Effects of distance dependence of exciton hopping on the Davydov soliton

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Abstract

The Davydov model of energy transfer in molecular chains is reconsidered assuming the distance dependence of the exciton hopping term. New equations of motion for phonons and excitons are derived within the coherent state approximation. Solving these nonlinear equations result in the existence of Davydov-like solitons. In the case of a dilatational soliton, the amplitude and width is decreased as a results of the mechanism introduced here and above a critical coupling strength our equations do not allow for localized solutions. For compressional solitons, stability is increased.

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I. INTRODUCTION

Davydov [1] formulated a model intended to explain an almost lossless energy transfer in quasi-one-dimensional biomolecular chains such as peptides, proteins and the DNA. The key element in the Davydov model is the coupling between excitons and phonons of the biomolecular chain. The starting point is typically the Hamiltonian given by

\[ H = \frac{1}{2} \sum_n \left[ \frac{p_n^2}{M} + W(u_n - u_{n-1})^2 \right] + \sum_n \left[ DA_n^\dagger A_n - J(A_{n+1}^\dagger A_n + A_{n+1}A_n^\dagger) \right] \]  

(1.1)

where the position of the \( n \)-th unit is

\[ x_n = dn + u_n \]  

(1.2)

with \( d \) denoting the equilibrium separation and \( u_n \) a displacement from equilibrium. Here, \( p_n \) is the associated momentum, \( W \) the elastic modulus and \( M \) the mass of the oscillating unit. The operators \( A_n^\dagger \) and \( A_n \) create and annihilate an exciton at site \( n \), respectively.

The constant \( D \) describes the energy of a single exciton on a given site while \( J \) refers to hopping of excitons between neighboring sites. Since both constants originate from the dipolar nature of the chain’s units it is obvious that they must be distance dependent. Hence, denoting the relative distances between two neighboring groups as

\[ r_{n,n+1} = |x_{n+1} - x_n| = d + u_{n+1} - u_n \]  

(1.3)

and

\[ r_{n,n-1} = |x_n - x_{n-1}| = d + u_n - u_{n-1} \]  

(1.4)

we assume that

\[ D = \Omega + D(r_{n,n+1}) + D(r_{n,n-1}) \]  

(1.5)

and analogously that

\[ J = J(r_{n,n+1}) + J(r_{n,n-1}). \]  

(1.6)
In most of the literature on the subject only the dependence of $D$ on the distance has been explicitly introduced. It is quite obvious, however, that $J$ should be inversely proportional to the third power of the distance (dipole-dipole interaction) and this for small displacements gives an approximately linear dependence of $J$ on the magnitude of the displacement. Hence, we can postulate that:

$$D(r_{n,n+1}) \approx D_0 + \chi_1(u_{n+1} - u_n)$$  \hspace{1cm} (1.7)$$
$$D(r_{n,n-1}) \approx D_0 + \chi_1(u_n - u_{n-1})$$  \hspace{1cm} (1.8)$$
$$J(r_{n,n+1}) \approx J_0 + \chi_2(u_{n+1} - u_n)$$  \hspace{1cm} (1.9)$$
$$J(r_{n,n-1}) \approx J_0 + \chi_2(u_n - u_{n-1})$$  \hspace{1cm} (1.10)$$

For a treatment of similar terms in a somewhat different spirit we refer the reader to Ref. [2].

First of all, let us note that $\chi_1$ is responsible for the existence of a localized solution called a Davydov soliton, and this fact is irrespective of the sign of $\chi_1$ [1]. For $\chi_1 > 0$, the molecular chain is locally compressed (compressional soliton) and for $\chi_1 < 0$, the soliton is of dilatational type (locally dilatated). This is not an uncommon situation in soliton bearing nonlinear lattices [3]. It is still an open question as to the value and the sign of $\chi_1$ (see for instance Ref. [4]). The constant $\chi_2$ is clearly negative since the interaction diminishes with distance. Scott [5] had estimated for peptide chains $\chi_2$ from the approximate relation $\chi_2 \approx 3J/d$ using $J \approx 7.8$ cm$^{-1}$ and $d \approx 4.5$ Å as $\chi_2 \equiv 1pN$. He also gave an estimate of $\chi_1 \approx 34pN$. These values will be used in subsequent numerical calculations. We will show in the sections that follow that keeping both $\chi_1$ and $\chi_2$ in the Hamiltonian results in equations of motion which differ from the standard Davydov system. It will be of interest to examine their solutions and find out whether solitons can be formed and what affects their properties.
II. THE MODEL HAMILTONIAN

