

## Model calculations for the phenomenon of nonlinear trapping in molecular aggregates

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(Received 27 May 1992)

We present model calculations to describe the phenomenon of nonlinear trapping in molecular aggregates such as can occur during excitation transfer from an antenna to the reaction center in a photosynthetic unit. Our calculations are analytical and proceed from the discrete nonlinear Schrödinger equation introduced recently as the appropriate transport instrument in the analysis of excitation transfer in the presence of strong interaction with molecular vibrations.

### I. INTRODUCTION

Trapping of quasiparticles constitutes an extremely important phenomenon in condensed matter physics. While widespread, it 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 gathered energy to the reaction center, i.e., the trap. Much work has been done on the trapping process.<sup>1-8</sup> Trapping has been sometimes modeled via the introduction of a capture or sink term in a variety of equations of motion for the moving entity.<sup>1-5</sup> The equations themselves have been the Master equation representative of completely incoherent, i.e., diffusive, motion,<sup>1,3</sup> the Schrödinger equation representative of purely coherent motion,<sup>4,5</sup> combined equations such as the generalized master equation<sup>3,6</sup> and the stochastic Liouville equation<sup>2</sup> capable of describing coupled coherent and incoherent transport, continuous-time random walk equations,<sup>7</sup> and even the linearized Boltzmann equation.<sup>8</sup> The modeling of the capture process has been done in several different ways and interesting names such as pendant models,<sup>1</sup> sink models, and substitutional models<sup>3,6</sup> have been assigned to the systems analyzed.

We describe here some work that we have been involved with recently in the *nonlinear* trapping of excitation. The nonlinearities that we are interested in are associated with polarons or solitons, and arise as a result of strong interactions of the moving quasiparticle with the vibrations of the solid. The basic equation of motion used to describe transport in the presence of such nonlinearities is the discrete nonlinear Schrödinger equation (DNLSE). This equation has been motivated, used, and reviewed recently.<sup>9-15</sup> The nonlinearity it entails is cubic in the quantum-mechanical amplitude of the moving excitation, and it can give rise to interesting phenomena such as localization, band narrowing, and self-trapping. In the present context, our interest lies in systems in which the trap alone possesses nonlinearity, the rest of the quasiparticle motion being linear. If excitation moves on a chain of sites  $m$ ,  $n$ , etc., via interactions taken to be nearest neighbor (of strength  $V$ ) for simplicity, and is trapped by a site which has the nonlinear behavior arising

from strong interactions with the vibrations mentioned above, it is natural to think of three different models.<sup>1,3</sup> In the first, one of the sites in the chain is itself the trap site. It is nonlinear in that the energy of the quasiparticle is lowered by an amount proportional to the probability of occupation of the trap site whenever the quasiparticle occupies the site. Thus,

$$i \frac{dc_m}{dt} = V(c_{m+1} + c_{m-1}) - \delta_{m,0} \chi |c_0|^2 c_0 \quad (1.1)$$

represents this model,  $c_m$  being the amplitude for the excitation to be on site  $m$ . For discussions of the microscopic origin of the nonlinear term, we refer the reader to the reviews mentioned above.<sup>13-15</sup> A different possibility would correspond to the situation in which the particle may move from one particular site, for instance, at  $m=0$ , to the trap site  $\theta$  which is considered to be external to the chain. One would then have

$$i \frac{dc_m}{dt} = V(c_{m+1} + c_{m-1}) + \delta_{m,0} W c_\theta \quad (1.2a)$$

to describe the evolution in what may be called the antenna part of our system, and

$$i \frac{dc_\theta}{dt} = W c_0 - \chi |c_\theta|^2 c_\theta \quad (1.2b)$$

to describe the evolution of the trap amplitude  $c_\theta$ . Of these two models, the first describes a trap which is embedded in the system, while the second involves communication of the antenna with an external trap. In particular, this communication is shared between the trap and a single antenna site in the model represented by (1.2). A third physical model is one in which this communication of the trap with the antenna occurs equally from all the antenna sites. We then have

$$i \frac{dc_m}{dt} = V(c_{m+1} + c_{m-1}) + W c_\theta, \quad (1.3a)$$

$$i \frac{dc_\theta}{dt} = W \sum_m c_m - \chi |c_\theta|^2 c_\theta. \quad (1.3b)$$

The first model was analyzed by Dunlap, Kenkre, and Reineker<sup>16</sup> via numerical calculations. They found that a

transition appears to occur as the nonlinearity parameter  $\chi$  crosses the value  $(3.2)V$ . We will remark on the second model elsewhere. The present paper examines the third model, i.e., (1.3).

