

Nonlinear Excitations in a Quantum Dimer

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1. Introduction

Nonlinear dynamical systems provide us with a relatively simple way to describe a rich collection of physical phenomena. Taking advantage of the descriptive power of nonlinear equations requires special justification, however, if the dynamical system of interest is a molecule. For any physical system, a nonlinear dynamical model is an approximation of the exact quantum-mechanical dynamics that comes from Schrödinger's linear wave equation. For molecular systems, we must ask what errors are involved in approximating Schrödinger's equation by a simpler but nonlinear model. We should also understand how interesting nonlinear phenomena are manifested in quantum-mechanical energy spectra, in order to test the predictions of nonlinear models against experimental evidence.

One classically-nonlinear phenomenon that is relevant to molecular systems is the tendency for the vibrational energy in a system of coupled oscillators to become localized. When the forces in coupled-oscillator system are nonlinear, it can be energetically favorable for vibrational energy to be concentrated on a single oscillator instead of distributed evenly over the system. Such localization of vibrational energy is observed experimentally in, for example, the C-H stretch vibrations of benzene [1], and is known in the physical chemistry literature as a local mode. Satisfactory quantum theories for local modes in small molecules have been developed [2,3].

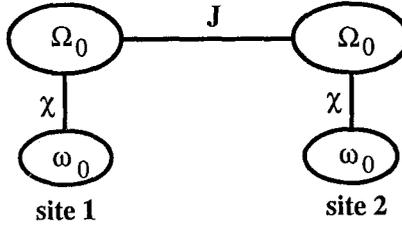
The work presented here is motivated by a related theory for localized and possibly mobile excitations in another type of molecular system: alpha helix protein. In 1973, Davydov proposed that interactions (which are nonlinear when described in terms of classical physics) between Amide-I ($\text{C}=\text{O}$) bond oscillations and the vibrations of adjacent hydrogen bonds could lead to stable coherent excitations in alpha helix sections of biological protein [4]. Although much theoretical work has been done since Davydov's original paper, most calculations are based on nonlinear approximations of the true quantum dynamics, for which precise estimates of the approximation errors are not known.

I am studying a model for the same classically-nonlinear interactions involved in Davydov's protein theory, but which is composed of only four coupled oscillators instead of the hundreds of bonds included in realistic protein models. For my system, it is possible to calculate the exact quantum dynamics by numerically solving the Schrödinger equation. These exact solutions can be used to evaluate the accuracy of nonlinear approximation methods. Here I will present some exact wavefunctions for this model and make a preliminary evaluation of the Discrete Self-Trapping Equation as a nonlinear approximation.

2. The Fröhlich-Einstein Dimer

The Fröhlich-Einstein Dimer (FED) is a system of four coupled oscillators, two with frequency Ω_0 , representing the Amide-I vibrations in a protein model, and two Einstein oscillators with frequency ω_0 , representing deformations of a surrounding molecular structure such as the stretching of hydrogen bonds in an alpha helix. The FED is shown schematically in Figure 1.

Figure 1:



This model is defined by a two-site version of the Fröhlich Hamiltonian used in Davydov's protein theory. For the case where a single quantum of Amide-I energy is present in the system, the FED energy operator can be written

$$H_{FED} = \sum_i [\hbar \omega_0 b_i^\dagger b_i + \chi \sqrt{\frac{\hbar}{2M \omega_0}} (b_i + b_i^\dagger) B_i^\dagger B_i] + J (B_1^\dagger B_2 + B_2^\dagger B_1),$$

where b_i (b_i^\dagger) is a lowering (raising) operator for excitations of the i^{th} Einstein oscillator and B_i (B_i^\dagger) is a lowering (raising) operator for excitations of the i^{th} Amide-I bond. The Einstein oscillators have a characteristic mass M and a spring constant w such that $\omega_0 = \sqrt{w/M}$. The displacement operator Y_i for the i^{th} Einstein oscillator is

$$Y_i = \sqrt{\frac{\hbar}{2M \omega_0}} (b_i + b_i^\dagger).$$

The strength of the intersite coupling between the two Amide-I bonds is given by the real parameter J . The magnitude of intrasite interactions between the Amide-I bond and the Einstein oscillator at each site is given by the real parameter χ .

