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Two exciton states in discrete and continuum alpha-helical proteins

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ABSTRACT

The dynamics of alpha-helical proteins is described by proposing a model Hamiltonian representing two exciton bound states. The dynamics is studied by constructing the equations of motion using a two exciton eigen-function in the discrete level. A numerical analysis shows the existence of two excitons in alpha-helical proteins and its propagation as solitons along the hydrogen bonding spines. The lattice model is also treated in the continuum limit which is a valid approximation in the low temperature, long wavelength limit. The resulting equation is studied using the multiple scale perturbation analysis which also shows the transfer of two exciton energy through alpha-helical proteins in the form of solitons with no change in velocity and amplitude.

1. Introduction

The alpha-helical structure of protein is one of the important secondary structures which consists of three chains of hydrogen-bonded peptide groups (HNCO) with associated side groups running along the direction of the helical axis with the sequence "...H–N–C=O...H–N–C=O...H–N–C=O..." where C=O represents the amide-I bond and the dotted lines represent hydrogen bonds. The leading role in the energy transfer in alpha-helical proteins is played by amide-I vibrations of atoms in the peptide groups. Davydov [1–5] suggested that nonlinear self-trapping could serve as a method of energy transport along quasi-one-dimensional chains of protein molecules through the formation of solitons moving without loss of energy. A soliton along the hydrogen bonding spines in alpha-helical proteins is formed as a result of the dynamical balance between the dispersion due to the resonant interaction of intrapeptide dipole vibrations and the nonlinearity provided by the interaction of these vibrations with the local displacements of the equilibrium positions of the peptide groups. In this context Davydov showed that the dynamics of alpha-helical proteins is governed by the completely integrable nonlinear Schrödinger (NLS) equation which possesses N-soliton solutions. Following Davydov's original suggestion, the model has been elaborated by many physicists to describe more accurately the dynamics of energy transfer through alpha-helical proteins at the classical and quantum levels [6–26]. These works include both analytical and numerical studies. In the same line, the effect of higher order interactions and excitations and interspine coupling on the dynamics of alpha-helical protein molecule has been studied both at the discrete and continuum levels by Latha et al. [27–32] in the recent past. Recently it is observed using ultrafast infrared spectroscopy, a N–H stretching mode self trapping in the poly-γ-benzyl-L-glutamate helix [33]. Two positive bands in the transient absorption spectrum have been assigned to self-trapped two-exciton states. It is suggested that the intrinsic anharmonicity of amide modes plays an important role when more than one amide excitation is present [34]. Since the energy of an amide double excitation is reduced in the anharmonic case, two excitons do not move independently, but rather form a bound self-trapped state. Studies on the dynamics of two quantum states have been reported earlier by Förner [35] and Kerr et al. [36]. The multi-exciton self-trapping in alpha-helical proteins has been studied recently [37–40] by the multiconfiguration time-dependent Hartree method for the time propagation of the exciton-chain vibrational wave function. In these studies only the linear and pump-probe infrared absorption spectra are calculated by numerical time propagation of the exciton-chain vibrational wave function. As analytical studies would give more information, in this Letter, we investigate the underlying dynamics of alpha-helical proteins with special consideration to two exciton states. We propose a model Hamiltonian using the second quantized operators of quantum field theory and derive the equations of motion after averaging the Hamiltonian using a suitable wave function and study the dynamics both in the discrete and continuum levels.

The Letter is organized as follows. In Section 2, we introduce the Hamiltonian for the two exciton states and study numerically the dynamics for specific choices of physical parameters. In Section 3, the lattice model is treated as a continuum chain and the equations of motion are constructed. The resulting equation is studied using multiple scale perturbation analysis and the details are presented in Section 4. The results are summarized in Section 5.

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2. Model and equations of motion

