NONLINEAR DYNAMICS OF POLARONS

V. M. KENKRE

Department of Physics and Astronomy
University of New Mexico, Albuquerque, NM 87131

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Nonlinear Dynamics of Polaronos

V. M. Kenkre
Department of Physics and Astronomy, University of New Mexico
Albuquerque, NM 87131, USA

Abstract

Recent work on the description of polaronos in condensed matter systems on the basis of the Discrete Nonlinear Schrödinger Equation (DNLSE) is reviewed. The microscopic origin of the DNLSE is discussed briefly. Analytical and numerical solutions, which elucidate well known polaronic phenomena, are presented, and typical applications to experiment are discussed in the context of neutron scattering, fluorescence depolarization, and muon spin relaxation. The extension of the analysis to the nonadiabatic domain, and the incorporation of finite temperature effects via stochastic procedures are discussed, and miscellaneous results such as the evolution of nonlinear trimers and Nmers and the theory of nonlinear trapping, and exciting phenomena such as Hopf bifurcation in the nonlinear nonadiabatic finite-temperature dimer are mentioned.

1. Introduction

This article deals with an aspect of polaronos which lies out of the customary routes of investigation of this subject. The reader will not meet here dressing transformations or path-integral methods - techniques which have surely received ample coverage in the rest of this Proceedings volume. Instead, the reader will find below a description of the analysis of several polaronic phenomena that has been carried out with the help of a relatively new transport instrument, the discrete nonlinear Schrödinger equation (DNLSE). The equation describes the time evolution of the polaron and is nonlinear in the amplitude of the occupation of site states. The article is set out as follows. A motivational introduction to the microscopic origin of the DNLSE is given in section 2. Consequences of the analytical solution of the equation for simple systems, which elucidate well known polaronic phenomena, are presented in section 3. Typical applications to experiment are discussed in section 4, with particular reference to neutron scattering, fluorescence depolarization, and muon spin relaxation. Generalizations of the equation to the so-called nonadiabatic domain,
which involve finite (as opposed to infinite) relaxation, are presented in section 5 along with an extension of the analysis to finite temperatures via stochastic methods. Section 6 consists of concluding remarks as well as brief mention of some miscellaneous work including the analysis of nonlinear trimers and N-mers, the theory of nonlinear trapping, and exciting phenomena such as Hopf bifurcation in the nonlinear nonadiabatic finite-temperature dimer.

2. Form and Physical Motivation for the Nonlinear Evolution Equation

In studying the evolution of the polaron, Holstein/1/ introduced an equation of motion with a cubic nonlinearity in the polaron amplitude, which he arrived at by eliminating the vibrations through a variational procedure. That equation was static, i.e., time-independent. The time-dependent version of that equation is identical, at least in essence, to an equation suggested many years later /2/ by Davydov and analyzed by Scott and collaborators /3/. In its simplest form, the equation is

\[ i \hbar \frac{dc_m(t)}{dt} = \sum_n V_{mn} c_n - \chi |c_m|^2 c_m \]  

(2.1)

The amplitude that the particle is at site m is \( c_m \). \( V_{mn} \) is the intersite matrix element which describes the transfer of the particle from site n to site m, and \( \chi \) is the nonlinearity parameter which describes the strong interactions with the lattice and lowers the site energy of the particle by an amount proportional to the product of \( \chi \) and the particle probability at site m. In order to understand the microscopic origin of the DNLSE, one may take as the point of departure the Schrödinger equation

\[ i \hbar \frac{d|\Psi(t)\rangle}{dt} = H|\Psi(t)\rangle \]  

(2.2)

for the ket \(|\Psi(t)\rangle\) of the moving particle with the Hamiltonian \( H \), and obtain, by multiplying (2.2) by the bra \(<m|\) associated with the state at site m in the basis of a localized states (such as the basis of Wannier states),

\[ i \hbar \frac{dc_m(t)}{dt} = \sum_n V_{mn} c_n + E_m c_m \]  

(2.3)

where the \( E \)'s and the \( V \)'s are respectively the diagonal and off-diagonal matrix elements of the Hamiltonian in the localized basis. If interactions with vibrations are present, the \( V \)'s and \( E \)'s are dependent on the vibrational coordinates. For simplicity, we will take \( V \) to be independent of the
vibrational coordinates and $E$ to depend linearly on them. If we further simplify by taking $E_m$ to be dependent only on a single vibrational coordinate $x_m$ associated with the site $m$ (for instance the coordinate which describes an internal vibration of the molecule located at $m$), we can write

$$i \hbar \frac{dc_m(t)}{dt} = \sum_n V_{mn} c_n - \text{const.} \cdot x_m c_m$$

(2.4)

The vibrational coordinate itself, which, in the absence of interactions, might have evolved sinusoidally as a simple harmonic oscillator coordinate with frequency $\omega$ and equilibrium position $0$, may be written, in the presence of interactions, to obey

$$\frac{d^2x_m}{dt^2} + \alpha \frac{dx_m}{dt} + \omega^2 x_m = -\text{const.} |c_m|^2$$

(2.5)

where the equilibrium position of the oscillator is changed by an amount proportional to the probability that site $m$ is occupied by the moving quasiparticle. Dissipation is represented by the rate $\alpha$. If a time scale disparity exists such that the vibrations are slaved by the quasiparticle probabilities, the time derivatives in (2.5) may be put equal to zero with the result that the vibrational coordinate is proportional to the probability of occupation of the quasiparticle. Equation (2.1) is then recovered.

The microscopic derivation of the DNLSE contains many subtleties which we will not comment on here for want of space. The above description of the origin of the DNLSE is meant to convey only its essential physical content.

