vt)], \tag{6·35}$$

$$\omega=[\omega^{(0)}(\bar{k})^2-(-1)^{\eta-1}\omega_1 g_1 a^2]^{1/2}=\omega_\eta(k), \tag{6·36}$$

$$k=\omega v/c_\eta(k)^2 . \tag{6·37}$$

Such a result is only a zeroth order approximation to Eqs. (6·30). However, this already contains the non-trivial result that the vibron soliton frequency band $\omega_\eta(k)$ has the width equal to that of $\omega^{(0)}(k)$ in contrast to the case of Eqs. (6·23) and (6·26) and that k should be regarded as a crystal momentum. A little more accurate result can be obtained from numerical solutions to Eq. (6·33). Qualitative features of the solutions can easily be obtained by translating the numerical solutions to Eq. (6·13′) to the present case. Here the separatrix corresponds to the solution (6·22), (6·23) and (6·24), and the same reasoning on the change of the KAM trajectories and the appearance of chaotic phases can be used. Here the chaotic phases correspond to some sort of random motion of moving solitons, for which the soliton momentum is not strictly defined.

Finally, the binding frequency $\omega_B(k)$ of solitons with momentum k is defined by the relation

$$\omega_B(k)=\begin{cases}\omega^{(0)}(k)-\omega_1(k)=\omega_{B1}(k) & \text{for case (1)}, \quad (6·38\text{a})\\ \omega_2(k)-\omega^{(0)}(k_2-k)=\omega_{B2}(k) & \text{for case (2)}. \quad (6·38\text{b})\end{cases}$$

This gives a measure of stability of vibron solitons or exciton solitons in comparison with vibrons or excitons, respectively. The soliton frequency band $\omega_\eta(k)$ has a particularly well-defined meaning if it appears outside the frequency band $\omega^{(0)}(k)$ of the quasi-particles. Within the framework of the results given by Eqs. (6·35), (6·36) and (6·37), this takes place for the case in which $\omega_{B\eta}(k)$ is larger than the width of $\omega^{(0)}(k)$.

§ 7. Vibron solitons in α-helical proteins and comparison with the Davydov theory

In the previous section we made a detailed study of vibron solitons as an application of our model system, a simplified version of which was studied in (I) to give an alternative view to Davydov solitons in α helical proteins. In this section a more detailed and improved discussion is given to test our vibron soliton theory and to show that Davydov's idea can be formulated in a more physically reasonable and quantitatively correct form by the present oscillator-lattice model in comparison with the original Davydov theory.[3] In order to make our discussion self-contained, we first show the α helix in Fig. 2. Without loss of essential features of the problem, we use here a highly idealized model of the α helix by confining ourselves to considering a single chain of peptide groups. Then ω_0 in Eq. (2·8) or (5·1) is the eigenfrequency of the amide-I vibration. The quantities q_n, μ and $L(n, m)$ are the normal coordinate of the amide-I vibration of the nth peptide group (nth

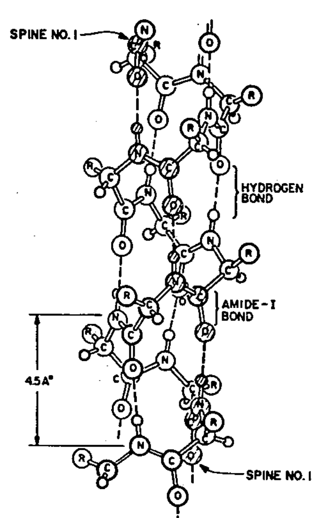

Fig. 2. Alpha-helix. The atoms of a single spine are cross-hatched.

amide-I oscillator), its effective mass and a dipole-dipole interaction force constant between the nth and mth amide-I oscillators, respectively. The quantities u_n, M and K in Eq. (2·2) are the longitudinal displacement of the nth peptide group, the mass of a peptide group plus residue and the force constant of a hydrogen bonding, respectively. The eigenfrequency ω_0 has energy of about 0.2 eV or 1650 cm^{-1} which is appropriate to store or transport the 10 kcal/mole or 0.43 eV of free energy released in the hydrolysis of adenosine triphosphate (ATP). We assume the amide-I vibration to be predominantly harmonic, so case (1) ($\eta=1$) considered in §§5 and 6 holds here.

