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A characteristic feature which exists in biologically important macro­
molecules such as proteins and DNA is their structural and dynamical
flexibility. This reflects the fact that many functional properties of
these molecules cannot be completely understood from the average struc­
ture as determined by x-ray analysis. For example, reaction rates of
enzymes may be correlated with the structural and dynamical flexibility
of proteins, while local structural fluctuations in DNA may be a part of
what proteins recognize. As is well known, recent development of nonli­
near science has yielded new and interdisciplinary concepts such as so­
litons, universal routes to chaos, fractals, pattern selection and so
on. Of these soliton problem has produced a unifying influence in natural science. The aim of this paper is to explore the utility of soliton concept in understanding the structural and dynamical properties of proteins.

2. MODEL DYNAMICAL SYSTEM

To simulate proteins, we consider a 1D oscillator system, in which each oscillator is linearly coupled with neighbouring ones and nonlinearly with lattice vibrations. The oscillator Hamiltonian $H_{osc}$ is given by

$$H_{osc} = \sum_n \left( (\frac{m q_n^2}{2}) + v(q_n) \right) - \sum_{n,n'} L(n,n') q_n q_{n'}$$

Here $q_n$, $v(q_n)$, and $L(n,n')$ are the normal coordinate of the nth oscillator with effective mass $m$, an on-site potential, and a force constant, respectively. Two types of lattice vibrations are considered, acoustic and optic vibrations, the former and the latter being given by the Hamiltonians

$$H_{La} = \sum_n \left( (\frac{M u_n^2}{2}) + Ku_n^2 \right)$$

and

$$H_{LO} = \sum_n \left( (\frac{M u_n^2}{2}) + Ku_n^2 \right)$$

respectively. Here $u_n$ and $K$ are the displacement of the nth molecule with molecular mass $M$ from its equilibrium position and a force constant respectively. Oscillator-lattice interactions are described by the Hamiltonians $H_{La}$ or $H_{LO}$ in which $V(q_n)$ is a function of $q_n^2$. For these two model systems equations of motion for the $q_n$'s and the $u_n$'s take the form

(i) case of acoustic phonons

$$m \ddot{q}_n + v'(q_n) - 2 \sum_{n'} L(n,n') q_{n'} + v'(q_n) (u_{n+1} - u_{n-1}) = 0, \quad (2.4a)$$

$$M \ddot{u}_n + Ku_n (u_{n+1} + u_{n-1} - 2u_n) - [V(q_{n+1}) - V(q_{n-1})] = 0, \quad (2.4b)$$

(ii) case of optic phonons

$$m \ddot{q}_n + v'(q_n) - 2 \sum_{n'} L(n,n') q_{n'} + v'(q_n) u_n = 0, \quad (2.5a)$$

$$M \ddot{u}_n + Ku_n V(q_n) = 0. \quad (2.5b)$$

If the velocity $v$ of nonlinear excitations under consideration is much smaller than the velocity of phonons in case (i) and it satisfies the relation $Mv^2 < Ku^2$ in case (ii), the factor $Mv^2$ can be neglected to give

$$u_{n+1} - u_n = -(1/K) [V(q_{n+1}) + V(q_n)] + (u_0/2)$$

for case (i) \quad \text{(2.6)}

$$u_n = -v(q_n)/K$$

for case (ii) \quad \text{(2.7)}

where $u_0$ is an integral constant. It is understood that the $u$'s here depend only on the secular part $V(Q_n^2)$ of $V(q_n) = V(q_n^2)$, where $Q_n$ and $Q_n^*$ are the negative and position frequency parts of $q_n$, respectively. Inserting Eqs. (2.6) and (2.7) back into Eqs. (2.4a) and (2.5a), respectively, we get equations of motion written entirely in terms of the $q$'s derivable from the following effective oscillator Hamiltonian

$$H_{eff} = \sum_n \left( (\frac{m q_n^2}{2}) + U(q_n^2) \right) - \sum_{n,n'} L(n,n') q_n q_{n'} + \sum_n W(q_n, q_{n+1})$$

where
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\[ U(q_n) = \begin{cases} v(q_n) + u_0 V(q_n) - (2/K) V(q_n)^2 & \text{for case (i)} \\ v(q_n) - (1/2K) V(q_n)^2 & \text{for case (ii)} \end{cases} \]  (2.9a)  (2.9b)

\[ W(q_n, q_{n+1}) = \begin{cases} -(1/K) V(q_n) [V(q_{n+1} - V(q_n)) & \text{for case (i)} \\ 0 & \text{for case (ii)} \end{cases} \]  (2.10a)  (2.10b)

