Chapter 2

Self-trapping and localization-delocalization transition due to discrete nonlinear Schrödinger equation

2.1 Introduction

In this chapter we deal with the dynamics of an exciton in nonlinear systems described by the discrete nonlinear Schrödinger equation [20,62–76,78,86]. Many interesting behaviors in the dynamics of the exciton described by discrete nonlinear Schrödinger equation are observed and will be discussed here. These interesting behaviors include the self-trapping transition (dynamical transition) [11–15,74,79,80,87–89], stationary transition [112] and condition for full delocalization [90] etc. For that purpose, we first consider the dynamics of an exciton in finite systems and then go over to extended systems. Even though a plethora of works has been done [77,79,80,83,84,86,89–93,95–97,99–103,105–115,117] on the self-trapping and the dynamics of an exciton whose dynamics can be adequately modeled by the discrete nonlinear Schrödinger equation, we present a few paradigms.
2.2 Nonlinear dimer

For an analytical understanding of the self-trapping transition we first consider the dynamics of an exciton in a two site (dimer) system described by the discrete nonlinear Schrödinger equation or discrete self-trapping equation (work done by Kenkre, et al. [12,80]). Furthermore, the dimer is both interesting in its own right and attainable experimentally. A well known example in the field of energy transfer is the stick dimer consisting of a variable discrete donor-acceptor system. Dimers [92], more generally systems of small size, occur 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 [109,110]. Therefore, calculation for dimer observables is not merely pedagogical in nature but has direct significance in experiments.

2.2.1 Degenerate dimer with adiabatic nonlinearities

The system we consider here is a degenerate nonlinear dimer with adiabatic nonlinearities [12]. By degeneracy we mean that the static site energies of the sites are same. The time evolution equations for the exciton at sites 1 and 2 of the nonlinear dimer are given by

\[ i \frac{dC_1}{dt} = VC_2 + \chi |C_1|^2 C_1 \]
\[ i \frac{dC_2}{dt} = VC_1 + \chi |C_2|^2 C_2 \]  

(2.1)

where, \( C_1(t) \) and \( C_2(t) \) are the probability amplitudes at sites 1 and 2 of the dimer respectively. \( V \) is the hopping matrix element between sites 1 and 2. As mentioned in chapter 1, the nonlinear term arises due to the interaction of the exciton with the lattice oscillators (or due to polaronic effect) under the adiabatic approximation [51]. The validity of the approximation holds good if the motion of the oscillators is assumed to be much faster than that of the exciton. The lattice oscillators are assumed to be Einstein oscillators (local harmonic oscillators). \( \chi \) is the coupling parameter for the nonlinearity. It is also assumed that the interaction at both the sites are of equal strength, i.e., the exciton interacts with both the oscillators with equal strength. Switching over to density
matrix, we defined \( \rho_{mn} = C_mC_n^* \). After some simple algebra, eq. (2.1) can be decoupled and finally yields

\[
\frac{d^2P}{dt^2} = AP - BP^3
\]  

(2.2)

where, \( P = \rho_{11} - \rho_{22} \) (the probability difference of the particle between two sites of the nonlinear dimer). \( A \) and \( B \) are integration constants and given as

\[
A = \left( x^2/2 \right) P_0(t=0) - 4V^2 - 2V\chi(\rho_{21} + \rho_{12})|_{t=0}, \quad B = \chi^2/2. \]

In the absence of nonlinearity, i.e., for \( \chi = 0 \), \( A = -4V^2 \) and \( B = 0 \), and the probability difference \( P(t) \) oscillates sinusoidally. But in the presence of nonlinearity, i.e., \( \chi \neq 0 \), quite different and rich behavior in dynamics is obtained.

![Fig. 2.1](image)

Fig. 2.1 \( P(t) \), probability of the particle to stay at site 1, is plotted as a function of time \( t \) for three values of \( \omega \). The values of \( \chi \) for dotted curve, solid curve and dashed curve are 3, 5 and 4 respectively. In this case \( V = 1 \).

If the particle (exciton) is initially populated entirely at the site 1, i.e., \( P(t=0) = 1 \), the constants \( A \) and \( B \) reduce to \( \chi^2/2 - 4V^2 \) and \( \chi^2/2 \) respectively. With this initial condition the eq. (2.2) has two completely different solutions for \( 0 < \chi/4V < 1 \) and \( \chi/4V > 1 \). The solutions are given by [12]

\[
P(t) = \begin{cases} 
  \text{cn} \left( 2Vt|k = \frac{\chi}{4V} \right) ; & 0 < \frac{\chi}{4V} < 1 \\
  \text{sn} \left( \frac{1}{2} \chi t|k = \frac{4V}{\chi} \right) ; & 1 < \frac{\chi}{4V}
\end{cases}
\]  

(2.3)
These functions are plotted in Fig. 2.1. It shows that for $\frac{\chi^2}{4V} = \frac{3}{4} < 1$, the exciton oscillates (solid curve) between two sites, i.e., $P(t)$ goes from -1 to +1. For $\frac{\chi^2}{4V} = \frac{5}{4} > 1$, $P(t)$ oscillates approximately between 0.6 and 1 (dotted curve) and thus, the particle prefers to be at the initially populated site. On the other hand, for $\chi = 4V$, the exciton takes infinitely long time to go over to the other site (dashed curve). Therefore, a transition takes place from free particle transport to a self-trapping of the particle at $\chi = 4V$.