We first compare the model Hamiltonian and a relevant field variable in the present theory and those in the Davydov theory.*) For this purpose we introduce creation and annihilation operators, b_n^+ and b_n, for the nth amide-I oscillator, rewriting q_n and p_n as

$$q_n=(2\mu\omega_0)^{-1/2}(b_n+b_n^+), \tag{7·1a}$$

$$p_n=(\mu\omega_0/2)^{1/2}(1/i)(b_n-b_n^+). \qquad (\hbar=1) \tag{7·1b}$$

In terms of the b_n's and the b_n^+'s Eq. (2·1) is rewritten as[5),**)]

$$H_{\text{osc}}=\sum_n \omega_0 b_n^+ b_n-\sum_{nm}\bar{J}(n,m)(b_n^+b_m+b_m^+b_n+b_n^+b_m^++b_nb_m), \tag{7·2}$$

where

$$\bar{J}(n,m)=L(n,m)/\mu\omega_0\equiv L(n,m)q_0^2\,. \tag{7·3}$$

On the other hand, the model Hamiltonian H_D for the amide-I oscillator system employed by Davydov takes the form

$$H_D=\sum_n \omega_0 b_n^+b_n-J\sum_n(b_n^+b_{n+1}+b_{n+1}^+b_n), \tag{7·4}$$

where J is a constant describing dipole-dipole interactions for nearest neighbour pairs of the oscillators. The principal difference of Eq. (7·2) from Eq. (7·4) is as follows: (i) The former contains the factor $(b_n^+b_m^++b_nb_m)$ in addition to $(b_n^+b_m+b_m^+b_n)$. (2) The quantity $\bar{J}(n,m)$ here is given in terms of the force constant $L(n,m)$ and the mean square displacement q_0^2. It is to be reminded that Eq. (7·4) itself is the model Hamiltonian originally used for Frenkel-type electronic excitons with transfer by exchange interactions, which is entirely of quantal nature, whereas Eq. (7·2) or (2·1) is classical in origin. The oscillator-lattice interactions and the lattice vibration Hamiltonian in the Davydov theory are given by the Hamiltonian

$$H_{\text{int}}=\chi\sum_n b_n^+b_n(u_{n+1}-u_{n-1}) \qquad (\chi=\text{const}) \tag{7·5}$$

and Eq. (2·2), respectively. Equation (7·5) is essentially of the same nature as Eq. (4·3). In studying the amide-I vibration we took the normal coordinate or the displacement field q_n as a relevant field variable, while the corresponding one in the Davydov theory is the probability amplitude a_n for finding a vibrational quantum in the nth amide-I oscillator subject to the constraint

*) Here comparison with the Davydov theory is made in its simplest form (see Davydov's text book cited in Ref. 3)).

**) $L(n,m)$ here is different from that in Ref. 5) by the factor 2.

$$\sum_n |a_n|^2 = 1 . \tag{7·6}$$

In the Davydov theory solitons are quantal entities, where number states are taken to be appropriate ones to describe solitons, while vibron solitons here are classical in nature, where in a certain sense phase states are considered as appropriate. Generally speaking, for such low energy excitations as those encountered in biological systems the phase-state description appears to be more appropriate.

These differences of the model amide-I oscillator Hamiltonian and the viewpoint on solitons are reflected in equations of motion obeyed by the solitons and soliton solutions. Starting from Eqs. (7·4), (2·2), and (7·5) and using the continuum approximation, Davydov directly arrived at the 1d NLS equation for $a_n \to a(x, t)$

$$i\frac{\partial a}{\partial t} + \frac{1}{2m_D}\frac{\partial^2 a}{\partial x^2} - (\omega_D + W_D)a + g_D|a|^2 a = 0 , \qquad (\hbar = 1) \tag{7·7}$$

with

$$\int (dx/a)|a(x, t)|^2 = 1 , \tag{7·6'}$$

where

$$\omega_D = \omega_0 - 2J , \quad m_D = 1/2Ja^2 , \quad g_D = 4\chi^2/K \quad \text{with } K^* \simeq K ,$$

$$W_D = (1/2)\sum_n [M\dot{u}_n{}^2 + K(u_{n+1} - u_n)^2]. \tag{7·8}$$

Aside from the factor W_D, one-soliton solutions to Eq. (7·7) with the normalization condition (7·6′) are given by

$$a(x, t) = \alpha \operatorname{sech}[a(m_D g_D)^{1/2}(x - vt)]\exp[-i(\omega t - kx)], \quad (v \ll c_s) \tag{7·9}$$

$$\alpha = a(m_D g_D)^{1/2}/2 , \tag{7·10}$$

$$\omega = \omega_D + (k^2/2m_D) - (g_D{}^2/16J) , \quad k = m_D v . \tag{7·11}$$