Based on the results of the previous section we rewrite the Davydo v Hamiltonian’s exciton part as

\[ H_{\text{exc}} = \sum_n [(\Omega + 2D_0) + \chi_1(u_{n+1} - u_{n-1})] A_n^\dagger A_n \]  

\[ - \sum_n A_n^\dagger [(J_0 + \chi_2(u_n - u_{n-1}))A_{n-1} + (J_0 + \chi_2(u_{n+1} - u_n))A_{n+1}] \]  

where the first term is responsible for on-site excitations and the second for hopping.

In the next stage we find the continuum limit of both the excitonic part \( H_{\text{exc}} \) given above and the phonon contribution \( H_{\text{ph}} \). To make the continuum limit we take:

\[ A_n \rightarrow A(x); \quad A_{n \pm 1} \approx A(x) \pm \frac{\partial A}{\partial x} dx + \ldots \]  

\[ u_n \rightarrow u(x); \quad u_{n \pm 1} \approx u(x) \pm \frac{\partial u}{\partial x} dx + \ldots \]  

and define

\[ J(x) \equiv J_0 + \chi_2 \frac{\partial u}{\partial x} dx \]  

\[ D(x) \equiv D_0 + \chi_1 \frac{\partial u}{\partial x} dx. \]

As a result, the phonon part of the Hamiltonian becomes:

\[ H_{\text{ph}} = \frac{1}{2} \int dx \left[ \frac{p^2(x)}{M} + W \left( \frac{\partial u}{\partial x} \right)^2 d^2 \right]. \]

The exciton contribution to the Davydo v Hamiltonian is found as

\[ H_{\text{exc}} = \int dx \left[ \tilde{\Omega} A^\dagger(x)A(x) + 2\chi_1 d \left( \frac{\partial u}{\partial x} \right) A^\dagger(x)A(x) \right] \]  

\[ - \int dx \left( J_0 + \chi_2 d \left( \frac{\partial u}{\partial x} \right) \right) \left[ 2A^\dagger(x)A(x) - \frac{\partial A^\dagger}{\partial x} \frac{\partial A}{\partial x} d^2 \right] \]

where we have denoted

\[ \tilde{\Omega} \equiv \Omega + 2D_0 \]

and the hopping part has been obtained from a symmetric form given by
which is explicitly hermitian.

Our next task is to derive equations of motion for the coupled phonon field \( u(x) \) and the exciton field \( A(x) \). This can be done using several approaches, e.g. through functional minimization, coherent state Ansatz, etc. In the following section we derive these equations by treating phonons classically and taking a special Ansatz for excitons.

### III. DERIVING THE EQUATIONS OF MOTION

In order to derive equations of motion we assume the phonons to be virtually classical so that Hamilton’s equations can be applied to \( u(x) \) and \( p(x) \). The exciton part is approximated by the expectation value of \( H_{\text{exc}} \) in the trial ground state

\[
|\psi\rangle = \int dx \, a(x) A^\dagger(x) |0\rangle
\]

where \( a(x) \) is a complex probability amplitude of an exciton wave and \( |0\rangle \) is the vacuum. Thus, the effective Hamiltonian used is

\[
H_{\text{eff}} = H_{\text{ph}} + \langle \psi | H_{\text{exc}} | \psi \rangle
\]

or explicitly:

\[
H_{\text{eff}} = \frac{1}{2} \int dx \left[ \frac{p^2(x)}{M} + W \left( \frac{\partial u}{\partial x} \right)^2 \right] + \int dx \left\{ \left[ -2J_0 + \Omega \right] + 2(\chi_1 - \chi_2) d \frac{\partial u}{\partial x} \right\} |a(x)|^2 + \left( J_0 + \chi_2 d \frac{\partial u}{\partial x} \right) \left| \frac{\partial a}{\partial x} \right|^2 d^2 \}
\]