This self-trapping can also be visualized from an alternative analysis. It is described below. The eq. (2.1) with the initial condition $P(t = 0) = \pm 1$ (the particle is initially placed at either of the two sites) takes the form

$$\frac{d^2P}{dt^2} = \left(\frac{\chi^2}{2} - 4V^2\right) P - \frac{\chi^2}{2} P^3$$

(2.4)

Eq. (2.4) can be thought of an equation describing the motion of a particle in the potential

$$U(P) = -(\frac{\chi^2}{2} - 4V^2) P^2 + \frac{\chi^2}{4} P^4$$

(2.5)

where $P$ is treated as the coordinate determining the position of the particle. The total energy of the particle is given by

$$\left(\frac{dP}{dt}\right)^2 + U(P) = \left(\frac{dP}{dt}\right)^2 \bigg|_{t=0} + U(P(t = 0)) = 4V^2 - \frac{\chi^2}{4}$$

(2.6)

From eq. (2.5) it is clear that the structure of the potential becomes a double well when $\chi^2 \geq 8V^2$. But the maximum of the potential appears at $P = 0$, therefore, when $U(P(t = 0)) \leq U(0)$, i.e., $\chi \geq 4V$, the thought particle gets confined in one of the wells depending on the initial condition. Thus, one of the turning points of the particle is at $P = 1$ and the other one lies between 0 and 1. This implies that $P(t)$ oscillates in the range $1 \leq P \leq 0$ for $\chi \geq 4V$. Otherwise $P(t)$ oscillates between -1 and 1. Thus, it is clear that a transition from free oscillation between the two site to a self-trapped motion takes place as $\chi$ goes beyond 4V. Furthermore, comparing the dynamics of the exciton in the nonlinear dimer with the dynamics of an exciton in an effective linear system, it has been found that the nonlinearity helps in reducing the hopping parameter from $V$ to $V_{eff} \approx V\pi/Ln[16/(1 - \chi^2/16V^2)]$ [12].
Kenkre et al. [80] further examined the effect of the nonlinearities on quasielastic scattering function in a dimer by the use of the exact solution as found earlier (eq. (2.3)). The calculation is appropriate to the scattering of probe particles such as neutrons off moving quasiparticle which interact with lattice vibration strongly enough to produce nonlinear effects while moving in the lattice. They have presented explicit expression for the scattering spectrum. They are seen to exhibit the phenomenon of motional narrowing even in the absence of true damping. Self-trapping transition also gets detected from the spectral function. It has also been found that the system has similarity with the case of a damped linear dimer. So, the nonlinearity introduces the effect of damping.

It is known that the nonlinear systems are highly sensitive to the initial condition. Therefore, Kenkre and his collaborators [119], further studied the dimer problem and found that if initially the particle is completely localized at one site, then the critical value of the nonlinearity, $\chi_{cr} = 4V$. On the other hand if the particle is initially fully delocalized, the critical value goes to infinity [108,119]. Furthermore, it has been found that the more localized the particle is initially, the smaller is the degree of nonlinearity required to self-trap the particle. In this study a different kind of transition in the self-trapped region has also been revealed. This is known as amplitude transition (see ref. [119]).

### 2.2.2 Nondegenerate dimer with adiabatic nonlinearities

So far we have talked about the degenerate nonlinear dimer. Now a brief discussion on nondegenerate, nonlinear dimer [86,91] will be made. By nondegeneracy we mean that both the sites of the dimer has different static site energies. Nothing much happens due to the nondegeneracy. Only when the nondegeneracy is of very small amount, the critical value of the trapping gets affected. That again depends on the initial condition. If the initially populated site has lower site energy, the particle faces a barrier and, therefore, less nonlinearity is needed to trap the particle. Otherwise, the situation reverses. For large amount of nondegeneracy, the particle gets confined in one site (initially populated site) and therefore, nonlinearity has no role to play. The interplay of nondegeneracy and the nonlinearity has been discussed in detail in the reference [26].
2.2.3 Nondegenerate dimer with oscillating hopping element and adiabatic nonlinearities

Throughout our earlier discussion, the hopping element between two sites of a nonlinear dimer is taken to be constant. What we are interested in is to consider the oscillatory hopping element between the two sites of a nondegenerate nonlinear dimer [90,97]. What we mean by nondegeneracy is defined earlier. This system is similar to a two level system (the individual levels are varying with time) where two levels are coupled to an oscillatory electric field. The dynamics of the exciton in this system will be governed by the following equations.

\[ i\frac{dC_1}{dt} = -(\epsilon_0/2 + \chi_1|C_1|^2)C_1(t) + V\cos(\omega t)C_2 \]
\[ i\frac{dC_2}{dt} = (\epsilon_0/2 - \chi_2|C_2|^2)C_2(t) + V\cos(\omega t)C_1 \]  

(2.7)

Here \( C_1(t) \) and \( C_2(t) \) are the probability amplitude of the exciton (quasiparticle) to stay at the sites 1 and 2 of the nonlinear dimer, respectively, at time \( t \). \( \epsilon_0 \) is the energy difference between the two sites (levels). \( \chi_1 \) and \( \chi_2 \) are the nonlinearity strengths at the sites 1 and 2, respectively. In this model the nonlinearity alters the effective site energies dynamically depending on the site-probability of the respective sites. \( V\cos(\omega t) \) is the laser field in the context of two level system. But here it couples the two sites sinusoidally with respect to time. In the absence of oscillation of the hopping element (laser field with zero frequency) and \( \chi_1 = \chi_2 = \chi \), the system is called nondegenerate and symmetric nonlinear dimer [26,97]. There are several studies on different kinds of such nonlinear systems and has been discussed earlier. In most of these systems nonlinearity induces a self-trapping transition at certain critical value of nonlinearity strength. But in some of the cases chaotic behavior of the electron has also been observed [15]. Here, we consider two cases: (i) \( \chi_1 = \chi_2 = \chi \) which we call the doubly nonlinear two site (DNTS) system and (ii) \( \chi_1 = \chi \) and \( \chi_2 = 0 \), which we call the singly nonlinear two site (SNTS) system.

DNTS system:

To observe the dynamics of the particle, initially placed at one of the two sites of a symmetric nonlinear dimer with the oscillating hopping element between the sites, one
has to solve eq. (2.7). But in the presence of nonlinearity analytical solution is not possible and therefore we solve them numerically. There are many ways to look at the localization-delocalization transition of the particle between two sites. For example we look at (i) the probability of the particle to stay at any of the two sites and (ii) the time averaged probability of the particle at any of the sites according to convenience. The time averaged probability of the particle at the \( m \)-th site is given as

\[
\langle P_m \rangle = \frac{1}{T} \lim_{T \to \infty} \int_0^T |c_m(t)|^2 \, dt,
\]

where \( m = 1, 2 \).

