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# Non-linearity, dissipation and transport in a molecular trimer

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**Abstract.** This study investigates the effects of dissipation on the quasi-particle transport in a degenerate molecular trimer in which the time evolution is described by the discrete non-linear Schrödinger equation. The standard procedure of introducing dissipation as a phase-destroying stochastic parameter through the corresponding Liouville–von Neumann equation is employed. A closed second-order integrodifferential equation describing the time evolution of the site occupation probability difference is derived in the simultaneous presence of non-linearity and dissipation for trimers in compact geometry subjected to specific initial conditions. The Painlevé property of the evolution equation is examined and it is found that the system is not of p type.

A conflict arising from the two opposing views existing in the literature on the effects of dissipation on non-linear dynamics in a closely related system is focused on. Both the resolution of this conflict and a description of trimer dynamics are provided by elucidating the effects of the interplay between dissipation and non-linearity through numerical experiments.

## 1. Introduction

In the field of condensed matter, the non-linear Schrödinger equation is largely used to describe the transport characteristics of particles and quasi-particles which interact with the vibrations of the ‘solid’ strongly enough to induce dynamic disorder [1–3].

In this context†, it may be written as

$$i\dot{c}_m(t) = \sum_{n=1}^N V_{mn} c_n(t) + [E_m - \chi|c_m(t)|^2]c_m(t) \quad (1)$$

where  $\hbar = 1$  and  $c_m(t)$  is the amplitude that the particle is at the state  $|m\rangle$  (e.g. a localized Wannier state centred on site  $m$  at time  $t$ ).  $V_{mn}$  is the intersite matrix element which describes the transfer of the particle from state  $|m\rangle$  to state  $|n\rangle$ . The effect of strong coupling between the particle and the vibrations of the ‘solid’ is to lower the site energy  $E_m$  of the particle by an amount proportional to the product of  $\chi$  (non-linearity parameter) and the probability  $|c_m(t)|^2$  of finding the particle at site  $m$ .  $N$  is the total number of sites. Solutions to equation (1) are not known in general for discrete systems of an arbitrary number of sites [4]. The integrability properties of the dimer ( $N = 2$ ) and trimer ( $N = 3$ ) cases have been extensively investigated in the absence of dissipation [5–7]. The dimer case has been furthermore

† It should be recalled that equation (1) holds in the ‘adiabatic limit’ of infinitely fast vibrational relaxation.

elaborated upon to gain insight into the physics of transport phenomena in extended systems [8, 9].

In this limit, the formation of localized (self-trapped) states provided that the non-linearity is strong enough has been well established.

The dimer case has also been chosen to understand the dynamical behaviour of discrete non-linear systems in the non-zero dissipation limit [10, 11]. In these studies, dissipation is introduced into a corresponding Liouville–von Neumann equation as a stochastic parameter causing dephasing of the dimer state evolution in both the site [10] and the symmetry-adapted [11] representations. In [10], it was concluded that *irrespective of the nature of non-dissipative dynamics the net effect of dissipation is to force the system to have a completely delocalized probability distribution*. On the other hand, Banacký and Zajac [11] have reported that, depending on the interplay of the non-linearity, dissipation and transfer parameters, the system may or may not be driven to the completely delocalized probability distribution.

We note, however, that in both analyses the point of departure is the full stochastic Liouville–von Neumann equation. Therefore, both should make predictions which are *a fortiori* independent of representation. One may refer to the appropriate references [12, 13] for a detailed discussion of this point for the case of the linear stochastic Liouville equation.

Consequently, we think that it is worthwhile to address this conflict. We shall resolve the conflict in the context of dissipative non-linear dynamics of a trimer with specific initial conditions. One of the purposes of introducing this trimer, rather than repeating the dimer analyses, is to investigate the dynamics in a more extended system than a dimer. Secondly, it allows direct comparison of the studied dynamics with the dimer cases in conflict, since the specific initial conditions chosen restrict trajectories to those of a dimer [5–7].