The on-site potential \( v(q) \) is modified into the effective one \( U(q) \) by the oscillator-lattice interactions, where nonlinear attractive potentials characterized by the factor \(-V(q)^2/K\) are induced. Two more effects exist for case (i). Namely, \( u_0 V(q_n) \) and \( W(q_n, q_{n+1}) \) represent a modification of \( v(q_n) \) due to the existence of strain field and phonon-assisted vibration transfer, respectively. In a sense, the result so obtained for low velocity nonlinear excitations, which appear to play a crucial role in nonlinear phenomena in biological systems, can be considered as arising from a coherent part of the oscillator-lattice interactions.

3. DYNAMICAL SELF TRAPPING OF VIBRONS

To study the effect of the nonlinear attractive potential, we put \( u_0 = 0 \) and neglect phonon-assisted vibration transfer for case (i). As the simplest yet most important model, we take

\[ v(q) = m \omega_0^2 q^2/2, \quad V(q) = Aq^2. \]  \( (3.1) \)

Here \( \omega_0 \) and \( A \) are an eigenfrequency of the oscillator and a coupling constant, respectively. An explicit expression for the effective on-site potential \( U(q) \) is then obtained as follows

\[ U(q) = \begin{cases} (m \omega_0^2/2) q^2 - (A^2/2K) q^4 & \text{for case (i)} \\ (m \omega_0^2/2) q^2 - (A^2/8K) q^4 & \text{for case (ii)} \end{cases} \]  (3.2a)  (3.2b)

We are particularly interested in localized modes induced by the nonlinear attractive potential appearing below the bottom \( \omega_1 = \omega(0)(0) \) of the vibron frequency band \( \omega(0)(k) = (\omega_0^2 - (2/m) \sum_n L(n) \exp(ikn))^{1/2} \) as shown in Fig.1. Here \( a \) is the lattice constant of the oscillator system. This is a self-trapped state of vibrons referred to as vibron solitons. Here we limit our discussion to case (ii), since Eqs. (3.2a) and (3.2b) are of the same form, and such solitons has been identified in red-shifted infrared spectra of amide I vibrons in crystalline acetonitrile or ACN (CH₃CONHCH₃)ₓ recognized as a quasi-poly-peptide system. In studying equations of motion for the \( q \)'s governed by Eq. (2.8) with \( U(q) \) given by Eq. (3.2b), we put \( q_n = \omega(t) \) with \( \phi_n = \omega_0 t \) and employ the rotating-wave approximation to obtain

\[ -Q_n + \omega_0^2 Q_n - (2/m) \sum_n L(n, n') Q_n' - (3A^2/2Km)|Q_n|^2 = 0 \]  (3.3)

with

\[ u_n = -(A/K)|Q_n|^2. \]  (3.4)

We seek solutions to this in the form \( Q_n = f_n \exp[-i(\omega t - kn)] \), where \( k \) and
\( \omega \) are real constants identified as the momentum and eigenfrequency of vibron solitons, respectively, while \( f_n \) is a real envelope function. Inserting this into Eq. (3.3) gives

\[
\frac{1}{2} f_n' + \left( \frac{W_0}{k} \right)^2 f_n' - (2L/m) \cos(ka) \left( f_{n+1} + f_{n-1} - 2f_n \right) - \left( \frac{3A^2}{2Km} \right) f_n^3 = 0
\]

(3.5a)

\[
2df_n' + (2L/m) \sin(ka) \left( f_{n+1} - f_{n-1} \right) = 0.
\]

(3.5b)

Here we employed a nearest neighbour approximation for \( L(n,n') \) with \( L=L(1) \). Except in the case of a continuum limit, where solutions to Eq. (3.5) have a form similar to those to the 1d nonlinear Schrödinger equation, the above equations cannot be solved analytically.