The values for the FED parameters considered here are those appropriate for the one-dimensional version of Davydov's protein model [5], with the values for χ and w taken to be the midpoints of the appropriate ranges of values. These parameter values are listed in Table I.

J	1.55×10^{-22}	Joules
χ	48.5×10^{-12}	Newtons
w	48.75	Newtons/meter
M	5.7×10^{-25}	kilograms

The calculations presented here for the parameters of Table I complement recent results which concentrate on systems with lower Einstein oscillator frequency (smaller ω_0) [6] and stronger intrasite coupling (larger χ) [7].

3. FED Quantum Dynamics

Three different descriptions of the FED quantum dynamics are presented here. First, for comparative purposes, the exact quantum theory for the classically-linear case $\chi = 0$ is described. For $\chi \neq 0$, we consider both the exact quantum theory and a nonlinear approximation called the Discrete Self-Trapping Equation. We look for the FED version of a Davydov soliton - a quantum-mechanical wavefunction for which there is initially a greater probability of finding the quantum of Amide-I energy on one of the two sites. Without loss of generality, we consider local modes on site 1.

3.1. The Zero-Interaction Limit ($\chi = 0$)

If the value of χ is set to zero, the two stationary quantum states of lowest energy for the FED are

$$\Psi_{\pm}(t) = \frac{1}{\sqrt{2}} (|1\rangle|0\rangle \pm |0\rangle|1\rangle) |0(Y_1)\rangle |0(Y_2)\rangle \exp\left(\frac{iE_{\pm}t}{\hbar}\right)$$

where $|1\rangle|0\rangle$ and $|0\rangle|1\rangle$ are harmonic-oscillator wavefunctions for the two Amide-I

bonds, with the single quantum of vibrational energy localized on site 1 and site 2, respectively. The factor $|0(Y_i)\rangle$ is a harmonic-oscillator ground state wavefunction for the i^{th} Einstein oscillator, with equilibrium position $Y_i=0$. The corresponding energies are $E_{\pm} = \pm J$.

3.2. The Discrete Self-Trapping Approximation

Most of the nonlinear approximations used on Davydov's model are based on assumptions about the form of the quantum wavefunctions. One commonly-used trial wavefunction is

$$\psi(t) = (c_1|1\rangle|0\rangle + c_2|0\rangle|1\rangle)|0(Y_1 - \beta_1)\rangle|0(Y_2 - \beta_2)\rangle \exp\left(\frac{iEt}{\hbar}\right) \quad (1)$$

when written specifically for the FED. Here, $|1\rangle|0\rangle$ and $|0\rangle|1\rangle$ are the Amide-I states discussed in the previous section, and c_1 , c_2 , β_1 and β_2 are time-dependent parameters. The Einstein oscillator harmonic-oscillator states have time-dependent equilibrium positions $\beta_i(t)$. The complex amplitudes c_1 and c_2 have the property that $|c_i(t)|^2$ gives the probability of finding an Amide-I excitation on site i at time t . In the jargon of Davydov soliton fanatics, this is the "D2 Ansatz" for the FED.

With the additional assumption that the Einstein oscillators respond instantaneously to changes in the Amide-I probabilities, the equations of motion for the parameters in the trial state (1) are

$$i\hbar \dot{c}_1 = -Jc_2 - \frac{\chi^2}{w} |c_1|^2 c_1 \quad (2a)$$

$$i\hbar \dot{c}_2 = -Jc_1 - \frac{\chi^2}{w} |c_2|^2 c_2 \quad (2b)$$

and

$$\beta_i = -\frac{\chi}{w} |c_i|^2. \quad (3)$$

The system (2a,b) is known as the Discrete Self-Trapping Equation (DST) [8]. The time-evolution of a local mode is obtained by integrating (2a,b) from an initial condition such that $|c_1| > |c_2|$. Because the trial state (1) is not general enough to include all the possible FED wavefunctions, (2a,b) will generally not give the exact quantum dynamics [9].