We now derive the equations of motion for the phonon field as

\[
\frac{\partial u}{\partial t} = \{ H_{\text{eff}}, p \} = \frac{p(x)}{M}
\]

and

\[
\frac{\partial p}{\partial t} = \{ H_{\text{eff}}, u \} = W d^2 \frac{\partial^2 u}{\partial x^2} + \frac{\partial}{\partial x} \left[ 2(\chi_1 - \chi_2) d |a|^2 + \chi_2 d^3 \left| \frac{\partial a}{\partial x} \right|^2 \right]
\]
where the curly brackets above indicate Poisson commutators. Differentiating eq. (3.4) with respect to time and utilizing eq. (3.5) we obtain

\[
\begin{align*}
\frac{\partial^2}{\partial t^2} - v_0^2 \frac{\partial^2}{\partial x^2} u(x, t) &= 1 \frac{\partial}{\partial x} \left[ 2(\chi_1 - \chi_2) d|a|^2 + \chi_2 d^3 \left| \frac{\partial a}{\partial x} \right|^2 \right] \\
\end{align*}
\] (3.6)

which is a wave equation for the displacement field with an additional term arising due to the coupling with excitons. The sound velocity \(v_0\) is defined as \(v_0 = d\sqrt{W/M}\).

We treat excitons quantum mechanically and hence use the Schrödinger equation

\[
i\hbar \frac{\partial}{\partial t} |\psi\rangle = H_{exc} |\psi\rangle
\] (3.7)

as an equation of motion. Here, \(H_{exc}\) is taken in the form given in eq. (3.4). It is easy to verify that, as a consequence, we obtain

\[
i\hbar \frac{\partial a}{\partial t} = \left[ (\tilde{\Omega} - 2J_0^+) + 2(\chi_1 - \chi_2) d \left( \frac{\partial u}{\partial x} \right) \right] a(x) - \frac{\partial}{\partial x} \left[ (J_0 + \chi_2 d \frac{\partial u}{\partial x}) \left( \frac{\partial a}{\partial x} \right) \right] d^2. \] (3.8)

We note that the two coupled equations, eqs. (3.6) and (3.8) resemble the Davydov set of equations. In fact, as \(\chi_2 \to 0\) the result agrees identically with Davydov.

Our next task is to solve these two equations with a specific objective of finding soliton solutions.

**IV. SOLVING THE EQUATIONS OF MOTION**

In the first step we postulate that

\[
u(x, t) = u(x - vt)
\] (4.1)

i.e. that the (real) displacement field is a travelling subsonic wave \((v < v_0)\) and

\[
a(x, t) = \exp[-iEt + i\alpha(x - vt)]a(x - vt)
\] (4.2)

which means that the complex exciton field travels with the same velocity \(v\) but also has internal oscillations. The energy of the soliton is not \(E\), since in our Ansatz, we have other
time dependent pieces. A more complete form is easy to obtain [1]. As a result, the two
equations become ordinary differential equations in the new coordinate \( \xi \equiv x - vt \). Thus,

\[
(v^2 - v_0^2)u'' = \frac{1}{M} \left[ 2(\chi_1 - \chi_2) d a^2 + \chi_2 d^3 (a')^2 \right] \quad (4.3)
\]

and

\[
\left[ -E + \tilde{\Omega} - 2J_0 - \frac{v^2}{4d^2 J_0} + 2 d(\chi_1 - \chi_2) u \right] a - d^2 \left[ (J_0 + \chi_2 du') a \right]' = 0 \quad (4.4)
\]

where the prime denotes differentiation with respect to \( \xi \). Note that as \( \chi_2 \to 0 \), eqs. (4.3) and (4.4) reduce to the original system of Davydov equations [1].