3. Some Consequences of the Nonlinear Evolution Equation

While $m,n$ in (2.1) are generally vectors in a lattice of appropriate dimensions (normally 3-d), the simplifying assumptions that the system is a chain and that the intersite interactions are nearest-neighbour in character reduce (2.1) to

$$\frac{dc_m(t)}{dt} = -i V (c_{m+1} + c_{m-1}) + i \chi |c_m|^2 c_m$$

(3.1)

In (3.1), and henceforth in this article, we put $\hbar = 1$. Analytic solutions of neither (2.1) nor (3.1) are known except in the continuum approximation or for spatially finite systems. We will show here the explicit solutions for the simple dimer, i.e. a system of only two sites. The DNLSE takes the form.
\[ \frac{dc_1}{dt} = -i V c_2 + i \chi |c_1|^2 c_1; \quad \frac{dc_2}{dt} = -i V c_1 + i \chi |c_2|^2 c_2 \quad (3.2) \]

In order to find the solutions of (3.2), we first convert (3.2) into the nonlinear Von-Neumann equation for the matrix elements of the density matrix \( \rho \), define the quantities \( p, q, \) and \( r \) through

\[ p = \rho_{11} - \rho_{22}; \quad q = i(\rho_{12} - \rho_{21}); \quad r = \rho_{12} + \rho_{21} \quad (3.3) \]

and eliminate \( q \) and \( r \) in favour of \( p \), the probability difference between the two sites. A closed equation for the latter is found to be

\[ \frac{d^2 p}{dt^2} = A \ p - B \ p^3 \quad (3.4) \]
\[ A = (\chi^2/2)p^2_0 - 4V^2 - 2V\chi \ r_0; \quad B = (\chi^2/2) \quad (3.5) \]

and can be solved in terms of Jacobian elliptic functions/4-7/. One can then determine \( q(t) \) and \( r(t) \) through

\[ r = r_0 + (\chi/4V)(p^2-p^2_0); \quad q = (1/2V)dp/dt \quad (3.6) \]

where (and henceforth) the subscript 0 denotes the value at \( t = 0 \).

The full solution of (3.4) for arbitrary initial conditions is given by

\[ p(t) = C \ cn \left[ (C\chi/2k)(t-t_0) \right] \ k = C \ dn \left[ (C\chi/2)(t-t_0) \right] \ 1/k \quad (3.7) \]

The arbitrary constant \( C \) and the elliptic parameter \( k \) satisfy

\[ C^2 = p^2_0 - \xi^2 + [\xi^4 + (4V/\chi)^2 q^2_0]^{1/2} \quad (3.8) \]
\[ 1/k^2 = 2 \left[ 1 + (1/C^2)(\xi^2 - p^2_0) \right] \quad (3.9) \]

where \( \xi \) is given by

\[ \xi^2 = (1/2)[(4V/\chi)^2 + (8V/\chi) r_0] \quad (3.10) \]
The starting time $t_0$ is usually zero but can be written in terms of the normal elliptic integral of the first kind in terms of $C$ and $k$.

To elucidate several physical effects it will suffice to consider particular cases of the general solution in which $(dp/dt)_0 = 0$:

$$p = p_0 \, cn[(p_0 \, \chi/2k) t \, | \, k] = p_0 \, dn[(p_0 \, \chi/2) t \, | \, 1/k] \quad (3.11)$$

$$k^2 = k_0^2 \, p_0^2 \left[ 1 + 2 \, k_0 \, r_0 \right]^{-1} = k_0^2 \, p_0^2 \left[ 1 \pm 2 \, k_0 \, (1 - p_0^2)^{1/2} \right]^{-1} \quad (3.12)$$

where $k_0 = \chi/4V$. Three cases of (3.11), (3.12) are of special interest: (i) initial localization ($p_0 = 1$), (ii) initial delocalization ($p_0 \neq 1$) with in-phase amplitudes, i.e. $r_0$ positive, and (iii) initial delocalization ($p_0 \neq 1$) with out-of-phase amplitudes, i.e. $r_0$ negative.

For the initially localized case (i), one finds $k = k_0$, and

$$p(t) = cn[2Vt \, | \, \chi/4V] = dn[(\chi/2) t \, | \, 4V / \chi] \quad (3.13)$$

Equation (3.13) contains rather interesting physics. The evolution of the nonlinear dimer is seen to be a combination of that of a degenerate and a nondegenerate linear dimer: If $\chi < 4V$, the nonlinear dimer behaves like the former, and full "ringing" of excitation occurs. If $\chi > 4V$, it emulates the latter and exhibits incomplete oscillations characteristic of the $dn$ function. The time evolution slows down as the nonlinearity is increased, and undergoes a transition at $\chi = 4V$ when $p(t)$ reduces to a sech curve which is non-oscillating. The transition can be said to be indicative of self-trapping since the oscillations do not cross the $p = 0$ region once $\chi$ exceeds the critical value $4V$. Equation (3.13) thus shows three important features of the nonlinear dimer: the "dynamic self-trapping transition" which occurs as the nonlinearity exceeds the critical value, effective energy mismatch between the two dimer sites for nonlinearities in excess of the critical value, and reduction of bandwidth or quasiparticle velocity (ringing frequency) with increase in nonlinearity for $\chi$ less than the critical value. The latter result can be shown particularly clearly by plotting the $\chi$-dependence of the particle "velocity" or bandwidth $V_{\text{eff}}$, defined as being proportional to the frequency of oscillations. It is proportional to the reciprocal of the complete elliptic integral of the first kind, and thus drops off sharply at the transition as the reciprocal of a logarithm:

$$V_{\text{eff}} = V[(2/\pi)K(\chi/4V)]^{-1} \approx V[\pi / \ln(16/1 - (\chi^2/16V^2))] \quad (3.14)$$
the second equality in (3.14) being valid close to the transition.

