

## Self-trapping on a dimer: Time-dependent solutions of a discrete nonlinear Schrödinger equation

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From the discrete nonlinear Schrödinger equation describing transport on a dimer we derive and solve a closed nonlinear equation for the site-occupation probability difference. Our results, which are directly relevant to specific experiments such as neutron scattering in physically realizable dimers, exhibit a transition from "free" to "self-trapped" behavior and illustrate features expected in extended systems, including soliton/polaron bandwidth reduction and the dependence of energy-transfer efficiency on initial conditions.

The discrete nonlinear Schrödinger equation, which describes a number of phenomena in condensed matter, nonlinear optics, and other fields of physics,<sup>1-7</sup> may be written quite generally as

$$dc_m(t)/dt = -iV(c_{m+1} + c_{m-1}) + i\chi|c_m|^2c_m, \quad (1)$$

where  $c_m$  is the amplitude for the system to be in state  $|m\rangle$ ,  $V$  is the interstate matrix element [assumed "nearest neighbor" in (1)] describing the linear evolution among the states  $|m\rangle$ , and  $\chi$  is the nonlinearity parameter. In the specific system of an electron or exciton in a crystal interacting strongly with phonons or vibrations,  $|m\rangle$  denotes the (localized) Wannier state centered on site  $m$ ,  $V$  is proportional to the bandwidth of the bare electron or exciton, and  $\chi$  is the energy lowering due to polaronic effects.

Equation (1) or similar equations have been written down or derived by a variety of people in a variety of contexts.<sup>1-7</sup> While solutions for its continuum limit are well known,<sup>7</sup> analytical solutions for the discrete chain are not known. We present here exact analytical *time-dependent* solutions for (1) for the case of a dimer, i.e., when  $m$  can take on values 1 and 2 only. Although easy to arrive at mathematically, the solutions are rich in physical insight. In particular, they illustrate explicitly a transition from free particle motion to self-trapping, dynamic energy mismatch, polaron/soliton bandwidth reduction, and other expected and conjectured features of the evolution described by (1) for extended systems. They also complement and extend the previous phase plane analysis.<sup>6</sup> Further, far from being an idealized system, the dimer is both interesting in its own right and attainable experimentally.<sup>8-10</sup> A well-known example in the field of energy transfer is the "stick dimer"<sup>8</sup> consisting of a variable distance donor-acceptor system. 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—and the efficiency of energy transfer is studied through measurements of fluorescence excitation, emission, and polarization spectra.<sup>8,9</sup> Another similar example in the field of energy transfer consists of excited dimers in aromatic hydrocar-

bon crystals such as 1, 2, 4, 5—tetrachlorobenzene,<sup>10</sup> studied with microwave probes via optically detected magnetic resonance. Dimers, more generally systems of small size, occur<sup>11</sup> also in the study of the motion of trapped hydrogen atoms among states associated with impurity atoms such as those of oxygen in metals (e.g., niobium). The motion of hydrogen atoms is studied in these systems with the help of quasielastic neutron scattering.<sup>11</sup> Calculations for dimer observables are therefore not merely pedagogical in nature but have direct significance in experiments.

To relate our results to previous studies of transport on molecular crystals and aggregates,<sup>12</sup> we first derive from (1) the corresponding Liouville-Von Neumann equation for the density matrix elements  $\rho_{mn}$ . It is trivial to show that (1) and its complex conjugate give

$$d\rho_{mn}/dt = -iV(\rho_{m+1n} + \rho_{m-1n} - \rho_{mn+1} - \rho_{mn-1}) + i\chi(\rho_{mm} - \rho_{nn})\rho_{mn}, \quad (2)$$

provided  $\chi$  is assumed real. A linear chain with varying site energies would obey (2) with the replacement of the final term  $i\chi(\rho_{mm} - \rho_{nn})\rho_{mn}$  by the energy mismatch term  $-i(E_m - E_n)\rho_{mn}$ , where  $E_m$  is the site energy at  $m$ . The effective dynamic energy lowering  $-\chi\rho_{mm}$ , which equals the product of  $\chi$  and the probability of occupation of site  $m$ , is thus completely evident in (2). From the special case of (2) for the dimer, a straightforward calculation consisting of the exact elimination of  $\rho_{12}$  and  $\rho_{21}$  leads to an *explicit, closed* nonlinear equation for the probability difference  $p(t) = \rho_{11} - \rho_{22}$ :

$$d^2p/dt^2 = Ap - Bp^3, \quad (3)$$

$$A = (\chi^2/2)p_0^2 - 4V^2 - 2V\chi(\rho_{21} + \rho_{12})_0, \quad B = (\chi^2/2). \quad (4)$$