![Graph](image)

**Fig. 2.2** \( P_1(t) \) (Probability of the particle to stay at site 1 at time \( t \)) is plotted as a function of time \( t \) for three values of \( \omega \). The values of \( \omega \) for dotted curve, solid curve and dashed curve are 5.91, 6 and 6.1 respectively. In this case \( \chi = 0 \) and \( V = 0.1 \).

The initial excitation is applied at site \( m = 1 \), i.e., \( |c_m(t = 0)|^2 = \delta_{m,1} \). To calculate this we have solved the coupled nonlinear differential equations numerically by using the fourth order Runge-Kutta Method. Here we have taken \( T = 3000 \) with discretized time interval \( \Delta T = 0.01 \) for summation. The numerical accuracy has been checked by using the probability conservation (\( |C_1|^2 + |C_2|^2 = 1 \)). It should be noted that in the case of perfect delocalization of the particle, the probability of the particle to stay at any of the two sites oscillates between 0 and 1. On the other hand when the time averaged probability of the
particle at both the sites is 0.5, the particle has equal probability to stay at both the sites and hence the particle is in a state of perfect delocalization. Through out our analysis in this section we have mostly used the above definition for the delocalization condition.

![Diagram](https://via.placeholder.com/150)

**Fig. 2.3** Plot of \( \langle P_m \rangle \) (time averaged probability at site \( m \)) for DNYS system as a function of frequency \( \omega \) for \( V = 0.1 \) and different \( \chi \) values. The upper curves are for \( \langle P_1 \rangle \) and the lower curves are for \( \langle P_2 \rangle \). Solid, dotted, small-dashed, long-dashed and dot-dashed curved are for \( \chi = 0, 0.5, 1, 2 \) and 3 respectively.

In Fig. 2.2 we have plotted the probability of the particle at site 1 for three different values of \( \omega \) when \( V < \epsilon_0 \). For example we have taken \( V = 0.1 \) and \( \epsilon_0 = 6 \). The dotted curve is for \( \omega = 5.91 \), the solid curve is for \( \omega = 6 \) and the dashed curve is for \( \omega = 6.1 \). We see that only the solid curve oscillates between 0 and 1. So it is clear that when \( V < \epsilon_0 \) the particle oscillates between the two sites only at the value of \( \omega = \epsilon_0 \) and indicating that perfect delocalization condition is reached. This condition is the resonance condition and \( \omega = \epsilon_0 = \omega_0 \) is the resonance frequency in the context of a two level system. We have also examined the situations with different values of \( V \). It is found that as \( V \) approaches \( \epsilon_0 \) the resonance is lost. This has been shown in earlier works [118].

In Fig. 2.3 we have plotted \( \langle P_m \rangle \) as a function of \( \omega \) for different values of \( \chi \). In this case \( \epsilon_0 = 6 \) and \( V = 0.1 \). In this figure upper curves are for \( \langle P_1 \rangle \) and lower ones are for \( \langle P_2 \rangle \). For \( \chi = 0 \) (solid curves) we find a sharp peak in \( \langle P_2 \rangle \) and a dip in \( \langle P_1 \rangle \) at \( \omega = \epsilon_0 \). We notice that both the time averaged probabilities touch each other at \( \omega = \epsilon_0 \) and have
values equal to 0.5. This value of frequency ($\omega_0 = \epsilon_0$) is the resonant frequency where perfect delocalization is obtained.

Fig. 2.4 Plot of time averaged probability $\langle P_m \rangle$ of DNTS system as a function frequency $\omega$ for $V = 0.6$. Other parameters are same as in Fig. 2.3. The upper curves are for $\langle P_1 \rangle$ and the lower ones are for $\langle P_2 \rangle$.

Fig. 2.5 Plots of the probability of the particle to stay at site 1 i.e., $P_1$ as a function of time $t$ for different values of $\omega$ in DNTS system. The value of $\omega$ for solid, dotted and dashed curves are 5.9, 6 and 6.1 respectively. Except this value of $\omega$ the values of $\langle P_1 \rangle$ and $\langle P_2 \rangle$ are near 1 (or greater than 0.5) and near 0 (or less than 0.5) respectively, which corresponds to the localization of the particle.
at site \( m = 1 \). For \( \chi = 0.5 \) (dotted curves) we find a sharp peak in \( \langle P_2 \rangle \) and a dip in \( \langle P_1 \rangle \) at the value of \( \omega \) which is larger than \( \omega = \epsilon_0 \). But, in this case the probabilities do not touch each other. If we increase the value of the nonlinearity strength the position of the peak and consequently the dip of the probabilities moves away from \( \omega = \epsilon_0 \). The difference between the peak of \( \langle P_2 \rangle \) and the dip of \( \langle P_1 \rangle \) also increases with the increasing \( \chi \). This is easily seen from the curves for \( \chi = 1 \) (small dash), \( \chi = 2 \) (long dash) and \( \chi = 3 \) (dot-dashed). It should be noted that the time averaged site-probabilities show the asymmetric behavior around the frequency where the peak and dip is observed. In the left side the variation is sharper than that in right side. This study shows that at the value of \( V = 0.1 \) we do not obtain the resonance condition (\( \omega_0 \)) where complete delocalization occurs for the values of nonlinearity strength studied here. But, if we increase the value of \( V \) we observe a significant change in \( \langle P_m \rangle \). This is shown in Fig. 2.4 for \( V = 0.6 \). In this case also the upper curves are for \( \langle P_1 \rangle \) and the lower ones are for \( \langle P_2 \rangle \). Here, the peak of \( \langle P_2 \rangle \) and dip of \( \langle P_1 \rangle \) has been shifted at \( \omega \sim \epsilon_0 \). This is obtained for \( \chi = 0.5 \) (dotted curves) and 1 (small-dashed curves). For \( \chi = 0 \) (solid curves) both the probabilities touch each other at the same value of \( \omega \) as obtained for \( V = 0.1 \) in Fig. 2.3. The only change observed is that the width of the peak and dip increases. For \( \chi = 0.5 \) and 1 the probabilities even cross each other near \( \omega = \epsilon_0 \). For \( \chi = 2 \) (long-dashed curves) and 3 (dot-dashed curves) we obtain the same kind of behavior as in Fig. 2.3 but here the difference between the peak of \( \langle P_2 \rangle \) and the dip of \( \langle P_1 \rangle \) decreases. Also the values of \( \omega \) where the peaks and dip are observed move closer to \( \omega = \epsilon_0 \). So, from these studies we see that even in the presence of nonlinearity we may obtain the resonance condition. Here also \( V \) plays an important role to bring the resonance in the system.