Here v is a parameter identified as the soliton velocity. We observe that Eq. (7·7) is identical in form to Eq. (6·27) for case (1) ($\eta = 1$), provided the factors ω_1, m_1 and g_1 are replaced by $\omega_D + W_D$, m_D and g_D, respectively. We make here one-to-one correspondence between μ, $L(l)$, K and A in our theory and J and χ in the Hamiltonian (7·4) and (7·5) in the Davydov theory. This can be done by (i) comparing Eqs. (7·2) and (7·4) with each other and (ii) comparing Eq. (4·3) with $v(q) = (A/2)q^2$ and Eq. (7·1a) with Eq. (7·5). In terms of ordinary units which will be used throughout the remaining part of this paper, a result of such a procedure is written as

$$L(1) = \mu\omega_0 J/\hbar , \qquad A = (2\mu\omega_0/\hbar)\chi . \tag{7·12}$$

Here $L(1)$ is the value of $L(l)$ which corresponds to nearest neighbour interaction. By the use of Eqs. (6·3), (6·15), (6·19), (7·12), one-to-one correspondence is then obtained between ω_1 and ω_D except the factor W_D and between m_1 and m_D in the limit $\omega_W/\omega_0 \ll 1$, where ω_W is the width of the frequency band $\omega^{(0)}(k)$. No such correspondence, however, exists for the coupling constant g and the soliton binding energy $E_B(k) = \hbar\omega_{B1}(k)$, the situation for the former being given by the relation

$$g_1 = 3g_D/q_0^2 \quad \text{with} \quad q_0^2 = \hbar/\mu\omega_0 . \tag{7·13}$$

This is due to the difference for the origin of the NLS equation. Namely, Eq. (7·7) is nothing but the Schrödinger equation obeyed by the probability amplitude a_n derivable from the exchange-type Hamiltonian H_D in the continuum limit, whereas Eq. (6·27) obeyed by the displacement field results from Eq. (6·1) in anharmonic lattice dynamics through two steps of approximation procedures, one being the rotating-wave approximation and the other the non-relativistic limit of the nonlinear Klein-Gordon equation obeyed by the complex field Q, in conjunction with the use of the continuum approximation. Due to these differences, the properties of the one-soliton solution and the soliton binding energy obtained here are different from those of the Davydov theory. Namely, the binding energy of the Davydov solitons takes a unique value since their amplitude is automatically given, whereas for vibron solitons the soliton amplitude is an arbitrary parameter and therefore the soliton binding energy increases as it increases.

In applying our theory to biological problems, our general recognition is that we should reserve spatial discreteness if it is possible for us to do so. Keeping this in mind, confining ourselves to the case $v \ll c_1$ as well as $v \ll c_s$ and assuming the anharmonicity of the amide-I vibration to be negligibly small, we present the following form of one-vibron-soliton solutions for α helical proteins

$$Q_n = \alpha \operatorname{sech}[\alpha\{3A^2/\mu c_1(k)^2 K\}^{1/2}(na - vt)]\exp[-i(\omega t - kna)], \tag{7·14}$$

$$\omega = [\omega^{(0)}(k)^2 - (3A^2/K\mu)\alpha^2]^{1/2} = \omega_1(k), \quad k = \omega v/c_1(k)^2 . \tag{7·15}$$