The solutions of (2a,b) are known for arbitrary initial conditions in terms of Jacobi elliptic functions [10,11]. For $c_1(0) = 1$ and $c_2(0) = 0$, the site 1 excitation probability evolves as

$$P_1(t) = |c_1(t)|^2 = \frac{1}{2}[1 + \text{cn}(u|k)]$$

where $\text{cn}(u|k)$ is the Jacobi elliptic function cn with argument $u = 2.94 t$ and modulus $k = .078$. This elliptic function oscillates between 1 and -1 with a frequency $\omega = 2.93 \text{ psec}^{-1}$. Assumption (3) about the Einstein oscillators implies

$$\langle Y_1(t) \rangle = A [1 + \text{cn}(u|k)],$$

where, for the Table I parameters, $A = -.497$.

3.3. Exact Quantum States of the FED

Because the two sites in the FED are identical, we can choose all stationary quantum states to be either symmetric or antisymmetric with respect to site exchanges. Using the coordinates

$$\delta = \frac{1}{\sqrt{2}}(Y_1 - Y_2) \quad \text{and} \quad \sigma = \frac{1}{\sqrt{2}}(Y_1 + Y_2),$$

the exact stationary states of the FED system can be written

$$\psi^\pm(t) = [f^\pm(\delta)|1\rangle|0\rangle \pm f^\pm(-\delta)|0\rangle|1\rangle] |m(\sigma + \frac{\chi}{\sqrt{2}w})\rangle \exp(\frac{iE^\pm t}{\hbar}),$$

where $|m(\sigma + \chi/\sqrt{2}w)\rangle$ is a harmonic oscillator state for the coordinate σ with equilibrium position $\sigma = -\chi/\sqrt{2}w$, and the \pm sign indicates whether the state $\psi^\pm(t)$ is symmetric or anti-symmetric. A particular function $f^+(\delta)$ ($f^-(\delta)$) corresponds to each symmetric (anti-symmetric) stationary state.

Shore [12] showed that a straightforward numerical calculation can be used to obtain the functions $f^\pm(\delta)$ in terms of the coefficients in the expansion

$$f^\pm(\delta) = \sum_{j=0}^{\infty} c_j^\pm |j(\delta)\rangle, \quad (4)$$

where $|j(\delta)\rangle$ is the j^{th} harmonic oscillator number state in the coordinate δ . The coefficients c_j^\pm are found by diagonalizing the matrices H^+ and H^- with elements

$$H_{jj}^\pm = \pm (-1)^{j+1} J + \hbar \omega_0 j - \frac{\chi^2}{4w}$$

and

$$H_{j+1,j}^\pm = H_{j,j+1}^\pm = \frac{1}{2} \left[\omega_0 \frac{\chi^2}{w} \right]^{1/2} \sqrt{j+1}.$$

Each of the eigenvectors of H^+ (H^-) gives the coefficients c_j^+ (c_j^-) in the expansion (4) corresponding to a symmetric (anti-symmetric) stationary state of the FED. The associated eigenvalue of H^+ (H^-) is the energy of that stationary state. The expansion coefficients and energies of the two lowest-energy FED eigenstates are listed in Table II.