To obtain the resonance frequency (\( \omega_0 \)) at a nonzero value of \( \chi \) we study here the time evolution of the site-probabilities (\( |e_m(t)|^2 \)). Keeping \( V, \epsilon_0 \) and \( \chi \) fixed (the values can be obtained from Fig. 2.3) we change the frequency \( \omega \) around \( \omega = \epsilon_0 \) and find the value of \( \omega_0 \) where the the site-probabilities oscillate approximately between 0 and 1. In this way one can easily find out the resonance frequency.

The site-probabilities do not oscillate between 0 and 1 at any frequency other than \( \omega_0 \). For comparison we have plotted the site-probabilities as a function of time for three different values of \( \omega \) including \( \omega = \epsilon_0 \) in Fig. 2.5 where the solid curve is for \( \omega = 5.9 \),
the dotted curve is for \( \omega = 6 \) and the dashed curve is for \( \omega = 6.1 \). Here we have chosen \( V = 0.6, \epsilon_0 = 6 \) and \( \chi = 1 \). We notice that the curve for \( \omega = \epsilon_0 = 6 \), oscillates approximately between 0 and 1. So for this case the resonance frequency \( \omega_0 = \epsilon_0 = 6 \), which is same as in the case of \( \chi = 0 \) (Fig. 2.2 and Fig. 2.3). Therefore, the resonance frequency is independent of \( \chi \). After noting that the resonance frequency is at \( \epsilon_0 \) we now vary the value of \( V \) for a given \( \chi \) to obtain the critical value of \( V = V_c \) at which we obtain the perfect delocalization. The time period of the oscillation of the site-probabilities increases with decreasing the value of \( V \). Below \( V_c \) we obtain the amplitude-transition of the site-probabilities in a conventional sense. For fixed value of \( \chi \) we find that \( V_c \) has negligible dependence on \( \epsilon_0 \). We find that for perfect delocalization we must have \( V/\epsilon_0 << 1 \) and \( \chi/\epsilon_0 << 1 \). The value of \( V_c \) increases linearly as a function of \( \chi \) (with a slope equal to 0.4714).

Fig. 2.6 Plot of critical value of \( V \) where the delocalization starts in the DNTS system for different values of \( \chi \). In this case we have taken \( \omega = \epsilon_0 = 6 \).

This is shown in Fig. 2.6. Here we have taken \( \omega = \epsilon_0 = 6 \). Keeping \( \epsilon_0 \) fixed if we increase \( \chi \) as well as \( V \) the time evolution of the site-probabilities do not oscillate between 0 and 1. For further increase of \( \chi \) and \( V \) we obtain chaotic behavior (see for details ref. [15,97]) where the time averaged probability \( \langle P_m \rangle \) fluctuates rapidly as \( \chi \) and \( V \) changed. This can be understood from Fig. 2.7 where we have plotted the time averaged
probability as a function of $\chi$ for different values of $V$. In this case we have taken $\omega = \epsilon_0 = 1$ (resonance frequency).

Fig. 2.7 Plot of $\langle P_m \rangle$ as a function of $\chi$ for DNTS system. The lower curves are for $\langle P_1 \rangle$ and the upper curves are for $\langle P_2 \rangle$. Here $\epsilon_0 = \omega = 1$. The value of $V$ for solid, dotted and dashed curves are 0.1, 0.3 and 0.5 respectively.

Here the upper curves represent $\langle P_1 \rangle$ and the lower ones represent $\langle P_2 \rangle$ for different values of $V$. The solid curves are for $V = 0.1$, the dotted curves are for $V = 0.3$ and the dashed curves are for $V = 0.5$. We also note that as $V$ increases, the range of $\chi$ where the motion of the electron becomes chaotic increases. However, here we have not located the region in the parameter space where the chaotic behavior starts occurring. Another interesting feature in the system is the occurrence of sharp self-trapping transition [12] of the probability of the initial excitation site at $\chi_{cr}$. If we increase $V$ the value of $\chi_{cr}$ also increases but the self-trapping becomes weaker. The self-trapping property is responsible for the asymmetric behavior in Fig. 2.8 where we have plotted the time averaged site-probability (the solid curve is for site 1 and the dotted curve is for site 2) as a function of $\omega$ at $V_c$. Both the probabilities merge at $\omega = \epsilon_0 = 3$. At this frequency they both have equal value 0.5. The smooth decrease of $\langle P_2 \rangle$ and increase of $\langle P_1 \rangle$ in the region of $\omega > \epsilon_0$ is obtained as we move away from this frequency. But, in the left side of the peak or dip of the probabilities (i.e., $\omega < \epsilon_0$) we obtain a sharp jump.
It is also clear from Fig. 2.7 that at $\omega_0 = \epsilon_0$, for each value of $V$ there is only one value of $\chi = \chi_{cr}$ where the time averaged probability at both the sites touch each other with $\langle P_1 \rangle = \langle P_2 \rangle = 0.5$. We have already seen that at the self trapping transition point $\chi$ and $V$ are related linearly. So, in other words we can say that for each value of $\chi$ there is only one value of $V = V_c$ where perfect delocalization of the particle takes place. Therefore, the in presence of nonlinearity we get the exact resonance (delocalization) condition $\omega_0 = \epsilon_0$ along with the value of $V = V_c \sim 0.4714\chi$.

**Fig. 2.8** Plot of $\langle P_m \rangle$ as a function of $\omega_0$ in DNTS system. The solid curve is for $\langle P_1 \rangle$ and the dotted curve is for $\langle P_2 \rangle$. Here $V = V_c = 0.04714, \chi = 0.1$ and $\epsilon_0 = 3$.