We consider a protein molecule which consists of peptide groups bonded in periodic arrays in three chains along the hydrogen bonding spine running parallel to the helical axis (alpha-helical secondary structure). Experimental results, however, show that the interspine coupling among the three hydrogen bonding spines is small compared to the intraspine coupling among adjacent peptide group of molecules [41]. Therefore it is expected that the study of the dynamics of a single hydrogen bonding molecular chain will almost reproduce the dynamics of the full alpha-helical protein molecular chain. We assume that the peptide group of the alpha-helical protein chain along the hydrogen bonding spine is located at nodes $n\epsilon$ $(n = 0, \pm 1, \ldots)$ where ϵ is the lattice spacing and consider molecular excitations along the spine in the form of dipoles. In this model we also include higher order excitations and interactions which describe the two exciton states and write the Hamiltonian in the dimensionless form using the second quantized operators as

$$\begin{aligned} H = \sum_n \big\{ & E_0 a_n^\dagger a_n - J\big(a_{n+1}^\dagger a_n + a_n^\dagger a_{n+1}\big) + E_1 a_n^\dagger a_n a_n^\dagger a_n \\ & + J_1\big(a_{n+1}^\dagger a_n a_{n+1}^\dagger a_n + a_n^\dagger a_{n+1} a_n^\dagger a_{n+1}\big)\big\} + \sum_q \hbar\omega_q b_q^\dagger b_q \\ & + \sum_{n,q}\big\{\hbar\omega_q a_n^\dagger a_n\big[\big(\chi_n^q b_q^\dagger + \chi_n^{q^*} b_{-q}\big) \\ & + a_n^\dagger a_n\big(\chi_{1n}^q b_q^\dagger + \chi_{1n}^{q^*} b_{-q}\big)\big]\big\}. \end{aligned} \tag{1}$$

In Hamiltonian (1), $a_n^\dagger$ (a_n) creates (annihilates) an exciton in the local basis state n and $b_q^\dagger$ (b_q) creates (annihilates) a vibrational quantum of wave vector q in the normal mode with frequency ω_q. The constant E_0 is the energy of a single exciton on a given site while J refers to hopping of excitons between neighboring sites. E_1 represents the two exciton energy of higher order (quadrupole type) excitations of the molecules in each unit cell and J_1, the quadrupole–quadrupole type coupling between the adjacent unit cells. These higher order terms describe two quanta of amide-I excitations since the energy source for the amide-I excitations in living systems is the hydrolysis of ATP which can generate two quanta of amide-I excitations. The phonon frequencies ω_q is the proportionality constant between longitudinal displacement and the corresponding restoring force. The exciton–phonon coupling constant χ_n^q and χ_{1n}^q indicates how strongly localized vibrational energy will induce distortion of the alpha-helix and also how strongly alpha-helix distortion will trap localized vibrational energy. It arises from modulation of amide-I (C=O stretching) energy by stretching of the adjacent hydrogen bond. The functional dependence of the phonon frequencies ω_q and the coupling coefficient χ_n^q and χ_{1n}^q on the phonon mode index q will vary from system to system. The detail of this dependence is unimportant to our present purpose, so we leave it unspecified.

The wave function for the collective excitation of the two exciton states may be sought in the form

$$\big|\psi(t)\big\rangle = \frac{1}{\sqrt{2}}\sum_n A_n(t) a_n^{\dagger 2} \exp\Big\{\sum_q\big[\beta_{q,n}(t) b_q^\dagger - \beta_{q,n}^*(t) b_q\big]\Big\}|0\rangle. \tag{2}$$

In Eq. (2), $|0\rangle$ represents the vacuum state wave function. $A_n(t)$ and $\beta_{q,n}(t)$ are considered to be dynamical variables to which Lagrange's equations of motion could be applied. We derive the equations of motion using the Lagrangian given by

$$L = \frac{i\hbar}{2}\left[\langle\psi|\frac{\partial}{\partial t}|\psi\rangle - \left[\frac{\partial}{\partial t}\langle\psi|\right]|\psi\rangle\right] - \langle\psi|H|\psi\rangle. \tag{3}$$

Let us for this moment introduce the normalization condition $\sum_n |\psi_n|^2 = 1$. Using Eqs. (1) and (2) in Eq. (3), we get

$$\begin{aligned} L = \sum_n \Big\{ & \frac{i\hbar}{2}\big[2A_n^*\dot{A}_n - 2\dot{A}_n^* A_n\big] - E_0|A_n|^2 + J_n^{(1)} A_n^* A_{n+1} \\ & + J_n^{(2)} A_{n+1}^* A_n - E_1|A_n|^4 - J_{1n}^{(1)} {A_{n+1}^*}^2 {A_n}^2 \\ & - J_{1n}^{(2)} A_n^{*2} A_{n+1}^2 + \sum_q\big\{\beta_{q,n}^*\dot{\beta}_{q,n} - \beta_{q,n}\dot{\beta}_{q,n}^* + \hbar\omega_q\big[|\beta_{q,n}|^2 \\ & - |A_n|^2\big(\beta_{q,n}^*\chi_n^q + \chi_n^{q*}\beta_{q,n}\big) - |A_n|^4\big(\chi_{1n}^q\beta_{q,n}^* + \chi_{1n}^{q*}\beta_{q,n}\big)\big]\big\}\Big\}, \end{aligned} \tag{4}$$