Here we have used Eqs. (6·35), (6·36) and (6·37) for case (1) and put $\gamma_1(k)=1$. In doing numerical test of our theory, we pay attention to the binding energy of vibron solitons. For this purpose, we first write the soliton binding energy $E_1(k) = \hbar\omega_1(k)$ in terms of χ and K, since these quantities and J were estimated numerically by Russian workers[9)~11)] and by Scott.[4)] Inserting the second of Eqs. (7·12) into Eq. (7·15) and measuring the squared soliton amplitude α^2 in units of the mean square displacement q_0^2 of the lattice-free oscillator, i.e., $\alpha^2 = q_0^2 y$, we get

$$E_1(k) = [E^{(0)}(k)^2 - (12E_0\chi^2/K)y]^{1/2} \tag{7·16}$$

with

$$E_1(k) = \hbar\omega_1(k), \quad E^{(0)}(k) = \hbar\omega^{(0)}(k), \quad E_0 = \hbar\omega_0 . \tag{7·17}$$

In the above equations y is a dimensionless quantity yet to be estimated. The binding energy $E_B(k)$ of solitons is therefore given by

$$E_B(k) = E^{(0)}(k) - [E^{(0)}(k)^2 - (12E_0\chi^2/K)y]^{1/2} . \tag{7·18}$$

For vibrons in α helical proteins and also those in most of molecular crystals, the width ω_W^2 of the vibron squared frequency band

$$\omega_W^2 = \omega^{(0)}(k_2)^2 - \omega^{(0)}(0)^2 = (8/\mu)\sum_{l=\text{odd}} L(l), \tag{7·19}$$

is much too small compared with ω_0^2. Equation (7·18) is then reduced to

$$E_B(k) \cong (6\chi^2/K)y . \tag{7·20}$$

The dimensionless factor y can be esitmated by the stability condition of the soliton squared frequency band that $\omega_1(k)^2$ as a whole should be separated from the squared vibron frequency band $\omega^{(0)}(k)^2$(see Fig. 3). By the use of Eqs. (7·15) and (7·19), this condition is written as

$$\alpha^2 > (8/3)(K/A^2) \sum_{l=\mathrm{odd}} L(l) \equiv \alpha_m^2 . \tag{7·21}$$

Inserting Eqs. (7·12) into Eq. (7·21) with the $L(l)$'s nonvanishing only for nearest neighbour pairs, we get the lower bound α_m of α as follows:

$$\alpha_m^2 = (2/3)(JK/\chi^2) q_0^2 . \tag{7·22}$$

This implies that

$$y \simeq (2/3)(JK/\chi^2) \equiv y_0 . \tag{7·23}$$

For the estimation of y_0 and the soliton binding energy, we adopt the numerical values of J, K and χ used by Scott in his detailed analysis of the Davydov theory[4] (see also Refs. 9)~11)):

$$J = 7.8\,\mathrm{cm}^{-1}, \quad K = 1.95 \times 10^4\,\mathrm{erg\,cm}^{-2}, \quad \chi = 3.4 \times 10^{-6}\,\mathrm{erg\,cm}^{-1} . \tag{7·24}$$

This gives

$$y_0 = 1.73 , \tag{7·25}$$

$$E_B(k) = 18.0 \times y\,\mathrm{cm}^{-1} \qquad \text{for Eq. (7·20).} \tag{7·26}$$

It is seen that y is of the order of unity and that the binding energy of vibron solitons is about 15~35 cm^{-1} for moderate value of y ($0.83 \le y \le 1.94$).

Until now, there is no experimental evidence for the existence of solitons in α helical proteins, in vivo or vitro. However, the evidence for solitons of similar nature does exist for acetanilide $(CH_3CONHC_6H_5)_x$ or ACN which is an organic solid having the structure somewhat similar to the α helical protains. In ACN two close chains of hydrogen-bonded amide groups run through the crystal. It is an interesting system because nearly planar amide groups display bond distances which are close to those found by polypeptides. Careri, Buontempo, Carta, Gratton and Scott[12] have shown that a band in the infrared spectrum that is red-shifted by about 15 cm^{-1} from the amide-I maximum at 1665 cm^{-1} may arise from amide-I solitons originally suggested by Davydov. These workers provided an explanation of this experimental result by using the Davydov theory. We wish to point out here that the frequency shift 15 cm^{-1}, which can be considered as the binding energy of solitons, lies in the range 15~35 cm^{-1} of the binding energy obtained above, although numerical values of χ and K given by Eq. (7·24) may be different from those of ACN. We close this section by comparing our result for the soliton binding energy with that given by Davydov theory, which we denote by E_{BD}. From Eqs. (7·8) and (7·11) it is obtained as follows:

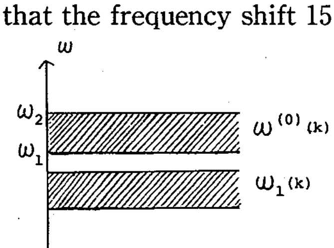

Fig. 3. Schematic feature of vibron soliton frequency band $\omega_1(k)$ which appears below the bottom of vibron frequency band $\omega^{(0)}(k)$.

$$E_{BD}=g_D{}^2/16J=\chi^4/K^2J\,. \tag{7·27}$$

The difference of natures of vibron solitons from Davydov solitons can also be seen by comparing the binding energy. Putting Eqs. (7·24) into Eq. (7·27), the numerical value of E_{BD} is given by

$$E_{BD}=1.15\,\mathrm{cm}^{-1}\,. \tag{7·28}$$

It is seen that soliton binding energy given by the Davydov theory is much too small compared with the result obtained in this paper. The Davydov theory gives the width E_W of the energy band of amide-I vibration excitons as follows:

$$E_W=4J=31.2\,\mathrm{cm}^{-1}. \tag{7·29}$$

It is seen that with such small binding energy almost all part of the soliton energy band is merged into the amide-I energy band. It appears that these numerical results also lend support to the advantage of our vibron soliton theory over the Davydov theory.

§ 8. Concluding remarks

We have shown that the exactly tractable oscillator-lattice system considered in this paper is rich in its structure and nonlinear excitations. It enables us to study the essential nonlinearity properties of the system without resorting to the conventional continuum approximation. Although the model system is fairly general, we limited our discussion to the case in which the on-site potential of the lattice-free oscillator system is of single-minimum type. Here the effect of nonlinear oscillator-lattice interactions is classified into two types: (1) One is to modulate vibrons, which are elementary excitations of the lattice-free oscillator system, to yield vibron solitons as a kind of envelope solitons. (2) The other is to produce coherent states of polar modes and kinks or topological solitons that are stabilized by nonlinear deformation of the lattice system. It was shown that the former provides us with one of the most natural models to elucidate the existence of solitons in α helical proteins as suggested by Davydov.[3] It was also shown that the latter can be considered as a working microscopic model to study Fröhlich's suggestion of biological activity.[1),2)]

Although we feel the model employed here is non-trivial for the study of the nonlinearity problem of the model itself and its implication to the problem of biological activity, it still suffers from several simplifications. Inclusion of the effect of phonon-mediated excitation transfer in the formulation, taking the existence of three spines in the α helix into account in the problem of vibron solitons, considering the effect of electric field on the polarization field, etc., are all likely to improve and refine the theory presented here. Another point worth mentioning is to do numerical calculations to solve differential-difference equations discussed in §6. Severals of these problems and other related ones will be studied in the near future.

Acknowledgements

It is a great pleasure for the author to dedicate this paper to Professor K. Tomita on the occasion of his retirement from Kyoto University.

Appendix A
—— Derivation of Eqs. (3·8) and (3·9) ——

From Eqs. (3·5) and (3·6) equations of motion obeyed by the q's are written as

$$\ddot{q}_n+\epsilon(x_n)^2(1-2q_n{}^2)^{-1/2}q_n-2\epsilon(x_n)\sum_m J(|x_m-x_n|)q_m$$
$$-D'(|a|)(\dot{u}_{n+1}-\dot{u}_{n-1})(\dot{q}_n/\epsilon)=0\,, \tag{A·1}$$

Inserting Eqs. (3·6) and (3·7) and retaining a term first order with respect to the u's in $\epsilon(x_n)^2$, we get

$$\ddot{q}_n+\epsilon^2(1-2q_n{}^2)^{-1/2}q_n-2\epsilon\sum_m J(n,\,m)q_m$$
$$+2[\epsilon(1-2q_n{}^2)^{-1/2}q_n-\sum_m J(n,\,m)q_m]D'(|a|)(u_{n+1}-u_{n-1})$$
$$-2\epsilon J'(|a|)[(u_{n+1}-u_n)q_{n+1}+(u_n-u_{n-1})q_{n-1}]-D'(|a|)(\dot{u}_{n+1}-\dot{u}_{n-1})(\dot{q}_n/\epsilon)=0\,. \tag{A·2}$$