This is also transparent from Fig. 2.8. So, we see that the resonance frequency remains same as in the absence of nonlinearity. This can be understood easily. By varying parameters when we obtain the situation of perfect delocalization, the effective energy difference $(\epsilon_0 + \chi_1 \langle P \rangle - \chi_2 \langle P_2 \rangle)$ between the two levels (energy difference between the two sites) oscillate about the value equal to $\epsilon_0$. Therefore, the particle on the average feels energy difference of $\epsilon_0$. Hence, the resonance frequency $(\omega_0)$ of the system becomes equal to $\epsilon_0$. We next study the localization-delocalization behavior of the exciton in the SNTS system.

**SNTS system:**
In SNTS system we assume that the site \( m = 1 \) has the nonlinearity strength \( \chi \) and the other site does not have any nonlinearity i.e. \( \chi_1 = \chi \) and \( \chi_2 = 0 \) in eq. (2.7).

Fig. 2.9 Plot of time averaged probability \( \langle P_m \rangle \) of SNTS system as a function of frequency \( \omega \) for \( V = 0.1 \) and different \( \chi \) values. The upper curves are for \( \langle P_1 \rangle \) and the lower curves are for \( \langle P_2 \rangle \). Solid, dotted, small-dashed, long-dashed and dot-dashed curved are for \( \chi = 0, 0.5, 1, 2 \) and 3 respectively.

Fig. 2.10 Plot of time averaged probability \( \langle P_m \rangle \) of SNTS system as a function frequency \( \omega \) for \( V = 0.6 \). The upper curves are for \( \langle P_1 \rangle \) and the lower curves are for \( \langle P_2 \rangle \). The \( \chi \) values for the curves from the right are 0, 0.5, 1, 2 and 3 respectively.
The initial excitation is applied at the nonlinear site \( i.e., |c_m(t = 0)|^2 = \delta_{m,1} \). To obtain the localization-delocalization transition we have studied the same quantities, \( i.e., \) time averaged site probabilities and the time evolution of the site probabilities as discussed in the previous section. We first study the time averaged site-probabilities as a function of frequency \( (\omega) \) of the field for different values of \( \chi \) and \( V \). This is shown in Fig. 2.9 where we have taken \( \epsilon_0 = 6 \) and \( V = 0.1 \). The upper curves are for \( m = 1 \) and the lower ones are for \( m = 2 \). In this case we find the same kind of behavior as for DNTS system ( see Fig. 2.2 ). But if we increase the amplitude of the field strength \( i.e., V \) we obtain results different (see Fig. 2.10) from DNTS system. For \( \chi = 0 \) ( left solid curves ) the system becomes two level linear problem. So, the resonance frequency should appear at \( \omega_0 = \epsilon_0 \). This is exactly obtained. But, if we increase the nonlinearity strength \( \chi \), \( \langle P_1 \rangle \) and \( \langle P_2 \rangle \) cross each other at the values of \( \omega \) other than \( \omega = \epsilon_0 \). This is shown for \( \chi = 0.5 \) ( left dotted curves ), 1 ( middle solid curves ) and 2 ( right dotted curves ) in Fig. 2.10. The values of peak of \( \langle P_2 \rangle \) and dip of \( \langle P_1 \rangle \) are \( \sim 0.5 \). So, we should expect that the resonance frequency should be observed around this region of \( \omega \). The frequency where the crossing of the probabilities observed increases with increasing the nonlinearity strength \( \chi \). However, for sufficiently large value of \( \chi \) ( shown by right solid curve for \( \chi = 3 \) ) we do not find the crossing in the time averaged probabilities. For further increase of \( \chi \) the difference between the peak and dip of the probabilities increases. The position of the peak and dip also moves towards \( \omega = \epsilon_0 \) for increasing of \( V \) ( compare Fig. 2.9 and Fig. 2.10 ). It should be noted that the crossing of the probabilities also occurs in DNTS system. Our next aim is to find out the resonance frequency \( (\omega_0) \) as well as \( V_c \) where the delocalization starts.

To obtain the resonance frequency \( \omega_0 \) and \( V_c \) we follow the same method as discussed in the previous section. Here we find the same kind of behavior as in DNTS system except \( \omega_0 \neq \epsilon_0 \) and \( V_c \) is different. For fixed value of \( \chi \) we find that \( (\omega_0 - \epsilon_0) \) and \( V_c \) approximately remain constant for arbitrary values of \( \epsilon_0 \) where perfect delocalization is obtained. If we increase the nonlinearity strength \( \chi \), \( (\omega_0 - \epsilon_0) \) and \( V_c \) increase linearly with slopes 0.5 ( dotted line ) and 0.2456 ( solid line ), respectively. This is shown in Fig. 2.11. From Fig. 2.11 we see that to get the resonance in the system for arbitrary values of \( \chi \), we have to satisfy the condition \( (\omega_0 - \epsilon_0) = 0.5 \chi \) and \( V = V_c = 0.2456 \chi \). So from these conditions
we find that to obtain resonance at $\chi = 0.5$, $V_c$ should be 0.1228 and the frequency of laser field should be $\omega = 6.25$.

Fig. 2.11 $(\omega_0 - \epsilon_0)$ and $V_c$ is plotted as a function of $\chi$ by dotted line and solid line respectively for SNTS system.

Fig. 2.12 Plot of $(P_m)$ as a function of $\chi$ for SNTS system. The solid curve is for $\langle P_1 \rangle$ and the dotted curve is for $\langle P_2 \rangle$. The values of $V, \omega$ and $\epsilon_0$ are taken such that resonance takes place. The values are taken as $V = 0.1228$, $\omega = 6.25$ and $\epsilon_0 = 6$.