This paper is outlined as follows. In Sec. II, we present the method of investigation, and obtain an analytic solution for arbitrary initial conditions. In Sec. III, we obtain exact solutions for the particular case of initial occupation of the antenna. Stationary states are discussed in Sec. IV. Concluding remarks form Sec. V.

## II. ANALYTIC SOLUTION FOR ARBITRARY INITIAL CONDITIONS

As is clear from (1.3), the model we analyze consists of an  $N + 1$  site system forming the antenna, which is a ring consisting of  $N$  sites, surrounding a central trap site. Intersite interactions involve only the nearest neighbors within the antenna, whereas the trap is coupled to all the antenna sites. Equations (1.3), which describe the evolution of this system, can be solved for arbitrary initial conditions. First, we perform the discrete Fourier transform on the  $c_n$  variables. We introduce the "Bloch state amplitudes"

$$c^k = \frac{1}{\sqrt{N}} \sum_{m=1,2,\dots}^N c_m e^{ikm}, \quad (2.1)$$

which can be inverted into the site amplitudes through

$$c_m = \frac{1}{\sqrt{N}} \sum_{k=0,2\pi/N,\dots}^{2\pi(N-1)/N} c^k e^{-ikm}. \quad (2.2)$$

Substituting (2.2) in the original equation (1.3a) gives

$$\dot{c}^k = -2iV(\cos k)c^k + \sqrt{N}W\delta_{k0}c_\theta. \quad (2.3)$$

We see that the equation for the zeroth Fourier component and the original equation (1.3b) form a closed system of two nonlinear equations:

$$\dot{c}_\theta = -i\sqrt{N}Wc^0 + i\chi|c_\theta|^2c_\theta, \quad (2.4)$$

$$\dot{c}^0 = -2iVc^0 - i\sqrt{N}Wc_\theta, \quad (2.5)$$

whereas the remaining Fourier components  $c^k$ ,  $k \neq 0$ , can be found trivially from the linear homogeneous equation (2.3).

It has been shown in previous work on the nonlinear dimer and other extended systems<sup>9-15</sup> that the analysis of equations such as (2.4) and (2.5) is facilitated by the introduction of the density matrix  $\rho$  explicitly. We rewrite the zeroth Fourier mode amplitude as  $c_s = c^0$ , define  $\rho_{\mu\nu} = c_\mu c_\nu^*$ , where the subscripts take on the values  $s$  and  $\theta$ , and introduce the quantities

$$\begin{aligned} P &= \rho_{\theta\theta}, \quad Q = i(\rho_{\theta s} - \rho_{s\theta}), \\ R &= (\rho_{\theta s} + \rho_{s\theta}), \quad S = \rho_{ss}. \end{aligned} \quad (2.6)$$

Straightforward calculations lead to

$$\dot{P} = -\dot{S} = wQ, \quad (2.7a)$$

$$\dot{Q} = -2w(P - S) - 2VR - \chi PR, \quad (2.7b)$$

$$\dot{R} = 2VQ + \chi PQ, \quad (2.7c)$$

where  $w$  is defined as  $\sqrt{N}W$ . The nonlinear system of Eqs. (2.7) has three integrals of motion:

$$I_1 = P + S, \quad (2.8)$$

$$I_2 = R - \frac{\chi}{2w}P^2 - \frac{2V}{w}P, \quad (2.9)$$

$$I_3 = 4P(P - I_1) + Q^2 + R^2. \quad (2.10)$$

The constants of motion  $I_1$  and  $I_3$  have a simple interpretation for the case of equal population of all antenna sites, represented by

$$c_n(0) = c_1(0), \quad n = 2, 3, \dots, N. \quad (2.11)$$

In this case,

$$I_1 = P + S = |c_\theta|^2 + |c_s|^2 = |c_\theta|^2 + \left| \frac{1}{\sqrt{N}} \sum_{m=1}^N c_m \right|^2 = |c_\theta|^2 + N|c_1|^2 = |c_\theta|^2 + \sum_{m=1}^N |c_m|^2 = 1, \quad (2.12)$$

$$\begin{aligned} I_3 &= 4P(P - 1) + Q^2 + R^2 = 4|c_\theta|^2(|c_\theta|^2 - 1) - (c_\theta c_s^* - c_s c_\theta^*)^2 + (c_\theta c_s^* + c_s c_\theta^*)^2 \\ &= 4|c_\theta|^2(|c_\theta|^2 + |c_s|^2 - 1) = 4|c_\theta|^2(|c_\theta|^2 + N|c_1|^2 - 1) = 0. \end{aligned} \quad (2.13)$$