The initially delocalized case (ii), in which \( p_0 \neq 1 \) and \( r_0 > 0 \), shows behaviour which is like that of case (i) with the exception that the oscillations of \( p \) are bounded by \( \pm p_0 \) rather than by \( \pm 1 \). However, the out-of-phase case (iii), in which \( r_0 < 0 \), introduces an additional transition in the time evolution as a result of the interplay of phases and nonlinearity. Since, \( r_0 = - (1-p_0^2)^{1/2} \), for \( \chi \) values which are large enough, it is possible to satisfy \( \chi / 4V = (1/2)(1-p_0^2)^{1/2} \). For this choice of the degree of nonlinearity and initial conditions, \( k \) in (3.12) is infinite, the system finds itself initially in one of its stationary states, and the probability of occupation of the sites remains unchanged from its initial value! A further increase in \( \chi \) makes \( k \) imaginary and \( p(t) \) is described by the Jacobian nd function. A striking characteristic of this transition is that, beyond the critical value of \( \chi \), a "repulsion" effect/5/ is exhibited in which the probability on the site with initially larger (smaller) occupation increases (decreases) in occupation and remains larger (smaller) than its initial value.

From among a multitude of further quantities that can be calculated for this exactly soluble system, we mention the stationary states/8/. They can be found from the general time evolution equation (3.4) by equating its right hand side to zero/6,7/. It is seen that, while the stationary states involve equal occupation on the two sites if \( \chi < 2V \), self-trapping, represented by the unequal occupation

\[
|c_{1,2}| = \left( \frac{1}{2} \right)^{\frac{1}{2}} \left\{ 1 \pm \sqrt{1 - \left( \frac{2V}{\chi} \right)^2} \right\}^{\frac{1}{2}}
\]

occurs when \( \chi \) exceeds the critical value \( 2V \).

4. Some Examples of Applications to Experiment

Applications of the nonlinear dimer analysis have been recently made to several experimental situations. They include, among others, neutron scattering off hydrogen atoms trapped at impurity sites in metals/9/. The atoms interact strongly with the lattice and exhibit polaronic effects. The scattering function of interest in the dimer is \( S(\pi, \omega) \) and, as a result of the Van Hove correlation analysis, is given basically as the Fourier transform of \( p(t) \) calculated above. For lack of space we refer the reader to ref. 5 for all details. The results are:
\[ S(\pi, \omega) = \pi[2kK(k)]^{-1} \left( \text{sech} \omega R_\omega \right) \left[ \delta(\omega - \omega_n) + \delta(\omega + \omega_n) \right] \] (4.1a)

\[ S(\pi, \omega) = (1/4V) \text{sech} \left( \omega \pi/4V \right) = (1/\chi) \text{sech} \left( \omega \pi/\chi \right) \] (4.1b)

\[ S(\pi, \omega) = \frac{\pi}{2K(1/k)} \left[ \delta(\omega) + \sum (\text{sech} \omega R_\omega) \left[ \delta(\omega - \omega_n) + \delta(\omega + \omega_n) \right] \right] \] (4.1c)

Cases a, b, c of equation (2.10) are respectively valid for \( \chi < 4V \), \( \chi = 4V \), and \( \chi > 4V \). \( K \) is the complete elliptic integral of the first kind, \( R_\omega \) equals \( (1/2V)K(k') \), and \( R_\omega(k) = (1/k)R_\omega(1/k) \). Both \( R_\omega \) and \( R_\omega(k) \) tend to \( \pi/4V = \pi/\chi \) at the transition. It should be noted that \( k \) equals \( \chi/4V \) throughout (4.1), that the index \( n \) runs from 0 to \( \infty \) in (4.1a) but from 1 to \( \infty \) in (4.1c), and that the frequencies \( \omega_n \) in (4.1a) are different from those in (4.1c). In (4.1a), i.e. on the "free" side of the transition, the \( \omega_n \) are given by

\[ \omega_n = (n+\frac{1}{2}) \left( 2\pi V/K(k) \right) \] (for \( \chi < 4V \))

where \( n \geq 0 \) as in the summation in (4.1a). In (4.1c), on the other hand, i.e. on the "self-trapped" side of the transition, the frequencies are given by

\[ \omega_n = n \left[ \pi \chi/2K(1/k) \right] \] (for \( \chi > 4V \))

with \( n \geq 1 \) as in the summation in (4.1c). Equations (4.1) represent interesting lineshapes. In the linear case one has two \( \delta \)-lines at \( \omega = \pm 2V \). An infinite number of \( \delta \)-lines appear for \( \chi = 0 \). They march towards the origin, decreasing both their spacing and their intensity as \( \chi \) increases, coalesce at the transition \( \chi = 4V \) into a finite (non-delta) sech shape, and split again into an infinite number of \( \delta \)-lines as \( \chi \) increases beyond the critical value \( 4V \). However, in addition to the lines marching away from the origin, and increasing in spacing and intensity, one now encounters (in the self-trapped region \( \chi > 4V \)) a \( \delta \)-peak at \( \omega = 0 \) which increases in intensity and represents the effective energy mismatch between the two sites after the transition has occurred. This entire behaviour is very much like the familiar motional narrowing phenomenon in a damped linear dimer. Further discussions on issues such as temperature effects on the neutron scattering will be found in ref. 5.