We next study the behaviour of time averaged probabilities as a function of $\chi$. This is shown in Fig. 2.12. The solid curve represents $\langle P_1 \rangle$ and the dotted one represents
\( \langle P_2 \rangle \). Other parameter values are taken such that resonance occurs at \( \chi = 0.5 \) for \( \epsilon_0 = 6 \), i.e., \( \omega = 6.25 \) and \( V_c = 0.1228 \). Here we find that \( \langle P_1 \rangle \) initially decreases and \( \langle P_2 \rangle \) increases with increasing value of \( \chi \). Then they both meet at \( \chi = 0.5 \) with the value 0.5. This implies that at \( \chi = 0.5 \) both the site-probabilities oscillate between 0 and 1 with time \( t \). For further increase of \( \chi \) we obtain a sharp self-trapping transition. Then \( \langle P_1 \rangle \) increases and \( \langle P_2 \rangle \) decreases gradually with increasing \( \chi \). Thus we find the localization of the particle at the initial excitation site with maximum probability. As the resonance frequency is different for different values of \( \chi \) we obtain the localization behavior in the region of \( \chi < 0.5 \) for the above case. The site-probabilities oscillate between 0 and 1 at \( \chi = 0.5 \) and the system is said to be in resonance condition. So, we see that the resonance condition for this case is given by the resonance frequency \( \omega_0 = \epsilon_0 + 0.5\chi \) along with the cut-off value of \( V = V_c \sim 0.2456\chi \). The dependence of resonance frequency on \( \chi \) can be understood easily. Under the perfect delocalization condition, the average energy difference between the two sites (levels) become \( \epsilon_0 + \chi_1\langle P_1 \rangle - \chi_2\langle P_2 \rangle = \epsilon_0 + 0.5\chi \) (on time average). Therefore, the resonance frequency of the system becomes \( \omega_0 = \epsilon_0 + 0.5\chi \). A sharp jump at the right side of \( \chi = 0.5 \) arises due the self-trapping transition which is the general property of the discrete nonlinear Schrödinger equation [12,14,15]. The same kind of asymmetric behavior is also observed in the plot of \( \langle P_m \rangle \) as a function of frequency of the oscillating field around the resonance frequency.

In short, the perfect delocalization (resonance) condition for a nondegenerate and symmetric (as well as asymmetric) nonlinear dimer with oscillating hopping element between the two sites (\( \approx \) two level system coupled with oscillating electric field) is obtained. The condition for perfect delocalization of the exciton is \( \omega_0 = \epsilon_0, V = 0.7414\chi \) in the DNTS system and \( \omega_0 = \epsilon_0 + \chi/2, V = 0.2456\chi \) in the SNTS system.

### 2.2.4 Nonadiabatic nonlinear dimer

It is also interesting to note that there were attempts to study the exciton dynamics without the adiabatic approximation [74,95,96,98,106,110,112–115]. Assuming that the oscillators are purely harmonic and coupled with the exciton dynamics, the dynamics of the exciton in the nonadiabatic dimer leads to chaos for some initial condition and
some parameter regime [15,95,96]. Some other interesting features are revealed when the oscillators coupled with the exciton dynamics are assumed to be damped harmonic oscillators [112]. The interesting features includes two kinds of transitions, namely, static and dynamic transitions at large time and small time limits respectively in the large damping limit. At large time limit, the probability of the exciton at both the sites becomes stationary. As long as $\chi < 2V$, the probability of the exciton at both the sites are $\frac{1}{2}$ but if $\chi > 2V$, then the probabilities reduces to $\frac{1}{2}[1 \pm \left(1 - \left(\frac{2V}{\chi}\right)^2\right)^{1/2}]$. This is named as static transition. On the other hand, at small time limit, the probability amplitude takes the form of cn and dn Jacobian elliptic function for $\chi < 4V$ and $\chi > 4V$ respectively as happened in case of adiabatic nonlinear dimer [12]. This is known as dynamic transition. Furthermore, to see the effect of temperature on the time evolution of the exciton, the damped harmonic oscillators are assumed to be in contact with a heat bath [113]. The bath contributes noise (in this case it is Gaussian white noise) to the system. The effect of temperature ($T$) is very prominent. If $T > 0$, the exciton escapes to the other site from the initially populated site. But there is a critical value of $T$ say $T_c$ (depending on the value of nonlinear strength) such that if $T < T_c$, the exciton takes huge time to be escaped from the initially populated site. For $T > T_c$, the exciton escapes very shortly and the particle gets delocalized. Therefore for $T < T_c$ the localization is robust for practical purposes. A great deal of study has been made along this line for both finite and infinite systems in the presence of noise [104–106,113,116].

2.3 Finite and infinite size systems with adiabatic nonlinearities

After an intensive discussion on nonlinear dimer, interest naturally goes over to larger nonlinear systems. So, the question is what happens to a nonlinear trimer and larger finite as well as infinite nonlinear systems. They will be discussed here in some detail. A system of trimer with closed as well as open boundary conditions has been studied in detail by several authors [15,16,87,88,108,120,121]. In general this system is nonintergable. But due to some symmetry depending on the initial condition, the system can be effectively
reduced to a dimer and can be solved exactly. For the exact solution we refer [87,88]. Only the trimer with closed boundary condition and N-mers with both closed and open boundary conditions will be discussed in this section. The equation of motions for the exciton in the N-mer system with closed boundary condition can be given by

\[ \begin{align*}
\frac{dC_n}{dt} & = V(C_{n+1} + C_{n-1}) + \chi|C_n|^2C_n; \quad 1 < n < N \\
\frac{dC_N}{dt} & = V(C_1 + C_{N-1}) + \chi|C_N|^2C_N \\
\frac{dC_1}{dt} & = V(C_2 + C_N) + \chi|C_1|^2C_1
\end{align*} \]  

(2.9)

where $C_n$ and $\chi$ are previously defined. $V$ is the hopping matrix element between nearest neighbor sites. For $N=3$, the system is a trimer. If the initial condition is given as $C_1(0) = 1$, $C_2(0) = 0$ and $C_3(0) = 0$, the sites 2 and 3 behaves alike due to the symmetry in the system (trimer) and hence $C_2(t) = C_3(t)$. Analyzing the eq. (2.9) along with the symmetric initial condition, the critical value of the nonlinearity, $(\chi_{cr})$, for the self-trapping transition comes out to be $6V$. Therefore, for the trimer case the larger amount of nonlinearity is needed to achieve the self-trapping. It again depends on the relative sign of $\chi$ and $V$. But we restrict our discussions to the case where $V > 0$ and $\chi > 0$. Another way of looking at the transition is to see the variation of the time averaged probability of the particle at the initially populated site as a function of $\chi$. Thus, for the trimer under consideration, the time averaged probability of the particle at the initially populated site shows sharp jump at $\chi = 6V$ [15].