Both these results are consequences of the conservation of total probability. Although the integrals  $I_1$  and  $I_3$  are not immediately connected to the probability conservation for general initial conditions, it is easy to check that they indeed remain constant during any evolution governed by (2.7). The constant  $I_2$  has well-known counterparts in the analysis of the nonlinear dimer<sup>9,13</sup> as well as of the trimer and  $n$ -mer.<sup>12</sup>

We now use the integrals of motion  $I_1$  and  $I_2$  to obtain a single equation for the primary variable of interest, viz.  $P$ , the probability of occupation of the trap site. Differentiating both sides of (2.7a), and using (2.7b) after

expressing  $S(t)$  and  $R(t)$  in terms of  $P(t)$  with the help of the constants  $I_1$  and  $I_2$ , respectively, we get

$$\frac{d^2P}{d\tau^2} = \frac{1}{2}(I_1 - \eta I_2) - (\xi I_2 + \eta^2 + 1)P - 3\xi\eta P^2 - 2\xi^2 P^3. \quad (2.14)$$

In (2.14), we have used the scaled time  $\tau = 2wt$  and have introduced the parameters

$$\xi = \frac{\chi}{4w}, \quad \eta = \frac{V}{w}. \quad (2.15)$$

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.

Multiplying both sides of (2.14) and  $dP/d\tau$  and integrating, we obtain

$$\left[ \frac{dP}{d\tau} \right]^2 = U(P) - U(P_0) + \left[ \frac{dP}{d\tau} \right]^2 \Big|_{\tau=0} \quad (2.16)$$

with  $P_0 = P(0)$ . The quartic potential  $U(P)$  reads

$$U(P) = \xi^2 P^4 + 2\xi\eta P^3 + h_2 P^2 + h_1 P, \quad (2.17)$$

where the constants  $h_1$  and  $h_2$  are linear combinations of  $I_1$  and  $I_2$  given by

$$h_1 = \eta I_2 - I_1, \quad (2.18)$$

$$h_2 = \xi I_2 + \eta^2 + 1. \quad (2.19)$$

The solution of (2.16) can be written in terms of the Weierstrass  $\mathcal{P}$  function as was done previously for a nonlinear nondegenerate dimer<sup>17</sup> as well as for the trimer and the  $n$ -mer:<sup>15</sup>

$$P(\tau) = P_0 - \frac{6U'(P_0)}{24\mathcal{P}(\tau; g_2, g_3) + U''(P_0)}. \quad (2.20)$$

In (2.20), the invariants  $g_2$  and  $g_3$  of the Weierstrass function are given by

$$g_2 = \frac{1}{9}h_2^2 + \frac{1}{2}h_1 - \xi^2 U(P_0), \quad (2.21)$$

$$g_3 = \frac{1}{216}h_2^3 - \frac{1}{16}\xi^2 h_2^2 + \frac{1}{24}\xi\eta h_1 h_2 - \frac{1}{4}\xi^2 [h_1 + \eta^2] U(P_0), \quad (2.22)$$

and  $U'$  and  $U''$  denote the derivatives of the potential  $U$ . The functions  $Q(\tau)$ ,  $S(\tau)$ , and  $R(\tau)$  can now be expressed in terms of the function  $P(\tau)$ :

$$Q(\tau) = 2 \frac{d}{d\tau} P(\tau), \quad (2.23)$$

$$R(\tau) = I_2 + 2\xi P^2(\tau) + 2\eta P(\tau), \quad (2.24)$$

$$S(\tau) = I_1 + P(\tau). \quad (2.25)$$

Recalling the definition (2.6), we find that the relative phase between  $c_\theta$  and  $c_s$  is determined by the equations

$$\cos\psi(\tau) = \frac{R(\tau)}{\sqrt{P(\tau)S(\tau)}}, \quad \sin\psi(\tau) = \frac{Q(\tau)}{\sqrt{P(\tau)S(\tau)}}. \quad (2.26)$$

Equations (2.20)–(2.26), together with

$$c^k(\tau) = c^k(0) \exp(-i\eta\tau \cos k), \quad k \neq 0 \quad (2.27)$$

constitute the solution of the full problem for arbitrary initial conditions.