As our second example of the applications of the analysis of the nonlinear dimer to experiment, we describe fluorescence depolarization/10/. The system under investigation is a variable-distance noninteracting donor-acceptor pair of molecules, a practical example being provided by the so-called "stick-dimers" in which poly-L-proline oligomers of controllable length are used to separate an \( \alpha \)-naphthyl group at the carboxyl end - the donor - from the dansyl group at the imino end - the acceptor -. In such systems the efficiency of energy transfer is studied through measurements of fluorescence.
excitation, emission and polarization spectra. On illumination, either of the molecules in the pair, assumed identical to each other in the simplest version of the analysis, may undergo electronic excitation. The direction of the induced dipole moment produced on the molecule through the process of excitation depends on geometrical factors and is generally different for the two molecules in the pair. For simplicity, we will assume the two dipole moments to be mutually perpendicular. One could, in principle, create an excitation of the dimer which is localized on one of the two molecules by shining (broad-band) light polarized in the direction of the dipole moment on that molecule. Varying the angle of the polarization of the incident light beam would result in varying the relative amplitude or probability of excitation of either molecule. The observable that has been studied/11/ is $f_s$, the steady-state degree of fluorescence polarization:

$$f_s = \frac{1}{\tau} \int_0^t dt f(t) e^{-t/\tau} \quad (4.4)$$

where $\tau$ is the lifetime of the excitation and $f(t) = (I_\parallel - I_\perp) / (I_\parallel + I_\perp)$ is the ratio of the difference and sum of $I_\parallel$ and $I_\perp$, the intensities of fluorescence polarized respectively parallel and perpendicular to the direction of the polarization of the incident light. In terms of $\phi$, the angle made by the polarization of the incident light with the induced dipole moment on molecule 1, $f(t)$ is given in terms of the density matrix elements of the dimer as

$$f(t) = p(t) \cos 2\phi + r(t) \sin 2\phi \quad (4.5)$$

The calculation of $p(t)$ and $r(t)$ from (3.7) and (3.6) respectively, followed by the use of (4.4) and (4.5), allows one to study $f_s$ as a function of the polarization angle $\phi$ for various degrees of the nonlinearity parameter $\chi$. For $\chi/4\chi = 0$, the system is linear and the integrated signal varies sinusoidally as a function of the polarization angle $\phi$. Minor changes occur in this variation for small nonlinearities until the ratio $\chi/4\chi$ equals 0.5. Peculiar dips now appear in the f-curve and there seems to be a "pinning" of the curve at 135°. A flattening of the dependence of $f$ on $\phi$ is characteristic of the transition. Striking effects of nonlinearity are the shift of the maximum of $f_s$ away from 135° and the "pinning" at 135°. We have not displayed the plots here. They can be found in ref. 10. The origin of the peculiar behaviour of fluorescence depolarization can be understood in terms of the features of the dimer solutions discussed in section 3 above. A detailed discussion of this origin can also be found in ref. 10.

As yet another example of the application of the DNLSE to experiment, we describe work done
on the effects of nonlinear transport evolution in spatially extended systems on muon spin relaxation/6,7,12/. Muons are often introduced into a solid as probe particles. In ferromagnetic crystals with magnetically inequivalent sites, a spin-polarized muon undergoes spin relaxation as a combined result of its motion and of the different Larmor frequencies at the different sites and may be looked upon as a quantum particle whose state evolves under the combined action of transport via nearest-neighbour matrix elements V from site to site, spin rotation under the Larmor frequencies, and strong interaction with the vibrations of the lattice. An earlier investigation/13/ took the so-called stochastic Liouville equation as the basic transport instrument. We replaced it by the discrete nonlinear Schrödinger equation (3.1), and calculated the x-component of the muon spin given by \( S_x(t) = \sum_m \frac{1}{2} [ \rho_m m^+ - + \rho_m m^+ - ] \), the summation being over all the sites of the 1-dimensional lattice, and the quantities summed being the density matrix elements between the + and - states at the same site. The + and - states are the Zeeman-split states differing in energy by \( \Delta \) (which is proportional to an applied static magnetic field). The muon is initially localized at a single site (\( m = 0 \)) and occupies the + and - states with equal probability and phase. The linear case (\( \chi = 0 \)) can be evaluated analytically and shows an eventual decay from its initial value \( \frac{1}{2} \to \frac{1}{2} \left( 1 - \left[ 1 + \left( 4V/\Delta^2 \right)^2 \right]^{-1/2} \right) \). We investigated this linear behaviour as contrasted with the nonlinear predictions of (3.1) which we obtained numerically. Wild oscillations of the muon spin component were seen along with distinct structure in the evolution, and the equilibrium value was seen to be reduced as a result of the nonlinearity/6,7,12/. These features, which arise from the apparent non-degeneracy and additional energy mismatch imposed by the nonlinearity, differ appreciably from the damping behaviour seen in the linear analysis/13/.

5. Nonadiabatic Generalizations and Stochastic Considerations

The DNLSE (2.1) which, in one form or the other, has been the point of departure for the studies reported thus far in this article, is the result of the coupled equations (2.4) and (2.5) for the quasiparticle (the polaron) and the vibrations, obtained under the assumption that the vibrations adjust infinitely fast to the state of the quasiparticle. If such a time scale disparity does not exist in the system studied, interesting new phenomena can occur. Those phenomena, and the associated extension of the investigations to non-zero temperatures, are the content of this section.