For $N > 3$ the system is genuinely nonintegrable and therefore the time averaged probability is seen as a function of $\chi$. It has been observed that for an open and small nonlinear chain, the $\chi_{cr}$ for self-trapping transition, is weakly dependent of the system size. But for a closed nonlinear chain, the critical value of $\chi$ for self trapping transition, depends strongly on the system size [15]. For both the cases a small window of $\chi$ exists just before the self trapping transition. In the small window of $\chi$, the exciton motion becomes chaotic [15]. This is because of the finite size effect of the nonlinear chain. As the chain size increases, the fluctuation reduces and for an infinite nonlinear chain, the fluctuation entirely disappears. The $\chi_{cr}$ for infinite nonlinear open chain is roughly $3.5V$. The effect of a cluster of nonlinear sites on the critical value of nonlinearity for self-trapping in one
dimensional chain has also been studied [79]. The self-trapping transition for an infinite linear chain with a single nonlinear site is also observed and found to be 3.22V [94,111]. The analytical support for this result is also presented in the ref. [111]. The dynamics of an exciton in the aperiodically ordered nonlinear lattices have also been studied [100–103]. The \( \chi_{cr} \) for two dimensional and three dimensional linear systems with a single impurity comes out to be 6.72V and 9.24V respectively [111]. But the two dimensional systems were not studied in detail. Two dimensional systems are however, more natural than one dimensional systems. We, therefore, study the self-trapping transition in two dimensional system due to the presence of one impurity more accurately and effect of more than one nonlinear impurities in the next section [122].

2.3.1 Two dimensional system with adiabatic nonlinearities

The dynamics of a quasiparticle such as electron or exciton in \( d \) dimensional solids influenced by lattice vibrations are described by (under adiabatic approximation)

\[
\frac{\text{d}C_n}{\text{d}t} = (\epsilon_n + \chi_n |C_n|^2)C_n + \sum_{\alpha} C_{n+1\alpha} \tag{2.10}
\]

where \( n=(n_1, n_2, n_3, \ldots, n_d)^T \) and \( 1_{\alpha} = (0_1, 0_2, 0_3, \ldots, \pm 1_{\alpha}, \ldots, 0_d) \). The summation over \( \alpha \) in eq. (2.10) considers only the nearest neighbors, although the hopping between any two sites can be included. All hopping matrix elements are taken to be same and the value has been set to unity without any loss of generality. \( C_n \) is the probability amplitude of the \( n \)th site at a time \( t \). \( \epsilon_n \) and \( \chi_n \) are respectively the site energy and the nonlinearity parameter associated with \( n \)th site. Our interest is to observe the dynamics of an exciton in two dimensional system. Therefore, in our case \( d = 2 \).

The dynamics is obtained by solving eq. (2.10). Since the eq. (2.10) is nonintegrable, Fourth order Runge–Kutta method is used to compute the probability amplitude. We use \( 10^4 \) time steps with a time interval 0.01. The conservation of the probability is checked at every step to ensure the accuracy of the result. To discern the self trapping transition we primarily examine the time average probability of the initially excited site as a function of \( \chi \). The time dependence of the probability of the initial site is considered in some cases. Furthermore, the dependence of the mean–square displacement(MSD) [117] of the
quasiparticle on $\chi$ and hence its velocity is studied. The MSD of a particle placed initially at a site $m$ in a $d$-dimensional Bravais lattice is

$$<|n - m|^2>(t) = \sum_n |n - m|^2 |C_n m(t)|^2$$

(2.11)

and in a perfect linear lattices this quantity grows as $t^2$ with a speed of $\sqrt{2d}$. In nonlinear lattices, the MSD grows ballistically but $<|n - m|^2>/t^2$ depends on the nonlinearity parameter [98]. Our results are presented below.

**Fig. 2.13** The plot of time averaged probability of the initially occupied site as a function of nonlinear parameter $\chi$. The lattice is a $7 \times 7$ square containing one nonlinear impurity in the middle and initial excitation has been put in the middle site of the lattice. The light solid curve corresponds to reflecting boundary condition ($\chi_{cr} \sim 6.82$), Dotted curve corresponds to semiperiodic boundary condition ($\chi_{cr} \sim 6.82$) and the heavy solid curve corresponds to the full periodic boundary condition ($\chi_{cr} \sim 6.87$).

**CASE I:** We consider a $7 \times 7$ square lattice with three types of boundary conditions, namely, (i) reflecting on both directions, (ii) semiperiodic (periodic in one of the directions) and (iii) fully periodic. A single nonlinear impurity is introduced in the middle of the lattice which is also the site for the initial excitation. For the reflecting and semiperiodic boundary conditions, we obtain the self trapping transition at $\chi_{cr} \sim 6.82$, where $\chi_{cr}$ denotes the critical value of $\chi$. In the other case $\chi_{cr} \sim 6.87$. The transition in this system is characterized by a lot of fluctuation in the time averaged probability of the initially occupied site followed by a steep rise to the asymptotic value (cf Fig. 2.13).
CASE II: When a finite size cluster (dimer and trimer) of nonlinear impurities is placed linearly in the middle of a 100 x 100 lattice and one of the end sites is initially occupied, we obtain $\chi_{cr} \sim 6.91$. In the one dimensional lattice with the same initial condition $\chi_{cr}$ is $\sim 4.2$. However, no cluster trapping transition [79] is observed in this case in sharp contrast to its behavior in the one dimensional lattice. On the other hand, for a perfectly nonlinear trimer (all three sites have same $\chi$) $\chi_{cr}$ rises to $\sim 6.98$, if the particle is placed initially at the middle of the trimer. No well defined self trapping transition is observed with this initial condition if the trimer is embedded in the one dimensional lattice.

![Fig. 2.14](image)

The plot of velocity of the particle as a function of $\chi$ in a self-expanding square lattice. The lattice contains nonlinearity($\chi$) at the middle and the initial excitation is applied there. At the critical value of nonlinearity parameter ($\chi \sim 6.82$) velocity jumps from a high value to a low value, there by indicating the transition.