To proceed we note that the second term in the square bracket of eq. (4.3) is much smaller
than the first one. This is on the account of the fact that for large solitons, \( a^2 \gg (a')^2 \). We
can then integrate eq. (4.3) once to yield

\[
u' \approx \frac{2(\chi_1 - \chi_2) d}{M(v^2 - v_0^2)} a^2. \quad (4.5)
\]

This can then be substituted into eq. (4.4) to give

\[
d^2 a'' - \frac{\Delta a}{J_0 + \gamma a^2} - \frac{\Gamma a^3}{J_0 + \gamma a^2} + \frac{2d^2 \gamma a}{J_0 + \gamma a^2} (a')^2 = 0. \quad (4.6)
\]

where, to simplify notation, we introduced the following symbols

\[
\gamma \equiv \frac{2\chi_2(\chi_1 - \chi_2) d^2}{M(v^2 - v_0^2)} \quad (4.7)
\]

\[
\Gamma \equiv \frac{4(\chi_1 - \chi_2)^2 d^2}{M(v^2 - v_0^2)} + \frac{v^2}{4J_0^2 d^2} \gamma \quad (4.8)
\]

and

\[
\Delta \equiv -E + \tilde{\Omega} - 2J_0 - \frac{v^2}{4J_0 d^2} > 0. \quad (4.9)
\]

Eq. (4.6) has two free parameters, \( E \) and \( v \) (the velocity of the soliton). The parameter
\( E \) is fixed by the requirement that the excitonic wave function be normalized, i.e.

\[
\frac{1}{a} \int a^2(z) \, dz = 1. \quad (4.10)
\]
Using the transformation
\[ y(a) \equiv \frac{da}{d\xi} \]  
we obtain from eq. (4.6)
\[ yy' + f(a) y^2 + h(a) = 0 \]  
where
\[ f(a) \equiv \frac{2\gamma a}{J_0 + \gamma a^2} \]  
and
\[ h(a) \equiv -\frac{\Delta a + \Gamma a^3}{J_0 + \gamma a^2}. \]  
Eq. (4.12) is a Bernoulli equation which can be completely integrated and its general solution is
\[ y^2 = \exp(-I)(a_1 - 2 \int_{a_0}^{a} h(\tilde{a}) \exp(I) d\tilde{a}) \]  
where
\[ I \equiv 2 \int_{a_0}^{a} f(\tilde{a}) d\tilde{a}. \]  
In our case
\[ I = 2 \ln(J_0 + \gamma a^2) \]  
and eq. (4.15) yields
\[ \left( \frac{da}{d\xi} \right)^2 = \frac{a_1 + J_0 \Delta a^2 + \frac{1}{2}(\Delta \gamma + J_0 \Gamma)a^4 + \frac{1}{3}\gamma \Gamma a^6}{(J_0 + \gamma a^2)^2} \equiv H(a). \]  
This final equation can be integrated numerically in terms of periodic and localized solutions. Note that for \( a_1 \neq 0 \) only singular or periodic solutions can be found. Before we present a complete analysis of the various solutions we note that in the limit of \( \chi_2 \rightarrow 0 \) we find the standard elliptic equation [7], i.e.
\[
\left( \frac{da}{d\xi} \right)^2 = \frac{c_0 + \Delta a^2 + \frac{\xi}{\xi} a^4}{J_0}
\]
(4.19)
since \( \gamma \to 0 \). Here, elliptic waves can be found in a standard way, and for \( c_0 = 0 \) we find the Davydov soliton as
\[
a(\xi) = \sqrt{-\frac{2\Delta}{\Gamma}} \sech \left( \sqrt{\frac{\Delta}{J_0}} \xi \right).
\]
(4.20)

V. ANALYSIS OF SOLUTIONS

In solving eq. (4.18), we assumed the values of model parameters consistent with those used for peptide chains \([4]\). These values are:

\[
\begin{align*}
W &= 40 \text{ N/m} \\
M &= 5.7 \cdot 10^{-25} \text{ kg} \\
d &= 4.5 \cdot 10^{-10} \text{ m} \\
\tilde{\Omega} &\approx 0.2 \cdot 10^{-19} \text{ J} \\
J_0 &= 1.55 \cdot 10^{-22} \text{ J}
\end{align*}
\]
(5.1)

For illustration purposes, we have chosen to investigate slow solitons \((v/v_0 \approx 0.02)\). Physical values for \( \chi_2 \) are on the order of \(-1 \) pN, and we will look at values within this range. Note that \( \chi_2 \) must be negative since dipole-dipole interaction decreases with separation. The value of \( \chi_1 \) is still an open question. Experiments seem to indicate that \( \chi_1 \approx 30 - 60 \) pN. This would correspond to a compressional soliton. On the other hand, theoretical estimates range from \(-60 \) to \(+25 \) pN raising the possibility of dilatational solitons \((\chi_1 < 0)\). Therefore, we will investigate both positive and negative values for \( \chi_1 \).