Two limits of (2.5) are particularly interesting: zero damping, and extremely large damping. Some exact solutions can be found for the former case/14/ for the dimer. The probability difference \( p(t) \)
shows cn or dn behaviour as in the adiabatic solutions discussed in section 3 and undergoes a characteristic new transition into a region where it equals the sum of a part which is proportional to the appropriate elliptic function (cn or dn), and a part which is proportional to the cube of the elliptic function. We will not discuss these solutions here for want of space. In the opposite limit of extremely large damping, to which we will restrict the analysis here, we will assume that the damping coefficient $\alpha$ is large enough to justify the neglect of the second derivative of the oscillator displacements. More formally, we will take the limit $\omega \to \infty$, $\alpha \to \infty$, $\omega^2/\alpha = \Gamma$. The evolution of the oscillator displacements $x$ towards their equilibrium positions now possesses a single characteristic "vibrational relaxation" time, viz. $\alpha/\omega^2 \equiv 1/\Gamma$, and (2.5) reduces to

$$dx_m/dt + \Gamma x_m = - \text{const.} |c_m|^2$$

(5.1)

Equation (5.1) describes the oscillator being driven by relaxation processes at rate $\Gamma$ to its dynamic equilibrium position which is decided by the state of the quasiparticle (polaron). Although the relaxation processes could actually be quite complex and involve vibrational dispersion and interactions with other degrees of freedom, we have assumed here that they may all be described through the single rate $\Gamma$.

The dimer (two-site) case of (2.4) and of (5.1) is, with $E$ a constant,

$$idc_1/dt = Vc_2 + E x_1 c_1$$

(5.2)

$$idc_2/dt = Vc_1 + E x_2 c_2$$

(5.3)

$$dx_1/dt + \Gamma x_1 = - (\chi \Gamma / E) |c_1|^2$$

(5.4)

$$dx_2/dt + \Gamma x_2 = - (\chi \Gamma / E) |c_2|^2$$

(5.5)

The first step in our analysis is the conversion of (5.2)-(5.5) into evolution equations for the density matrix elements which describe the quasiparticle, and the suitably normalized difference of the displacements $\gamma(t) = - (E/\chi)[x_1(t) - x_2(t)]$ which describes the oscillators. The quasiparticle equations are:

$$d\rho_{12}/dt = iVp + i\chi \rho_{12} \gamma$$

(5.6)

$$d\rho_{21}/dt = - iVp - i\chi \rho_{21} \gamma$$

(5.7)

$$dp/dt = i2V (\rho_{12} - \rho_{21})$$

(5.8)
The second step is to obtain from them an equation for \( p \) alone which is coupled to the evolution of \( v \):

\[
\begin{align*}
\frac{d^2 p(t)}{dt^2} + 4V^2 p &= -2V \chi y(t) r_0 - \chi^2 y(t) \int_0^t ds y(s)[dp(s)/ds] \\
\frac{dy(t)}{dt} + \Gamma y(t) &= \Gamma p(t)
\end{align*}
\] (5.9) (5.10)

If the vibrational relaxation rate \( \Gamma \) is infinitely large, one may substitute \( y = p \) in (5.10), notice that the integral can be evaluated to yield the characteristic cubic term in \( p \), and obtain the results of the usual adiabatic analysis (see section 3). When the relaxation rate is not taken to be infinitely large, a number of new results are found. Thus, for the simplest initial condition that the two oscillators are in their equilibrium positions in the absence of the quasiparticle, i.e. \( x_1(0) = x_2(0) = 0 \), and the quasiparticle is placed on one of the sites: \( |c_1(0)|^2 = 1 \), \( |c_2(0)|^2 = 0 \), it is found that, in this nonadiabatic dimer, the probabilities of the two site states settle at long times into constant values which are the stationary state probabilities of the adiabatic dimer discussed in section 3. For \( \chi \ll 2V \) these values equal 0.5. For \( \chi \gg 2V \) they are given by \( \frac{1}{2}[1 \pm (1 - (2V/\chi)^2)^{1/2}] \). It is also found that, for values of the damping rate \( \Gamma \) which are large enough (with respect to other rates such as \( V \) in the system), the evolution of the probabilities first follows the Jacobian elliptic function dynamics of the adiabatic dimer and then settles into the stationary state values. Thus, one observes that, for appropriately large values of \( \Gamma \), the variation of the nonlinearity parameter \( \chi \) shows the coexistence of two transitions: the static transition at \( \chi = 2V \) and the dynamic transition at \( \chi = 4V \). The former is reflected in the long time behaviour in that the asymptotic value of the probabilities is 0.5 for \( \chi < 2V \) but different from 0.5 for \( \chi > 2V \). The latter is seen in the short time behaviour in that the probabilities are characteristic of the \( cn \) function and oscillate on both sides of 0.5 for \( \chi < 4V \) but are characteristic of the \( dn \) function and oscillate only on one side of 0.5 for \( \chi > 4V \). It is further found that, for \( \chi > 2V \), whether the long time limit of the probability of occupation of a given site is \( \frac{1}{2}[1 + (1 - (2V/\chi)^2)^{1/2}] \) or \( \frac{1}{2}[1 - (1 - (2V/\chi)^2)^{1/2}] \), is a function of the value of the relaxation rate \( \Gamma \). Thus, a variation in \( \Gamma \) causes the equilibrium value to switch back and forth between the two options.