However for a 100 x 100 square lattice we find a very sharp transition at $\chi_{cr} \sim 6.81$ due to a single nonlinear impurity at the middle site irrespective of the boundary conditions. A similar type of transition at $\chi_{cr} \sim 6.82$(cf. Fig. 2.14) is obtained from the self–expanding lattice while previously reported result for this case $\sim 6.72$ [111].

The reported value of $\chi_{cr}(3.22)$ for the one dimensional self-expanding lattice is also obtained by gradually reducing the hopping to zero in one of the directions. The self trapping transition is also obtained at the reported value from a finite square lattice(say,
100x100) using the same procedure. We further find that $\chi_{cr}(W) \simeq 3.22 + 3.6W$, and $0 \leq W \leq 1$ defines the ratio of the hopping integrals in two directions. Similarly, we get a straight line with different intercept and slope for the same lattice with same $\chi$ at all sites. However, the time averaged probability at the trap–site reaches slowly to the asymptotic value.

CASE III: If the middle site as well as its nearest neighbor sites are nonlinear with same value of $\chi$ in a 100 x 100 square lattice with the initial excitation at the middle site, we obtain $\chi_{cr} \sim 7.12$. By extending the similar type nonlinearity to its next nearest neighbors, we obtain $\chi_{cr} \sim 7.18$ for the same initial condition. For the fully nonlinear lattice with all sites having same $\chi$ we obtain $\chi_{cr} \sim 7.17$ for both the semiperiodic and fully periodic boundary condition. Again the excitation is placed at the middle site initially. The self–expanding lattice with the same initial condition yields $\chi_{cr} \sim 7.18$ (cf. Fig. 2.15). This shows that the motion of the quasiparticle in the neighborhood of the self trapping transition is mostly confined to the near neighbors of the initial site. We ascribe this to the restriction in our model that the quasiparticle can directly tunnel only to the nearest neighbors.

![Fig. 2.15](image)

Fig. 2.15 The time averaged probability of the initial site versus $\chi$ is shown for a 100 x 100 square lattice. Left most solid curve corresponds to the system with one nonlinear impurity at the middle site ($\chi_{cr} \sim 6.82$). Light dotted curve corresponds to the system with a nonlinear dimer placed in the lattice with one site of the dimer at the middle of the lattice ($\chi_{cr} \sim 6.91$). Middle solid curve corresponds to the system with a nonlinear trimer embedded in the lattice,
where the middle site of the trimer coincides with the middle of the lattice ($\chi_{cr} \sim 6.98$). Middle dotted curve refers to the system with same $\chi$ at the middle site as well as its nearest neighbor sites of the lattice ($\chi_{cr} \sim 7.12$). The solid curve in the extreme right corresponds to the system with same $\chi$ at the middle, nearest neighbors and next nearest neighbor sites of the lattice ($\chi_{cr} \sim 7.17$). The dotted curve in the extreme right corresponds to the system where all sites are nonlinear with same $\chi$ ($\chi_{cr} \sim 7.18$).

To explain our main results we first note that the tunneling between two sites, albeit decreases with the increase in the ratio of their site energy difference ($\Delta \epsilon$) to the hopping strength ($V$), goes truly to zero iff this ratio $|\frac{\Delta \epsilon}{V}|$ goes to infinity. Since, the coordination number ($Z$) of the Bravais lattice increases with its dimensionality, the escape probability of the quasiparticle from the initial site through the tunneling to the nearest neighbors increases. This reduces the on site probability, reducing in consequence the site-energy of the nonlinear impurity in our model. So, the effective $|\frac{\Delta \epsilon}{V}|$ reduces. On the other hand, $|\frac{\Delta \epsilon}{V}|$ must attain the same critical value for the self trapping transition to occur. Hence, the value of $\chi_{cr}$ increases with the increase in the dimensionality. We further note that the effective tunneling between two nonlinear sites is more than between a nonlinear site and a perfect site. So, the escape probability from the initial site will increase due to any increase in the nonlinear nearest neighbors. By the above argument we should then expect that the $\chi_{cr}$ will increase with the increase in the nonlinear nearest neighbors. For a linear cluster of nonlinear impurities with the initial excitation at the end site, the initial site has one nonlinear nearest neighbor. This increases to two and four respectively in a nonlinear trimer and in the square lattice with the nearest neighbor nonlinearity with the initial excitation at the middle site. So, the expected trend is observed.

The absence of a cluster–trapping transition in a finite size linear clusters of nonlinear impurities in a square lattice is also due to the enhancement of the escape probability. If we just keep the nearest neighbors and treat all the perfect sites as a single site, the effective hopping to this site increases by $\sqrt{(Z - 1)}$. This then implies that the escape probability through the perfect sites will increase at least by this factor. This will affect the site–energy difference. So, the $\chi_{cr}$ for this transition will shift towards the $\chi_{cr}$ for the self trapping transition.
Near the self trapping transition of the quasiparticle a few neighboring sites determine its dynamics. So, an accurate estimation of $X_{cr}$ can be obtained from relatively small samples. $X_{cr}$ is also strongly influenced by the probability of escape of the quasiparticle from the trap-site. A quantitative estimation of this aspect is, however, desirable. This work is in progress.

2.4 Summary

In summary, we have reviewed on the self trapping transition in nonlinear dimer (both degenerate and nondegenerate case), nonlinear trimer, finite nonlinear chain (with both closed and open boundary condition) and infinite nonlinear chain. Nonlinearity arises due to the interaction of the exciton (quasiparticle) with the lattice vibration. In most of cases adiabatic approximation is employed. In other wards, the motion of the lattice oscillators are assumed to be much faster with respect to the motion of the exciton. We have shown the full delocalization (resonance) condition [90] for the exciton in a adiabatic and nondegenerate nonlinear (singly as well as doubly nonlinear) dimer. Here the hopping element is assumed to be oscillatory with respect to time. The resonance condition may be useful in the process of energy transfer in biological systems. A brief discussion on the nonadiabatic nonlinear dimer has also been made. The effect of temperature [113] on the localization and delocalization of the exciton on nonadiabatic dimer is discussed. Studies made on the self trapping transition due to a single adiabatic nonlinear impurity in one, two and three dimensional systems are discussed. Finally, the effect of nonlinear neighbors on the self-trapping transition in two dimensional system is presented [122].