### III. ANALYSIS OF THE CASE OF ZERO INITIAL OCCUPATION OF THE TRAP

Equation (2.16) can be used to find the occupation probability of the trap site for arbitrary initial conditions.

However, the character of the evolution of the system can be appreciated better by considering special cases and investigating the nonlinear potential  $U(P)$  corresponding to them. Let us consider the situation  $c_\theta(0) = 0$  and  $c_n(0) = 1/\sqrt{N}$ , which corresponds to the trap being unoccupied and to a uniform distribution of the initial probability among the antenna sites. In this case, we have

$$P(0) = Q(0) = R(0) = \frac{dP}{d\tau} \Big|_{\tau=0} = 0, \quad S(0) = 1. \quad (3.1)$$

The constants we have introduced in Sec. II have the simple values

$$I_1 = 1, \quad I_2 = 0, \quad h_1 = -1, \quad h_2 = \eta^2 + 1, \quad (3.2)$$

and the nonlinear potential has the form

$$U(P) = P[\xi^2 P^3 + 2\eta\xi P^2 + (\eta^2 + 1)P - 1] = P U_1(P), \quad (3.3)$$

where

$$U_1(P) = \xi^2 P^3 + 2\eta\xi P^2 + (\eta^2 + 1)P - 1. \quad (3.4)$$

The evolution starts from the point  $P=0$ , where  $U(P)=0$ . Since  $U'(0) = -1 < 0$ , the motion proceeds in the direction of positive  $P$ . Except for the case  $\eta = -\xi$ , which means that the antenna intersite interaction and the scaled antenna-trap interaction are equal in magnitude and opposite in sign, the system never reaches the point  $P=1$  corresponding to full occupation of the trap site, since  $U(1) = (\xi + \eta)^2 \geq 0 = U(0)$ . We also have

$$U_1(1) = (\xi + \eta)^2 \geq 0 > -1 = U_1(0), \quad (3.5)$$

which leads to the conclusion that there exists at least one positive root  $P_1$  of  $U_1(P)$  between  $P=0$  and  $P=1$ :

$$U_1(P_1) = 0, \quad 0 \leq P_1 < 1 \quad (3.6)$$

The motion is thus confined to the interval between the points  $P=0$  and  $P=P_1$ , where  $P_1$  is the smallest of the values which fulfill (3.6). The confining interval is traversed periodically in both directions during the evolution. The length of the interval varies with the parameters  $\xi$  and  $\eta$  and can undergo an abrupt change if another root of  $U_1$  appears between  $P=0$  and  $P=1$ . Obviously, because  $U_1$  has different signs in the points  $P=0$  and  $P=1$ , the total number of roots between these two points must be even. The necessary and sufficient condition for  $U_1$  having three real roots is that the discriminant  $\Delta$  of the third-order equation  $U_1(P)=0$  is smaller than zero.<sup>18</sup> In addition to the parameter  $\xi = \chi/4w$  introduced earlier, we define

$$\alpha = \frac{\chi}{4V}. \quad (3.7)$$

Then, for  $U_1(P)$  given by (3.4), the condition reads

$$\Delta = 4 \left[ \frac{1}{\xi^2} - \frac{1}{3\alpha^2} \right]^3 + \frac{1}{27} \left[ \frac{2}{\alpha^3} + \frac{1}{\xi^2} \left[ \frac{2}{\alpha} + 3 \right] \right]^2 < 0. \quad (3.8)$$

The inequality (3.8) is fulfilled if and only if

$$9 + \frac{8}{\alpha} > 0$$

and

$$\beta_- \geq \xi^2 \geq \beta_+,$$

where

$$\beta_{\pm} = \left[ -\frac{1}{\alpha^2} - \frac{9}{2\alpha} - \frac{27}{8} - \frac{(9\alpha+8)^{3/2}}{8\alpha^{3/2}} \right]^{-1}. \quad (3.10)$$