While the nonadiabatic problem has to be solved numerically for arbitrary values of the relaxation rate, a number of analytic insights can be gained through a reasonable approximation. The Laplace transform of (5.10) is

\[
y(\epsilon) = y(0)/(\epsilon + \Gamma) + p(\epsilon)/(1 + \epsilon / \Gamma)
\] (5.11)

where \textit{italics} denote Laplace transforms and \( \epsilon \) is the Laplace variable. If \( 1/\Gamma \) is smaller than all
characteristic times of the system, and if one is interested in the evolution only at long times 
\( t \gg 1/\Gamma \), one may expand \((1 + \epsilon/\Gamma)^{-1}\) in powers of \( \epsilon/\Gamma \) and retain the lowest term. At long times, the initial value term in (5.11) may be neglected, to yield

\[
y(\epsilon) \approx p(\epsilon)(1 - \epsilon/\Gamma) \approx p(\epsilon)\exp(-\epsilon/\Gamma)
\]  
(5.12)

The oscillator displacement difference \( y(t) \) thus follows the quasiparticle probability difference \( p(t) \) with a phase lag

\[
y(t) \approx p(t - 1/\Gamma) \approx p(t) - (1/\Gamma)dp(t)/dt
\]  
(5.13)

We then obtain a closed damped nonlinear equation for the probability difference valid for arbitrary initial conditions but for long times. Much can be learnt from the analysis of that equation/15/.

In addition to the evolution to the stationary states and the coexistence of the two transitions discussed above, striking effects of the interplay of initial phases and nonlinearity has also been observed in the nonadiabatic dimer/16/. For instance, if the initial value of the probability on one of the sites is taken to be 0.51 and that on the other 0.49, the evolution depends markedly on whether the two site amplitudes are initially in phase or our of phase. The probability of the initially occupied site tends to its stationary state value for long times in both cases However, if the amplitudes are initially in phase, wild oscillations are seen in the probability whereas, if they are initially out of phase, the evolution is relatively tame. A variation of the initial phase continuously from 0 to \( \pi \) shows an intriguing switching phenomenon: the eventual (stationary) state to which the dimer tends at large times switches as the intital phase is changed, there being contiguous blocks of initial phase for which the state the systems tends to is the same. The physical significance, particularly for extended systems, is that a quasiparticle placed in one location in a crystal could find itself self-trapped at quite different locations in the crystal, the precise spot of such self-trapping being dependent sensitively on the initial phase. This remarkable finding has relevance to the eventual localization of electronic excitations in biological systems such as photosynthetic units/17/.

The study of the stability of the nonlinear structures inherent in these analyses is of obvious importance. The relevant investigations have ben carried out by extending the theory to finite temperatures with the help of a Langevin/Fokker-Planck equation procedure/18/. Stochastic forces which constitute white Gaussian noise are added to the right hand sides of the oscillator displacement
equations (5.4), (5.5), or equivalently to (5.10):

\[
\begin{align*}
\frac{dp}{dt} &= 2Vq \\
\frac{dq}{dt} &= -2Vp - \chi r y \\
\frac{dr}{dt} &= \chi q y \\
\frac{dy}{dt} &= -\Gamma(y-p) + F(t)
\end{align*}
\]  

(5.14a)  
(5.14b)  
(5.14c)  
(5.14d)

Equations (5.14) constitute a Langevin set. It is converted into a Fokker-Planck system, and a Kramers analysis of the escape rate is carried out. It is found that, at finite temperatures, the system escapes from the localized states into which it would settle forever at zero temperature. However, the escape rate displays Arrhenius behaviour: it is negligible at low temperature and increases sharply above a characteristic temperature which is given by $\chi/4k_B$ where $k_B$ is the Boltzmann constant. Details of this analysis may be found in ref. 18.

As a result of the Fokker-Planck analysis a new nonlinear stochastic Liouville equation has also been introduced/19/. It incorporates into a single equation behaviour which is nonlinear, nonadiabatic, and stochastic, the equation being closed in the quasiparticle (polaron) variables. While space limitation prevents us from discussing it here in any detail, we state its form for the dimer:

\[
\begin{align*}
\frac{dp}{dt} &= 2Vq \\
\frac{dq}{dt} &= -2Vp - \chi r p + (2V\chi/\Gamma)qr - \alpha q \\
\frac{dr}{dt} &= \chi qp - (2V\chi/\Gamma)q^2 - \alpha(r-r_{eq})
\end{align*}
\]  

(5.15a)  
(5.15b)  
(5.15c)

Here, $r_{eq}$ is the thermal equilibrium value of $r$, and $\alpha$ is a rate which attempts to drive the system to the thermal state. A high temperature expression/19/ for this rate is $(2\chi/\Gamma)k_BT$.

6. Miscellaneous Results and Concluding Remarks

There is a plethora of additional results, many of them fascinating, that have been obtained from the DNLSE for a diversity of models and a variety of situations. We refer the reader to several other more detailed reviews/6,7/ that have been published recently on the subject. Here we will merely mention that the results obtained include work on (i) rotational polarons/20/, (ii) anharmonic potentials and nonlinear restoring forces/6,7,21/, (iii) nonlinear memories and generalized master
equations/22/, (iv) interplay of nonlinearity and disorder/6,7/, (v) exact analysis of some spatially extended systems/23,24/, (vi) nonlinear trapping/25,26/, and (vi) bifurcations and intermittent behaviour/27/ in the nonadiabatic nonlinear finite temperature systems. We refer briefly to the last three of these classes of results.