Let us pay attention to stationary localized modes for which \( k=0 \) and \( f_n \) is time-independent. A red-shifted absorption band at about 1650 cm\(^{-1}\) in ACN as shown in Fig. 2 can be considered as being due to such solitons.1) Equation (3.5a) then reduces to

\[
\left( \frac{W_0}{k} \right)^2 f_n' - (2L/m) (f_{n+1} + f_{n-1}) - \left( \frac{3A^2}{2Km} \right) f_n^3 = \omega^2 f_n',
\]

(3.6)

while (3.5b) is automatically satisfied. In terms of lattice Green's functions

\[
G(n,n';\omega) = \frac{1}{\pi} \sum_k \frac{\exp(ik(n-n')a)}{k \omega(k^2 - \omega^2)^2}.
\]

(3.7)

and the soliton amplitude \( b \) defined by \( f_n = b w_n \) with max \( |w_n| = 1 \), Eq. (3.7) is rewritten as

\[
w_n = \left( \frac{3A^2}{2Km} \right) \sum_{n'} G(n,n';\omega) w_{n'}^3.
\]

(3.8)

This is treated by using a successive approximation. We pay particular attention to a spatially symmetric or \( \sigma \)-like mode \( w_n = w_{-n} \) localized at \( n=0 \). Here the assessment of the localization of the localized mode is required by estimating numerical values of \( L, m, A \) and \( K \), in addition to the amide I frequency \( \omega_0 = 1665 \) cm\(^{-1}\). Making one-to-one correspondence to the theory in ref. [1] based on the Davydov theory,2) we get

\[
J = (\hbar L/m) \omega_0 = 3 \sim 4 \ \text{cm}^{-1}, \quad K = 1.3 \times 10^4 \ \text{N/m},
\]

\[
\chi = (\hbar A/2m) \omega_0 = 6 \times 10^{-11} \ \text{N}, \quad \hbar \omega_1 = 1665 \ \text{cm}^{-1}.
\]

In terms of \( \varepsilon = (\hbar \omega_0 - \hbar \omega)/2J \) and \( \gamma = (m \omega_0 / \hbar) b^2 \), the lattice Green's function \( G(n,n';\omega) = G(n-n;\omega) \) is written as

\[
G(n;\omega) = B \left( 1 + \varepsilon \right)^{1/2} \left[ 1 + \varepsilon + \left( 1 + \varepsilon \right)^{1/2} \right]^{-1/2} \left[ 1 + \varepsilon + \left( 1 + \varepsilon \right)^{1/2} \right]^{-1},
\]

(3.9)

where

\[
B = (3/2) (\chi^2 / KJ) = 7.5 \text{ for } J = 3 \ \text{cm}^{-1} \text{ and } 5.6 \text{ for } J = 4 \ \text{cm}^{-1}.
\]

(3.10)

The yet undetermined factor \( \gamma \) is taken to be 1/2. This corresponds to the soliton amplitude associated with the zero-point motion of the amide I vibration. As the first order approximation, we assume that the localized mode is strongly localized at the site \( n=0 \). Equation (3.8) then
reduces to
\[ 1 - (3A^2b^2/2Km)G(0; \omega) = 0 \quad \text{or} \quad \xi = \zeta (B^2y^2+1)^{1/2} - 1. \quad (3.11) \]

Inserting the numerical values obtained above to this, we get \( \xi = 2.9 \) for \( J=3 \text{ cm}^{-1} \) and 2.0 for \( J=4 \text{ cm}^{-1} \). The binding energy \( E_B = h(\omega_1 - \omega) \) of solitons, which corresponds to a red-shift frequency of amide I absorption line in ACN, is \( E_B = 17.4 \text{ cm}^{-1} \) for \( J=3 \text{ cm}^{-1} \) and 16.0 \text{ cm}^{-1} \) for \( J=4 \text{ cm}^{-1} \). The quantity \( \{1+\xi + [(1+\xi)^2-1]^{1/2} \}^{-1} \), which is a measure of the localization of the vibron solitons, is 0.13 and 0.17 for these two values of \( J \). This implies that our first order approximation is actually a good approximation, and we do not need to proceed any more. The soliton binding energy so obtained is in good agreement with the experimental result obtained by Careri et al. \(^1\) Here we have not yet specified optical phonons with which the amide I vibration in ACN couples. These may be phonon modes involving proton motion. It is seen from Eq.(3.4) that a local strain field or coherent phonon field is accompanied with stationary vibron solitons.

REFERENCES


K-dV方程式の一般的座標変換

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ソリトン方程式と呼ばれる方程式の中には適当な変換によって結びつけられるものがある。その一例として、Konno-Ichikawa-Wadati方程式 \(^1\)

\[ \theta_t + \cos^2 \theta (\sin \theta) \xi \xi = 0 \quad (1) \]

は、Ishimori \(^2\)によって見付けられた変換

\[ \begin{cases} 
\xi = \int^x \cos \theta \, dx \\
\tau = t 
\end{cases} \quad (2) \]

によって次ののようなmodified K-dV方程式

\[ \theta_t + \frac{1}{2} \theta_x^2 + \theta_{xxx} = 0 \quad (3) \]