where

$$J_n^{(1)} = J\exp\left\{\sum_q\left(\beta_{q,n}^*\beta_{q,n+1} - \frac{1}{2}|\beta_{q,n}|^2 - \frac{1}{2}|\beta_{q,n+1}|^2\right)\right\}, \tag{5}$$

$$J_n^{(2)} = J\exp\left\{\sum_q\left(\beta_{q,n+1}^*\beta_{q,n} - \frac{1}{2}|\beta_{q,n+1}|^2 - \frac{1}{2}|\beta_{q,n}|^2\right)\right\}, \tag{6}$$

$$J_{1n}^{(i)} = \frac{J_1}{J}J_n^{(i)}, \quad i = 1, 2. \tag{7}$$

We may now derive equations of motion for the parameters A_n, A_n^*, $\beta_{q,n}$ and $\beta_{q,n}^*$ using the Lagrange's equation of motion

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{G}_n}\right) - \frac{\partial L}{\partial G_n} = 0, \tag{8}$$

where G represents A_n, A_n^*, $\beta_{q,n}$ or $\beta_{q,n}^*$. Using the Lagrangian (4), the equations of motion can be written as

$$\begin{aligned} i\hbar\dot{A}_n = {} & E_0 A_n + 2E_1|A_n|^2 A_n - J_n^{(1)} A_{n+1} + 2J_{1n}^{(1)} A_n^* A_{n+1}^2 \\ & - J_n^{(3)} A_{n-1} + 2J_{1n}^{(3)} A_n^* A_{n-1}^2 \\ & + \sum_q\big\{\hbar\omega_q\big[A_n\big(\chi_n^q\beta_{q,n}^* + \chi_n^{q^*}\beta_{q,n}\big) \\ & + 2|A_n|^2 A_n\big(\chi_{1n}^q\beta_{q,n}^* + \chi_{1n}^{q^*}\beta_{q,n}\big)\big]\big\}, \end{aligned} \tag{9}$$

$$\begin{aligned} i\hbar\dot{\beta}_{q,n} = \sum_q \Big\{ & A_n^* A_{n+1}\left(\beta_{q,n+1} - \frac{1}{2}\beta_{q,n}\right)\big(-J_n^{(1)} + J_{1n}^{(1)} A_n^* A_{n+1}\big) \\ & + \frac{1}{2}A_{n+1}^* A_n\beta_{q,n}\big(J_n^{(2)} - J_{1n}^{(2)} A_{n+1}^* A_n\big) \\ & - A_n^* A_{n-1}\left(\beta_{q,n-1} - \frac{1}{2}\beta_{q,n}\right)\big(J_n^{(3)} - J_{1n}^{(3)} A_n^* A_{n-1}\big) \\ & + \frac{1}{2}A_{n-1}^* A_n\beta_{q,n}\big(J_n^{(4)} - J_{1n}^{(4)} A_{n-1}^* A_n\big) \\ & + \hbar\omega_q\big(\beta_{q,n} + |A_n|^2\chi_n^q + |A_n|^4\chi_{1n}^q\big)\Big\}, \end{aligned} \tag{10}$$

where

$$J_n^{(3)} = J\exp\left\{\sum_q\left(\beta_{q,n}^*\beta_{q,n-1} - \frac{1}{2}|\beta_{q,n}|^2 - \frac{1}{2}|\beta_{q,n-1}|^2\right)\right\}, \tag{11}$$

$$J_n^{(4)} = J\exp\left\{\sum_q\left(\beta_{q,n-1}^*\beta_{q,n} - \frac{1}{2}|\beta_{q,n-1}|^2 - \frac{1}{2}|\beta_{q,n}|^2\right)\right\}, \tag{12}$$

$$J_{1n}^{(i)} = \frac{J_1}{J}J_n^{(i)}, \quad i = 3, 4. \tag{13}$$

The other two equations are found to be the complex conjugates of Eqs. (9) and (10) respectively. The set of coupled equations (9) and (10) represents the dynamics of alpha-helical proteins in