Here the subscript 0 denotes the initial value (at  $t=0$ ).<sup>13</sup> In the absence of the nonlinearity, i.e., for  $\chi=0$ , the coefficient  $A$  equals  $-4V^2$ ,  $B$  vanishes, and the probability difference  $p$  oscillates sinusoidally. In the presence of the nonlinearity, however, the behavior is profoundly different and quite rich as we shall see below.

Considering first the simple initial condition that only

one of the two sites is occupied initially, we see that  $p_0 = 1$  (or  $-1$ ), the off-diagonal elements of the density matrix are zero initially, and (4) reduces to

$$A = (\chi^2/2) - 4V^2, \quad B = (\chi^2/2). \quad (5)$$

Equation (3) with (5) has two completely different solutions according to the value of  $\chi/4V$ . For  $0 \leq \chi/4V < 1$ , the probability difference displays oscillations about the value 0, represents complete transfer from one site to the other, and is given by

$$p(t) = cn(2Vt | k = \chi/4V), \quad (6)$$

whereas, for  $\chi/4V > 1$ , the probability difference oscillates only on one side of 0, represents incomplete intersite transfer, i.e., relative trapping as would be characteristic of an energy mismatch, and is explicitly given by

$$p(t) = dn(\frac{1}{2}\chi t | k = 4V/\chi), \quad (7)$$

where  $k$  is the respective elliptic parameter of the Jacobian elliptic functions  $cn$  and  $dn$ . There is thus a transition at  $\chi = 4V$  between free particle transport and self-trapping of the particle.

The evolution of the probabilities and the transition are shown in Fig. 1. Starting with  $\chi = 0$ , we see that the particle oscillates between the two sites with period  $\pi/V$ . As  $\chi$  increases, the oscillations of the particle begin to depart from trigonometric behavior. They follow the  $cn$  function which, for small  $\chi/4V$ , can be approximated by  $[\cos u + (k^2/4)(\sin u)(u - \sin u \cos u)]$  with  $u = 2Vt$ ,  $k = \chi/4V$  [see curve (a) of Fig. 1]. The  $cn$  function is periodic with interval

$$4K(k) \equiv 4 \int_0^{\pi/2} d\vartheta (1 - k^2 \sin^2 \vartheta)^{-1/2}.$$

Therefore, the period of the oscillations of the particle is  $T = 2K(k)/V$ . It increases as  $\chi/4V$  increases and, for small  $\chi/4V$ , may be expressed as  $T = (\pi/V)[1 + (1/2\pi)$

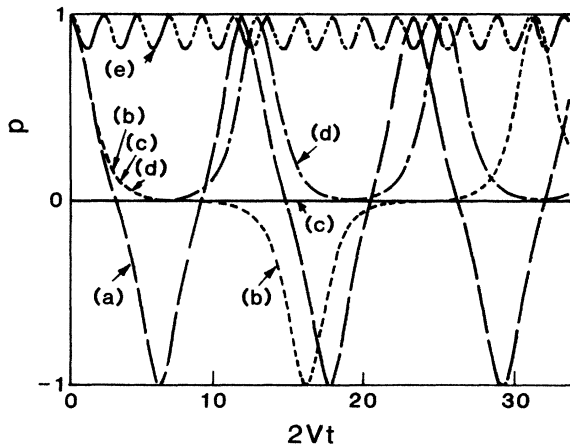


FIG. 1. The difference in the probabilities of occupation of the two sites in a dimer plotted as a function of time  $t$  for various values of  $\chi/4V$ : (a) 0.95, (b) 0.9995, (c) 1, (d) 1.0001, (e) 1.75. Curves (a) and (b) are indicative of free particle motion, (c) describes the transition, and (d) and (e) represent self-trapping behavior [see Eqs. (6) and (7)].