To ensure that all three roots of  $U_1$  lie between 0 and 1, we impose another condition, viz.,

$$0 \leq p_{\max} \leq p_{\min} \leq 1, \quad (3.11)$$

where

$$p_{\max} = -\frac{1}{3} \left[ \frac{2}{\alpha} + \left( \frac{1}{\alpha^2} - \frac{3}{\xi^2} \right)^{1/2} \right], \quad (3.12)$$

$$p_{\min} = -\frac{1}{3} \left[ \frac{2}{\alpha} - \left( \frac{1}{\alpha^2} - \frac{3}{\xi^2} \right)^{1/2} \right], \quad (3.13)$$

are, respectively, the values of  $P$  at the local maximum and minimum of  $U_1$ . Because  $U_1(\pm\infty) = \pm\infty$ , if  $U_1$  has three real roots, we must have  $U_1(p_{\max}) > 0$ ,  $U_1(p_{\min}) < 0$ , and  $p_{\max} \leq p_{\min}$ . It is now obvious that all roots of  $U_1$  lie between 0 and 1 if and only if  $p_{\max}$  and  $p_{\min}$  fulfill (3.11). Such a condition implies

$$\alpha < 0, \quad \frac{1}{\xi^2} > 1 - \left[ \frac{1}{\alpha} - 2 \right]^2. \quad (3.14)$$

Different shapes of the potential shown in Fig. 1 correspond to different regions in the  $(\alpha, \xi)$  plane. We stress the physical meaning of the parameters used in the plots: they represent, as (2.15) and (3.7) show, the value of the nonlinearity relative to the antenna intersite transfer and to the antenna-trap transfer, respectively. The abrupt change of the confining interval mentioned above is illustrated in Fig. 2. The depicted situation corresponds to  $\alpha = -1$  and three different values of the parameter  $\xi$ . For  $\xi = 2.25$ , the shape of the potential confines the changes of trap probability to the interval from  $P=0$  to about  $P=0.3$ . As one lowers the trap nonlinearity and takes  $\xi = 2.0$ , the motion still takes place between the probability values  $P=0$  and  $P=0.5$ . This means that the excitation is confined primarily to the antenna. However, as the nonlinearity is lowered further, and  $\xi$  assumes values only slightly smaller than 2.0,  $P$  oscillates between 0 and 1. We now have a delocalized state and much more efficient transfer of the excitation to the trap. This type of transition takes place whenever we cross the line  $\xi = \beta$  in the parameter space.

The detailed analysis of the trapping process for initial occupation of the antenna that we have presented above can be repeated easily for the case of the initial occupation of the trap. More involved initial conditions involving unequal distribution among the antenna sites can also be treated with the help of the expressions derived in Sec. II. We have taken the antenna sites to be energetically