**Exact Results for some Spatially Extended Systems**

The methods of analysis used in section 3 to obtain exact solutions in two-site systems can be extended to some larger systems including trimers and a class of extended systems termed N-mers/23,24/. The analytical calculations that have been carried out have addressed some stationary states and the time evolution for some initial conditions. The nonlinear trimer considered is a completely symmetric one, with energetically degenerate sites, and with a single intersite transfer interaction $V$ between any two sites. The general N-mer is also a totally symmetric system of the same kind. The counterpart of the form (3.1) of the DNLSE is

$$\frac{dc_m(t)}{dt} = -i V \sum_n c_n + i V c_m + i \chi |c_m|^2 c_m$$

(6.1)

The summation in (6.1) is over *all* the n's in the system, the terms summed being 3 for the trimer and N for the N-mer. The corresponding density matrix equation takes the form

$$\frac{d\rho_{mn}(t)}{dt} = -i V \sum_s (\rho_{sn} - \rho_{ms}) + i \chi (\rho_{mm} - \rho_{nn}) \rho_{mn}$$

(6.2)

For special initial conditions, represented, for the trimer, by $c_1(0) = c_{10}$, where $c_{10}$ is a real number for simplicity, and $c_2(0) = c_3(0) = s[(1/2)(1-c_{10}^2)]^{1/2}$ where $s = \pm 1$, solutions can be found explicitly. One defines/23,24/ the quantities

$$p = \rho_{11} - 2 \rho_{22}; \quad q = i (2)^{1/2} (\rho_{12} - \rho_{21}); \quad r = (2)^{1/2} (\rho_{12} + \rho_{21})$$

(6.3)

and, following methods similar to those developed in section 3 above, obtains a closed equation for $p$:

$$\frac{d^2p}{dt^2} = -2 \gamma_0 - 6 \gamma_1 p - 6 \gamma_2 p^2 - 2 \gamma_3 p^3$$

(6.4)

where the $\gamma$'s are functions of the system parameters and initial conditions. Solutions can be found explicitly/23,24/. They have been used to study the stationary states as well as time averages of the
system quantities and have been applied to experiment.

Similar considerations have been applied to Nmers. Exact solutions can be found for initial conditions in which the N sites are divided into two groups, one of $m_A$ sites and the other of $m_B$ sites, with $N = m_A + m_B$, the initial distribution of the quasiparticle being identical within all sites of each group. One generalizes (6.3) to

$$p = m_A \rho_{AA} - m_B \rho_{BB}; \quad q = i(m_A m_B)^{\frac{1}{2}}(\rho_{AB} - \rho_{BA}); \quad r = (m_A m_B)^{\frac{1}{2}}(\rho_{AB} + \rho_{BA})$$

(6.5)

so that, as in the trimer case, $p^2 + q^2 + r^2 = 1$ is obeyed. Equation (6.4) is again obtained, the coefficients of the various terms being represented by different combinations of the system parameters and initial conditions. Once again, explicit solutions can be found. We refer the reader to refs. 23, 24 for all further details and exhibit only the stationary states that have been found to obey

$$\chi [N^2 \chi(1-\eta^2)]^{-1} = [\eta(1-p_0^2)^{\frac{1}{2}} - s p_0 (1-\eta^2)^{\frac{1}{2}}]/[2(p_0 - \eta)(1-p_0^2)^{\frac{1}{2}}]$$

(6.6)

where $= \eta(m_A \cdot m_B)/N$.

**Nonlinear Trapping**

Trapping of quasiparticles constitutes an extremely important phenomenon in condensed matter physics, and is of particular interest in areas of investigation such as photosynthesis, in which the harvesting of energy necessary for the operation of the reaction centers is followed by the process of the transfer of the harvested energy to the reaction center, i.e., the trap. Much work has been done on the trapping process. Trapping has been sometimes modelled via the introduction of a capture or sink term in a variety of equations of motion for the moving entity. The equations of motion have been the Master equation representative of completely incoherent, i.e. diffusive, motion, the Schrödinger equation representative of purely coherent motion, combined equations such as the generalized master equation and the stochastic Liouville equation capable of describing coupled coherent and incoherent transport, and even the linearized Boltzmann equation. The modelling of the capture process has been done in several different ways/23-25/. We will describe here, very briefly, some investigations that have addressed the effect of nonlinearity in the capture process. Let us assume that an excitation moves on a chain of sites m,n, etc. via interactions taken to be nearest neighbour (of strength V) for simplicity, and is trapped by a site which has the nonlinear behavior arising from strong interactions with vibrations leading to the nonlinearity described by the cubic term in the DNLSE. Two models of
capture suggest themselves naturally. In the first, one of the sites in the chain is itself the trap site and possesses the cubic nonlinearity:

\[ \frac{dc_m(t)}{dt} = -i \sum \left( c_{m+1} + c_{m-1} \right) + i \delta_{m,0} \chi |c_0|^2 c_0 \]  

(6.7)

In the second, the excitation moves in a region of space which may be termed the antenna, and communicates with a trap which is external to the antenna and not embedded in it. A simple example of this latter situation is one in which the antenna sites all communicate equally with the external trap. Surely, there are a number of other models which are both physical and relevant which we do not mention here. The second model we have referred to is represented by

\[ \frac{dc_m(t)}{dt} = -i \sum \left( c_{m+1} + c_{m-1} \right) - i \frac{c_0}{W} c_B \]  

(6.8)

\[ \frac{dc_B(t)}{dt} = -i \sum c_m + i \chi |c_B|^2 c_B \]  

(6.9)

Numerical calculations on the first model have shown\(^{26}\) that a transition appears to occur as the nonlinearity parameter \(\chi\) crosses the value \((3.2)V\). The second model\(^{27}\) can be solved analytically and will be commented on below.