In the case of compressional solitons \((\chi_1 > 0)\), qualitatively nothing special happens. Including the effect of \( \chi_2 \) simply enhances the stability of the soliton. This can be understood as follows. With \( \chi_2 < 0 \), we see from eq. (4.7) that \( \gamma > 0 \) which immediately implies that the denominator of \( H(a) \) given in eq. (4.18) is increased. This means that in the compressed chain, the effective \( J_0 \) is larger.
If $\chi_1 < 0$, it follows that $\gamma < 0$. In this case, the soliton is dilated and the dipole-dipole interaction is weakened which can lead to a destabilization of the soliton itself.

We have examined how the form of the localized solution (soliton) changes with the value of $\chi_2$. This is illustrated in Fig. 1, where we see a gradual sharpening effect at the peak of the soliton solution starting from the standard Davydov form at $\chi_2 = 0$. The soliton disappears at a relatively low value of $\chi_2 \simeq -1.34 \text{pN}$, well within the range of physically acceptable values. This effect has been carefully investigated through analysis of the numerator and denominator of $H(a)$ appearing in eq. (4.18). As previously mentioned, $a_1 = 0$ is required for solitary wave solutions to exist. Of utmost importance to what follows is the location and reality of the roots of the numerator in $H(a)$. Obviously a double root exists at $a = 0$, and the remaining four roots are pairwise symmetrical with respect to sign reversal. We shall label the squares of these roots simply as $a^2 = r_1, r_2$. With this in place, we note that the singularity in the denominator of $H(a)$ coincides with $r_1 = r_2$ at a point $\chi_2 = \chi_{2r}^c$. We have determined that the value of $\chi_{2r}^c$ at which the solitonic solutions are destroyed is given by

$$\chi_{2r}^c = \frac{2J_0\chi_1}{3\Delta - \frac{\nu^2}{4J_0d^2} + 2J_0}. \quad (5.2)$$

Substituting the parameter values from eq. (5.1) into eq. (5.2) we find that for our system $\chi_{2r}^c = -1.34 \text{ pN}$ which is close to what is physically expected. The role of $\chi_2$ in changing the topology of $H(a)$ is clearly illustrated in Fig. 2. We show in Fig. 3 the region of stable solitons as deduced from the relative position of the roots of the numerator of $H(a)$ and the zero of the denominator.

**VI. CONCLUSION**

This paper has discussed the distance dependence of exciton hopping in the Davydov model. Two cases needed to be discussed separately. In the case of compressional solitons ($\chi_1 > 0$), soliton stability was enhanced simply because in the soliton, the average distance
between molecules was decreased, leading to a higher hopping probability. If this was the case in peptide chains, the conclusions reached through thermal stability studies of the standard Davydov model (Ref. [4] and others therein) might be unduly pessimistic.

The second case of $\chi_1 < 0$ corresponds to a dilatational soliton. Here there exists a critical value of $\chi_2$, beyond which Davydov-like solitons cease to exist. This critical value is surprisingly close to physical values and therefore it is to be expected that thermal fluctuations at physiological temperatures would destroy the soliton.

By including this important physical effect, we have arrived at a new set of equations which possess solitons. These new solutions are clearly relevant to the physics of poly-peptide chains.

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FIGURES

FIG. 1. The plot of soliton profiles for various values of \( \chi_2 \) (in pN). The dashed line is the Davydov soliton \( (\chi_2 = 0) \). Note how for \( \chi_2 = -1.33 \) pN, the soliton becomes sharply peaked.

FIG. 2. The change in the plot of \( H(a) \) for various values of \( \chi_2 \) (in pN) corresponding to those used in Figure 1. The plot with \( \chi_2 = 0 \) is the standard Davydov case.

FIG. 3. The location of squares of the roots, \( r_1 \) and \( r_2 \), of the numerator in \( H(a) \) (see eq. (4.18)) and the singularity (dashed curve) in the denominator of \( H(a) \) plotted as a function of \( \chi_2 \). Note that \( \chi_2^{cr} \) delineates the boundary of the soliton region.
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