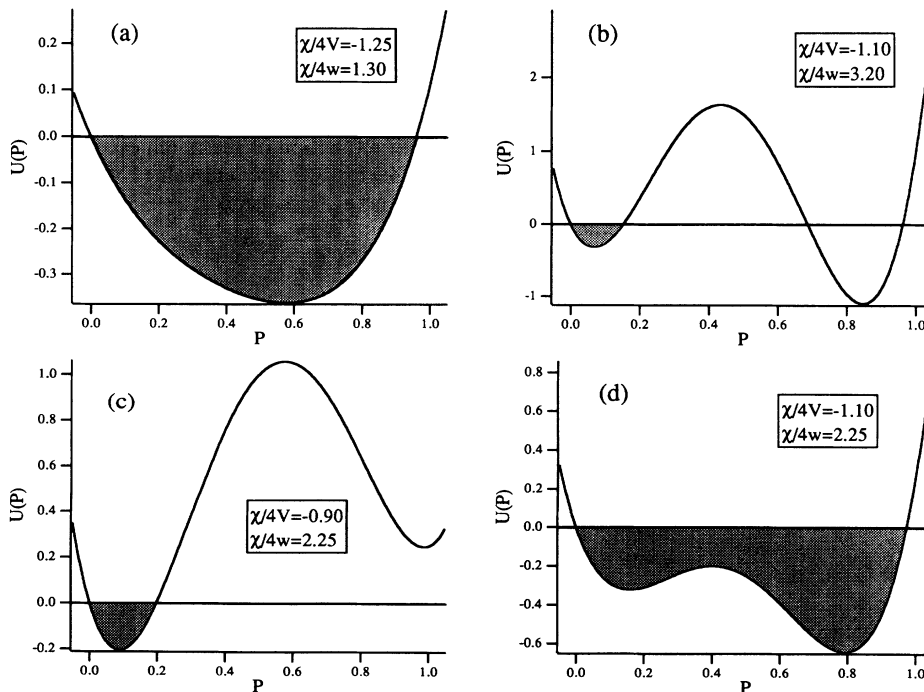


FIG. 1. Quartic potential  $U(P)$  determining the evolution of the excitation probability  $P$  for the trap site in the case of no initial trap occupation, for various values of the parameters. The shaded regions represent the intervals in which the system motion occurs. We see that, depending on the values of the system parameters, the system may be confined to the vicinity of  $P=0$  [as in (b) and (c)] or can reach values close to  $P=1$  [as in (a) and (d)]. The former corresponds to inefficient trapping while the latter describes the kind of situation that would be desirable in a photosynthetic unit.

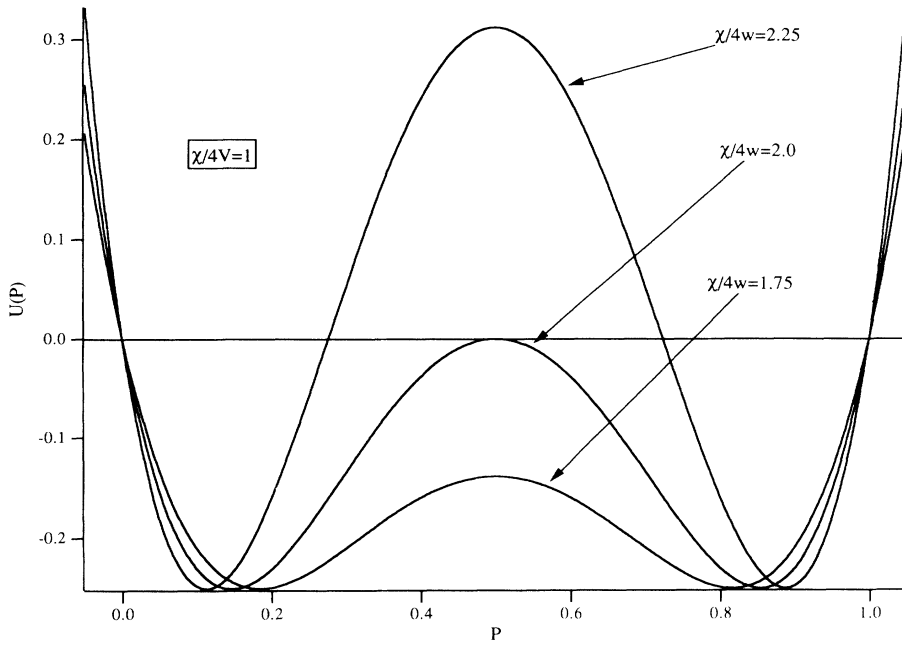


FIG. 2. Potential  $U(P)$  for parameters values near the transition between localized and delocalized states. The values of the probability  $P$  are confined to the left well of the potential (as is the case for  $\chi/4w = 2.25$  and  $\chi/4w = 2.0$ ) unless the value at the central peak is smaller than 0 (as is the case for  $\chi/4w = 1.75$ ).