Due to inequality (3·2) the second term in the square bracket in the second line of the above equation can be neglected compared with the first term. Furthermore, since time variation of the u_n's is much too small compared with that of the q_n's, i.e., $D'(|a|)\dot{u}(\dot{q}/\epsilon) \ll \epsilon^2 q,\ \epsilon D'(|a|)uq,\ \epsilon Jq,\ \epsilon J'(|a|)uq$, the last term can also be neglected. Equation (A·2) then is reduced to

$$\ddot{q}_n+\epsilon^2(1-2q_n{}^2)^{-1/2}q_n-2\epsilon\sum_m J(n,\,m)q_m$$
$$+2\epsilon D'(|a|)(1-2q_n{}^2)^{-1/2}q_n(u_{n+1}-u_{n-1})$$
$$-2\epsilon J'(|a|)[(u_{n+1}-u_n)q_{n+1}+(u_n-u_{n-1})q_{n-1}]=0\,. \tag{A·3}$$

It is easily seen that Eq. (A·3) is derivable from Eqs. (3·8) and (3·9).

Appendix B
—— An Approximate Treatment of Eq. (4·2) ——

In contrast to Eq. (4·5), Eq. (4·2), as it stands, is not exactly tractable. Here we approximate the last term in Eq. (4·2) as

$$2\lambda(q_{n+1}-q_{n-1})q_n\to\lambda(q_{n+1}^2-q_{n-1}^2) \tag{A·4}$$

and use Eqs. (4·12) and (4·13) to obtain

$$K^*\{\cosh[a(d/d\xi)]-1\}u+\sinh[a(d/d\xi)][V(q)-\lambda q^2]=0\,. \tag{A·5}$$

It is seen that this approximation procedure yields the renormalization of $v(q)$ as

$$V(q)\to V(q)-\lambda q^2\equiv V^*(q). \tag{A·6}$$

Approximate solutions to Eq. (4·2) are then given by Eq. (4·7) with K and V replaced by K^* and V^*, i.e.,

$$u_{n+1}-u_n=(1/K^*)[V^*(q_{n+1})+V^*(q_n)]+(u_0/2). \tag{A·7}$$

Inserting these equations back to Eq. (4·1), we get

$$\mu\ddot{q}_n+v'(q_n)+u_0[V'(q_n)-\lambda(q_{n+1}+q_{n-1})]-2\sum_m L(n,m)q_m$$
$$-(1/K^*)[2V^*(q_n)+V^*(q_{n+1})+V^*(q_{n-1})]$$
$$+(2\lambda/K^*)\{[V^*(q_{n+1})+V^*(q_n)]q_{n+1}+[V^*(q_n)+V^*(q_{n-1})]q_{n-1}\}=0\,. \quad (\mathrm{A}\cdot 8)$$

References

1) H. Fröhlich, Collective Phenomena **1** (1973), 101.
2) H. Bilz, H. Büttner and H. Fröhlich, Z. Naturforsch. **36B** (1981), 208.
3) A. S. Davydov, *Biology and Quantum Mechanics* (Pergamon Press, 1982), chap. VII and references cited therein; Sov. Phys. -Usp. **25** (1982), 899 and references cited therein.
4) A. C. Scott, Phys. Rev. **26A** (1982), 578; in *Proc. 7th Kyoto Summer Institute on Dynamical Problems in Soliton Systems* (Springer-Verlag, 1985) and references cited therein.
5) S. Takeno, Prog. Theor. Phys. **71** (1984), 395.
6) G. Kemeny, J. Theor. Biol. **48** (1974), 231.
7) For a preliminary discussion, see S. Takeno, Prog. Theor. Phys. **69** (1983), 1798.
8) See for example, V. I. Arnold, *Mathematical Methods of Classical Mechanics* (Springer-Verlag, New York-Heidelberg-Berlin, 1980), Appendix 8.
9) N. A. Nevskaya and Y. N. Chirgadze, Biopolymers **15** (1976), 637.
10) V. A. Kuprievich and Z. G. Kudritskaja, cited in Ref. 4).
11) V. A. Kuprievich and V. E. Klymenko, Mol. Phys. **34** (1977), 1287.
12) G. Careri, U. Buontempo, F. Carta, E. Gratton and A. C. Scott, Phys. Rev. Lett. **51** (1983), 304.