Consider the antenna to be formed by a finite number \(N\) of sites arranged in a ring. A discrete Fourier transformation applied to (6.8) results in replacing the antenna site states by Bloch states only one of which is coupled to the trap state, thus reducing the problem effectively to one which can be solved analytically by the methods of section 3. It can be shown\(^{27}\) that the probability of the trap site, which we will call \(P\), obeys

\[ \frac{dp}{d\tau} = \left( \frac{1}{2} \right) \left( \eta l_2 - \left( \xi l_2 + \eta^2 + 1 \right) p - 3\xi \eta p^2 - 2\xi^2 p^3 \right) \]  

(6.10)

where \(w\) is the reduced trapping matrix element \(W/(N)^{1/2}\), the scaled time \(\tau\) and the parameters \(\xi\) and \(\eta\) are

\[ \tau = 2w\tau ; \quad \xi = \chi/4w ; \quad \eta = V/w \]  

(6.11)

and the \(I\)'s are constants of the motion. The parameter \(\xi\) measures the amount of nonlinearity relative to the (scaled) interaction matrix element for transfer of excitation between the antenna and the trap. The parameter \(\eta\) measures the motion of the excitation within the antenna relative to the extent of its
transfer from the antenna to the trap. Equation (6.10) can always be solved in terms of Weierstrassian elliptic functions and a completely general solution to the problem obtained for arbitrary initial conditions. Also of use are stationary states involving equal distribution of the excitation among the antenna sites. The trap probability in such stationary states can be shown to obey

\[ P(P-1)[(2V/w) + (\chi/w)p]^2 + (1-2P)^2 = 0 \]  

(6.12)

A number of insights into the trapping problem can be gained through this analysis.

**Hopf Bifurcation and Other Phenomena**

The set of equations (5.15) have been arrived at by extending the DNLSE to nonadiabatic, finite temperature situations through a blend of analytic arguments and physical assumptions. The system they describe reduces to the trivial linear dimer if \( \chi \) vanishes along with \( \alpha \), to the high-temperature damped linear dimer if \( \chi \) vanishes but \( \alpha \) does not, to the nonlinear adiabatic dimer if \( \chi \) is finite but \( \Gamma \) is infinite and \( \alpha \) vanishes, to a relatively crude extension/30/ of the nonlinear dimer to dissipative situations if \( \chi \) is finite but \( \Gamma \) is infinite and \( \alpha \) vanishes, and to the nonlinear nonadiabatic dimer if \( \chi \) and \( \Gamma \) are finite and \( \alpha \) vanishes. Evolution showing a complete combination of the elliptic function evolution of the adiabatic dimer for short times, followed by a selftrapping swing into the localized stationary states of the dimer for longer times, which is itself followed by a delocalization and symmetrical spreading over the two sites characteristic of thermal fluctuations, has been exhibited and commented on in ref. 19. Exciting new behaviour, which occurs when the thermal equilibrium value of \( r \), viz. \( r_{\text{eq}} \), is *not* taken to vanish as a result of high temperatures, will now be mentioned here briefly.

For vanishing \( \alpha \), the probability difference \( p \) oscillates and then tends to the stationary value which is 0 if the nonlinearity parameter is small enough and finite (corresponding to a localized state) if it is large enough. As \( \alpha \), which may be said to be proportional to temperature, increases, the detrapping effect is seen: \( p \) tends to 0 at larger times even for large nonlinearities. As \( \alpha \) increases further, a surprising burst of \( p \) occurs for a short time, and the burst recurs after a time period. The bursts become more frequent with further increase of \( \alpha \) and behaviour that *appears* chaotic occurs. Phase space plots in the \( p-q \) plane show, at this point, that a limit cycle has been reached as \( p \) (as well as \( q \)) oscillates steadily between two finite values. A further increase in \( \alpha \) destroys the limit cycle, and stable dissipative behaviour is recovered, as \( p \) and \( q \) tend to vanishing values while \( r \) tends to \( r_{\text{eq}} \).
Phase-space and time plots of \( p, q, \) and \( r \) in the various regions described produce striking pictures. The pictures and the analysis will be found in ref.27. Here we make brief mention of a few points regarding the analysis. The reason for the rich behaviour that emerges from (5.15) when \( r_{\text{eq}} \) is taken to be non-zero is quite simple: this term serves as a driving agent in the nonlinear system. In order to understand the basic features of the dependence of the system evolution on \( \alpha \), we linearize the system around the stationary states. Calling the deviations of \( p, q, r \) from the stationary state values as \( \Delta p, \Delta q, \) and \( \Delta r \), we obtain, to first order in small quantities,

\[
\begin{align*}
\frac{d\Delta p}{dt} &= 2V\Delta q \\
\frac{d\Delta q}{dt} &= -2V\Delta p - \chi r_{\text{eq}}\Delta p + (2V\chi/R) r_{\text{eq}}\Delta q - \alpha \Delta q \\
\frac{d\Delta r}{dt} &= -\alpha \Delta r
\end{align*}
\]  

(6.13a)  

(6.13b)  

(6.13c)

Clearly, stability is decided by whether the real parts of all the eigenvalues of the matrix relevant to (6.13) are negative or positive. Straightforward calculations show that the condition for stability is

\[
\alpha > (\chi/R) r_{\text{eq}}
\]  

(6.14)

When \( \alpha \) changes from values greater than \((\chi/R) r_{\text{eq}}\) to values smaller than this value, the eigenvalues of the relevant matrix, which are complex conjugate to each other, cross the imaginary axis (the real part changes sign from negative to positive) and the stationary solution loses its stability, producing bursts and other interesting behaviour. The application of these features to the prediction of observations such as fluorescence depolarization is under way.

There is little more that needs be said in conclusion in this article. It should be thoroughly clear that the discrete nonlinear Schrödinger equation is a powerful, useful and immensely rich transport entity, waiting to be investigated, explored, and utilized. It is hoped that many polaronic phenomena will be investigated in the future with its help.

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