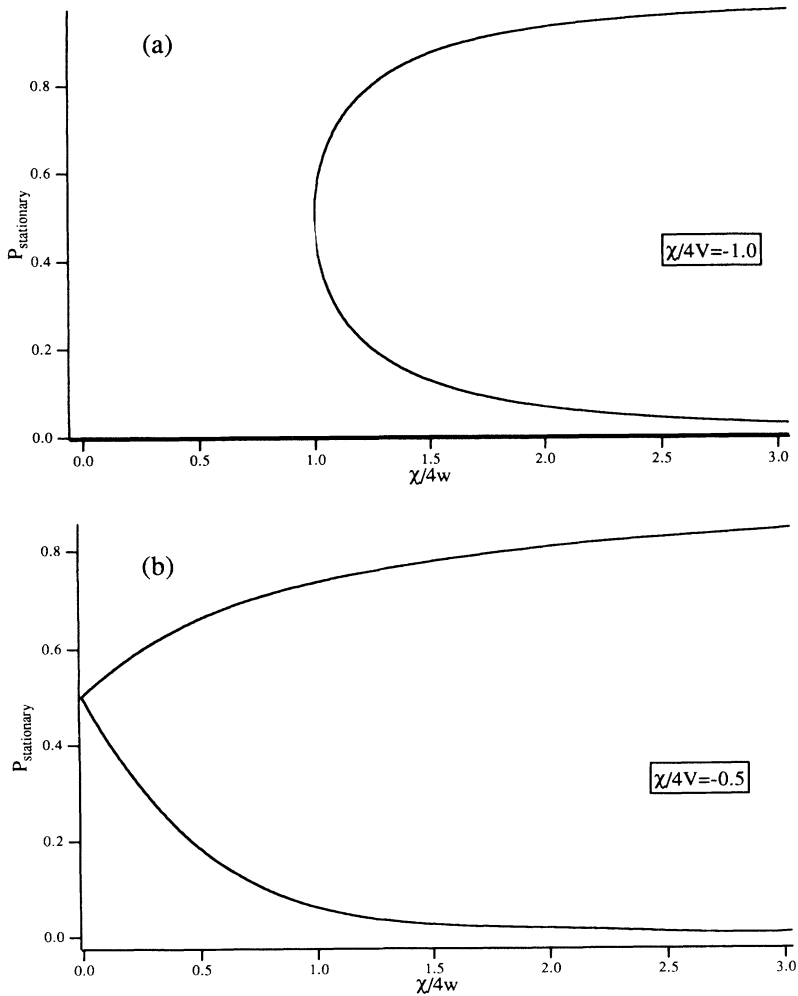


FIG. 3. Trap probability in the stationary state as a function of the nonlinearity parameter  $\chi/4w$  for two different values of the parameter  $\alpha$ : (a)  $\alpha = -1.0$  and (b)  $\alpha = -0.5$ .

degenerate relative to the trap site. The inclusion of an energy difference has some interesting consequences which will be reported on elsewhere.

#### IV. STATIONARY STATES

The stationary states of our system are obviously of interest. If we introduce dissipation explicitly into the system by following the method of Ref. 10, we are guaranteed to find the system evolving at large times to the stationary states of the (dissipationless) system of equations (1.3). We can find these states in the standard manner by writing

$$c_\theta = \bar{c}_\theta \exp(-i\Omega t), \quad c_n = \bar{c}_n \exp(-i\Omega t), \quad (4.1)$$

where  $\Omega$  is the energy of the stationary state. An equivalent, and practically easier, method<sup>13</sup> of obtaining them is by putting the left-hand sides of (2.7) equal to zero. We get

$$Q=0, \quad 2w(S-P)=2VR+\chi PR. \quad (4.2)$$

The solutions can be determined particularly easily in the case of homogeneous antenna occupation, i.e.,  $c_n=c_1$ . As we know, in this case,  $I_1=1$  and  $I_3=0$  [cf (2.12) and (2.13)]. Using these integrals to eliminate  $S$  and  $R$  in favor of  $P$ , we get, from (4.2),

$$P(P-1) \left[ \frac{2V}{w} + \frac{\chi}{w} P \right]^2 + (1-2P)^2 = 0. \quad (4.3)$$

Equation (4.3) has allowed us to study the dependence of the stationary state trap probability on a variety of parameters involving the nonlinearity. Of the large number of possible graphical outputs of our study, we have shown in Fig. 3 the dependence of the stationary state trap probability  $P$ , i.e., the solution of (4.3), on the nonlinearity parameter  $\xi=\chi/4w$ , for two values of the ratio  $\alpha=\chi/4V$ .

#### V. CONCLUSIONS

We have presented here some model calculations for nonlinear trapping. The evolution in the antenna sites is assumed to occur via the ordinary (linear) Schrödinger equation. Nonlinearity arising from strong interactions with vibrations is assumed to exist at the trap site. The form of the nonlinearity is as given by the discrete nonlinear Schrödinger equation. The geometrical configuration of the trapping process is as modeled by a

number of earlier authors, for instance, Lakatos-Lindenberg, Hemenger, and Pearlstein.<sup>1</sup> The method of solution follows our earlier work on the discrete nonlinear Schrödinger equation and consists of writing nonlinear density matrix equations and obtaining solutions for the quantity of interest such as the trap probability.