State	Energy	c_0	c_1	c_2	c_3	$c_{j>4}$
ψ^+	-1.76×10^{-22} Joules	.704	-.060	.005	.000	.000
ψ^-	1.25×10^{-22} Joules	.698	-.113	.009	-.001	.000

It is significant that the coefficients c_j are not the same for the two states in Table II. This means that unlike for $\chi = 0$, one cannot generate the anti-symmetric state by "anti-symmetrizing" the symmetric state. Another difference between the two states is that while the energies of both are lower than the $\chi = 0$ values $E^\pm = \pm 1.55 \times 10^{-22}$ Joules, the anti-symmetric state has been lowered $.30 \times 10^{-22}$ Joules while the symmetric state has been lowered only $.21 \times 10^{-22}$ Joules. These observations indicate that an accurate characterization of a superposition wavepacket requires knowledge of *all* the stationary states involved in the superposition. Often in studies of larger systems only the lowest-energy eigenstate is computed.

4. Local Mode Wavepackets

For $\chi = 0$ and for the $\chi \neq 0$ exact calculations, the two lowest-energy stationary states are used to construct a nonstationary wavepacket that concentrates the Amide-I excitation probability on site 1 at time $t = 0$. In each case, the site 1 excitation probability $P_1(t)$ oscillates periodically in time for $t > 0$. Four quantities are used to characterize the local mode wavefunctions in order to make comparisons between the exact results, the linear limit, and the DST approximation. These quantities are: a) the expectation of the energy for the localized wavepacket $\psi_L(t)$, that is, $\langle \psi_L(t) | H_{FED} | \psi_L(t) \rangle$, b) the initial site-1 excitation probability $P_1(0)$, c) the corresponding Einstein oscillator displacement $\langle Y_1(0) \rangle$, and d) the frequency ω at which $P_1(t)$ oscillates. These four quantities are listed in Table III for the three cases of interest.

Table III: FED Local Modes				
Case	$\langle H_{FED} \rangle$	$P_1(0)$	$\langle Y_1(0) \rangle$	ω (1/psec)
Linear ($\chi = 0$)	0	1	0	2.94
DST ($\chi = 48.5$ pN)	$-.24 \times 10^{-22}$ Joules	1	-99 pm	2.93
Exact ($\chi = 48.5$ pN)	$-.25 \times 10^{-22}$ Joules	.998	-1.05 pm	2.85

4.1. Effects of Nonzero χ

The local modes of the FED show three effects of the Amide-I/Einstein-oscillator interaction (the classical nonlinearity).

1. The average energy of a local mode wavepacket decreases for $\chi \neq 0$.
2. The stationary state wavefunctions deform so that the expectation of the coordinate Y_i is correlated with the probability of amide-I excitation $P_i(t)$.
3. The frequency at which the quantum probability oscillates between two sites decreases. In terms of quantum-mechanical data, this corresponds to a decrease in the splitting between the two lowest energy levels of the FED system.

These qualitative effects are found both in the exact quantum theory and in the DST approximation.

The wavepacket created from the exact stationary states in Table II was the simple linear combination

$$\Psi_L(t) = \frac{1}{\sqrt{2}}(\Psi^+(t) + \Psi^-(t)).$$

This wavepacket gives $P_1(0) = .998$, the largest value possible for a superposition of the first two exact states. Theoretically, the two lowest-energy quantum states may be combined in any normalized superposition. A wavepacket for which the contribution from Ψ^+ is larger than that from Ψ^- will give a smaller maximum value for $P_1(t)$ but the wavepacket will have a lower average energy. For any superposition of Ψ^+ and Ψ^- , $P_1(t)$ oscillates at the frequency $\omega = 2.85 \text{ psec}^{-1}$.

4.2. Errors in the DST Approximation

The DST approximation underestimates the effects of nonzero χ : the DST gives an average energy which is slightly higher than exact value, an Einstein oscillator displacement which is smaller than the exact value, and a probability transfer frequency which is greater than the exact value. In addition, the DST equation gives no indication that in the exact quantum theory a superposition of the two lowest-energy stationary states can give at most $P_1(t) = .998$.

It is not possible to make quantitative conjectures about the quantum dynamics of extended systems based on the results presented here. However, this information about the qualitative features of the FED wavefunctions and their relation to the DST approximation may be useful knowledge to those using such approximations to study more complicated systems.

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