$\times (\chi^2/16V^2)$ . As  $\chi$  approaches very close to  $4V$ , the oscillations of the particle show a marked departure from trigonometric behavior. The  $cn$  function can now be approximated by

$$[\text{sech}(u) - (\frac{1}{4})(1 - k^2)(\tanh u \text{sech } u)(\sinh u \cosh u - u)]$$

with  $u = 2Vt$ ,  $k = \chi/4V$  [see curve (b) of Fig. 1]. The period of the  $cn$  function becomes enormous as the particle oscillates sluggishly between the two sites. The logarithmic approximation to  $K(k)$  is appropriate here and the period of the oscillations of the particle is given by  $T = (1/V) \ln\{16/[1 - (\chi^2/16V^2)]\}$ .

The motion of the particle between the two sites for  $\chi < 4V$  described above and depicted in curves (a) and (b) of Fig. 1 is characteristic of free particle behavior. When  $\chi$  equals  $4V$ , the equalization of the probabilities of the two sites follows exactly the sech evolution:

$$p(t) = \text{sech}(2Vt) = \text{sech}(\chi t/2), \quad (8)$$

and the period of the oscillation is infinite. This is the transition between free behavior and self-trapped behavior, and it corresponds to curve (c) of Fig. 1.

As  $\chi$  increases beyond the transition, the oscillations are described by the  $dn$  function [see (7)]. In this region, for  $\chi$  not too different from  $4V$ , it can be approximated by  $[\text{sech}(u) + (\frac{1}{4})(1 - k^2)(\tanh u \text{sech } u)(\sinh u \cosh u + u)]$  with  $u = \chi t/2$ ,  $k = 4V/\chi$  [see curve (d) of Fig. 1]. In this region, the probability difference never crosses 0. Increasing  $\chi$  has now two effects: The amplitude of the oscillations decreases and the period also decreases. Near the transition, the period may be written as  $T = (4/\chi) \times \ln\{16/[1 - (16V^2/\chi^2)]\}$ . Far away from the transition, as  $\chi/4V$  approaches infinity, the oscillations follow a trigonometric evolution, i.e., can be approximated by

$$p(t) = 1 - (8V^2/\chi^2) \sin^2(\chi t/2). \quad (9)$$

This is precisely the evolution of the probability difference in a linear dimer with a true energy mismatch: The amplitude decreases with an increase in the amount of the energy mismatch. The period of the oscillations is  $T = 2\pi/\chi$ . This self-trapped particle behavior is depicted in curves (d) and (e) of Fig. 1. In the limit as  $\chi/4V$  tends to infinity, the particle is entirely self-trapped as the amplitude (and also the period) of the oscillations becomes zero.

It is instructive to study the potential curves corresponding to (3). With the convention that  $[dp(t)/dt]^2 + U(p) = \text{constant}$ , we have

$$U(p) = (B/2)p^4 - Ap^2. \quad (10)$$

The condition for the double minima to appear is  $A \geq 0$ , i.e.,  $\chi^2 \geq 8V^2$ . The condition for the transition from free to self-trapped behavior to occur is, however,  $\chi^2 \geq 16V^2$ . This condition corresponds graphically to the value of  $U(p)$  at the starting point ( $p = \pm 1$ ) becoming equal to its value at the central extremum (the maximum at  $p = 0$ ), i.e.,  $U(\pm 1) = U(0)$ .