We have shown the general method of solution, studied in detail the case of initial antenna occupation—which has special relevance to areas such as photosynthesis—and have obtained explicitly the stationary state trap probability. The latter is a clear indicator of the dependence of the trapping efficiency on nonlinearity parameters. We stress here that, unlike what is done in most studies of trapping, we have not assumed the trap site to provide any external sink rate in our model. The self-trapping phenomenon inherent in the discrete nonlinear Schrödinger equation is itself responsible for the capture of the excitation. The analysis is applicable to physical systems in which excitation in reaction centers (traps) interacts much more strongly with vibrations than excitation in the antenna sites.

We comment in passing on an interesting characteristic of our model which is apparent even when the evolution is *linear*. Since the antenna sites are all energetically equivalent to the trap site, we appear to have a problem of transfer between a pair of degenerate states: the trap state on the one hand and the entire antenna “state” on the other. However, if we diagonalize the part of the Hamiltonian which describes the motion in the antenna, we can obtain the  $N$  Bloch states which are the antenna eigenstates, each labeled by the value of the quasimomentum  $k$ , lying between 0 and  $\pi$ . It is easy to see, then, that the trap state will transfer excitation only to a single Bloch state, indeed the one with  $k=0$ . There will be no other interactions in the system of the trap state and the  $k$  states. Now we clearly have a situation of excitation transfer between two *nondegenerate* states: the trap state and the  $k=0$  antenna state, which differ in energy by the amount  $2V$ . This energy difference equals half the bandwidth for excitation transfer within the antenna. Surely, calculations, if carried out exactly in either picture, will give correct (equivalent) results. However, if approximations are introduced for analytic tractability in a complex system, inequivalences might indeed arise. One sees that there would be considerable sensitivity of the results to the energy difference between the trap state and the antenna states.<sup>19</sup>

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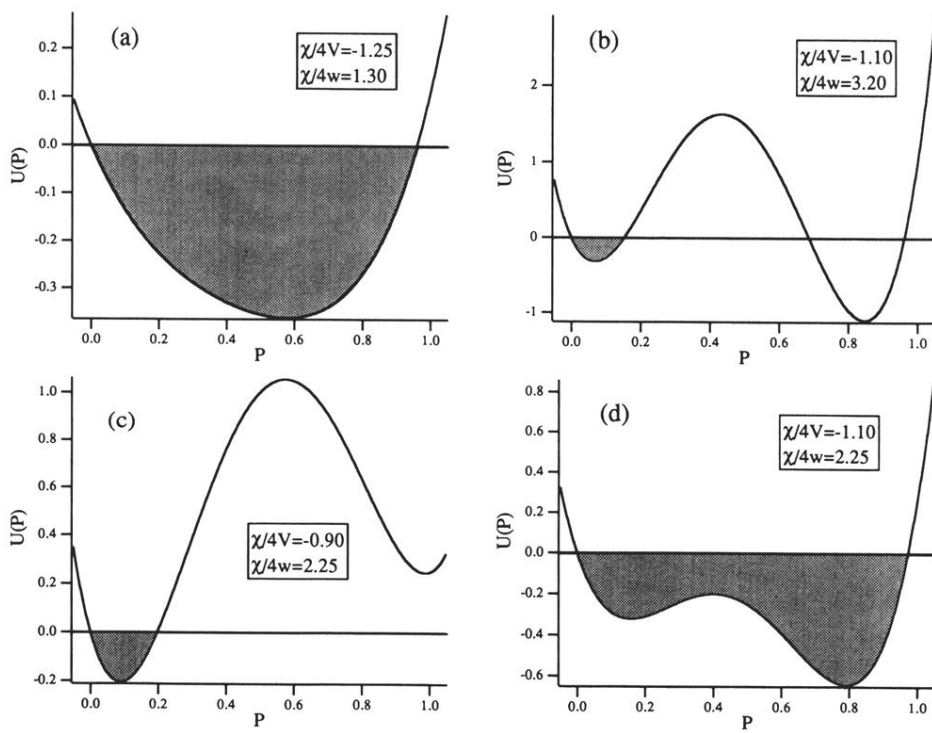


FIG. 1. Quartic potential  $U(P)$  determining the evolution of the excitation probability  $P$  for the trap site in the case of no initial trap occupation, for various values of the parameters. The shaded regions represent the intervals in which the system motion occurs. We see that, depending on the values of the system parameters, the system may be confined to the vicinity of  $P=0$  [as in (b) and (c)] or can reach values close to  $P=1$  [as in (a) and (d)]. The former corresponds to inefficient trapping while the latter describes the kind of situation that would be desirable in a photosynthetic unit.