In the small polaron literature<sup>1,3,4,12,14</sup> the carrier-phonon interaction (which gives rise to  $\chi$ ) is said to reduce the effective bandwidth of the carrier from  $V$  to  $V_{\text{eff}}$  (we suppress the constant factor which is 4 for an infinite

linear chain and 2 for a dimer). The reduced polaron bandwidth  $V_{\text{eff}}$  is typically written as  $Ve^{-S}$ , where  $S$  is the "Franck-Condon overlap factor" and is proportional to the square of the carrier-phonon interaction. This reduction, which represents a lowering of the velocity of the carrier, while an integral and important part of the analysis of Holstein<sup>1</sup> and of that of a number of other workers<sup>3,4,12,14</sup> in the field, does not appear to be present in the treatment of Davydov.<sup>2</sup> The question of whether it is or is not a natural consequence of the discrete nonlinear Schrödinger equation is thus an important one. Our analysis above shows explicitly that such a reduction does indeed occur, at least for the dimer. We define  $V_{\text{eff}}$  as the value of the intersite matrix element  $V$  required in a linear dimer ( $\chi=0$ ) to result in the same period of intersite oscillations of the probability as the period in the nonlinear dimer. The effective bandwidth thus drops off sharply at the transition as the reciprocal of a logarithm:

$$V_{\text{eff}} = V[2/\pi]K(\chi/4V)^{-1} \\ \approx V\{\pi/\ln[16/1 - (\chi^2/16V^2)]\} . \quad (11)$$

The approximate equality [the second relation in (13)] holds only near the transition. The dependence of the effective bandwidth (or velocity) over the entire free particle range is plotted in Fig. 2.

The detailed discussion above is based on the initial condition that the particle occupies one of the two sites completely at  $t=0$ , i.e., on (5). The solution for *arbitrary* initial condition, wherein  $A$  is given by (4), can be written formally as

$$p(t) = Ccn[(C\chi/2k)(t-t_0) | k] \\ = Cdn[(C\chi/2)(t-t_0) | 1/k] , \quad (12) \\ 1/k^2 = 2 + (1/C^2)[(4V/\chi)^2 \\ + (8V/\chi)(\rho_{21} + \rho_{12})_0 - 2p_0^2] , \quad (13)$$

the  $cn$  and  $dn$  in (12) being related to each other via the Jacobi reciprocal transformation, and  $t_0$  and  $C$  being arbitrary constants determined by the initial values of  $p$  and  $dp/dt$ . The explicit dependence of the effective velocity or frequency on the initial state is clear from (13).

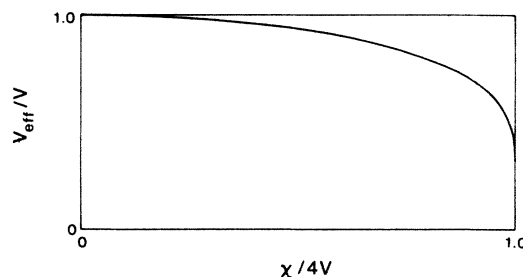


FIG. 2. The ratio of the effective bandwidth for motion between the dimer sites to the bare bandwidth plotted as a function of  $(\chi/4V)$  showing a logarithmic reduction near the transition [see Eq. (11)].

General investigations such as the study of self-trapping for *delocalized* initial conditions, and the explicit reduction of the time-dependent solutions presented here to stationary solutions<sup>6</sup> for the dimer, can be carried out easily from (12) and (13). Space does not permit us to remark in detail on them or on the interesting results that have emerged<sup>15</sup> from the application of the dimer analysis to experiments such as neutron scattering and fluorescence depolarization in physically realizable systems. Those considerations will be reported elsewhere.<sup>15</sup>

In summary, we have derived a closed nonlinear equation for the time dependence of the probability difference  $p(t) = \rho_{11}(t) - \rho_{22}(t)$  and demonstrated that its exact solutions exhibit (i) the transition from free to self-trapped behavior, (ii) the effective energy mismatch resulting from the nonlinearity in an equation which is otherwise translationally invariant, (iii) the reduction of the solitonic/polaronic bandwidth, i.e., of the effective velocity or frequency of the carrier, and (iv) the explicit dependence of the effective velocity or frequency on the initial state, which is an exclusive characteristic of nonlinear evolution.

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<sup>13</sup>One connection of Eq. (6) to the results of Ref. 6 is that, in terms of the "total energy"  $E$  of Ref. 6,  $A$  is given by  $-2\chi E - (\chi^2/2) - 4V^2$ .

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