## 2. Time evolution of the site occupation probability difference

Equation (1) and its complex conjugate can be written as a Liouville–von Neumann equation for the density matrix elements  $\rho_{mn}(t) = c_m(t)c_n(t)^*$  in the site representation

$$\dot{\rho}_{mn}(t) = -i \sum_{\beta} [V_{m\beta} \rho_{\beta n}(t) - \rho_{m\beta}(t) V_{\beta n}] + i\chi [\rho_{mm}(t) - \rho_{nn}(t)] \rho_{mn}(t) \quad (2)$$

where the site energies are assumed to be identical (degenerate).

The net effect of dissipation is to destroy the phase of the quasi-particles. The standard procedure for describing phase-destroying processes is to add terms to equation (2) which cause a decay in the off-diagonal elements of the density matrix [14]. The resulting non-linear adiabatic Liouville–von Neumann equation assumes the form

$$\begin{aligned} \dot{\rho}_{mn}(t) = & -i \sum_{\beta} [V_{m\beta} \rho_{\beta n}(t) - \rho_{m\beta}(t) V_{\beta n}] + i\chi [\rho_{mm}(t) - \rho_{nn}(t)] \rho_{mn}(t) \\ & - \alpha (1 - \delta_{mn}) \rho_{mn}(t) \end{aligned} \quad (3)$$

with  $\alpha$  being the rate of dephasing of the off-diagonal density matrix elements.

The system considered is a degenerate molecular trimer in compact geometry in which all sites are connected with equal intersite matrix elements. Using (3), it is straightforward to write the time evolution of the density matrix elements of a compact trimer explicitly by setting all the  $V$ 's equal.

Under a certain class of initial conditions, it is possible to convert the set of trimer equations obeying (3) into a closed second-order integrodifferential equation for the time evolution of the site occupation probability difference (SOPD).

This particular class of initial conditions is defined such that the SOPD between a pair of sites of the trimer is zero at all times and can be satisfied if any two of the sites are initially excited with equal probability. In the derivation below, it will be assumed that site 1 is excited with a certain probability  $\rho_{11}(0)$  and that the sites 2 and 3 share the remaining probability equally, i.e.  $\rho_{22}(0) = \rho_{33}(0)$ . It should be noted that two commonly employed experimental initial conditions, i.e. complete localization ( $\rho_{11}(0) = 1$ ) and complete delocalization ( $\rho_{ii}(0) = \frac{1}{3}$ ,  $i = 1, 2, 3$ ) follow as two special cases of the initial conditions defined above.

It then becomes possible to define the SOPD as  $p(t) = \rho_{11}(t) - \rho_{22}(t) = \rho_{11}(t) - \rho_{33}(t)$ , since  $\rho_{22}(t) - \rho_{33}(t)$  will always remain zero. In addition to  $p(t)$ , the real variables  $q(t)$ ,  $r(t)$  and  $s(t)$  can be defined in terms of the density matrix elements as

$$q(t) = i[\rho_{21}(t) - \rho_{12}(t)] = i[\rho_{31}(t) - \rho_{13}(t)]$$

$$r(t) = \rho_{21}(t) + \rho_{12}(t) = \rho_{31}(t) + \rho_{13}(t)$$

$$s(t) = \rho_{23}(t) + \rho_{32}(t).$$

The set of trimer equations obeying (3) can now be written in terms of these new variables as

$$\dot{p}(t) = -3Vq(t) \quad (4a)$$

$$\dot{q}(t) = 2Vp(t) + V[r(t) - s(t)] + \chi p(t)r(t) - \alpha q(t) \quad (4b)$$

$$\dot{r}(t) = -Vq(t) - \chi p(t)q(t) - \alpha r(t) \quad (4c)$$

$$\dot{s}(t) = 2Vq(t) - \alpha s(t). \quad (4d)$$

The solutions to (4c) and (4d) are

$$r(t) = r(0) \exp(-\alpha t) - VI_1 - \chi I_2 \quad (5a)$$

$$s(t) = s(0) \exp(-\alpha t) + 2VI_1 \quad (5b)$$

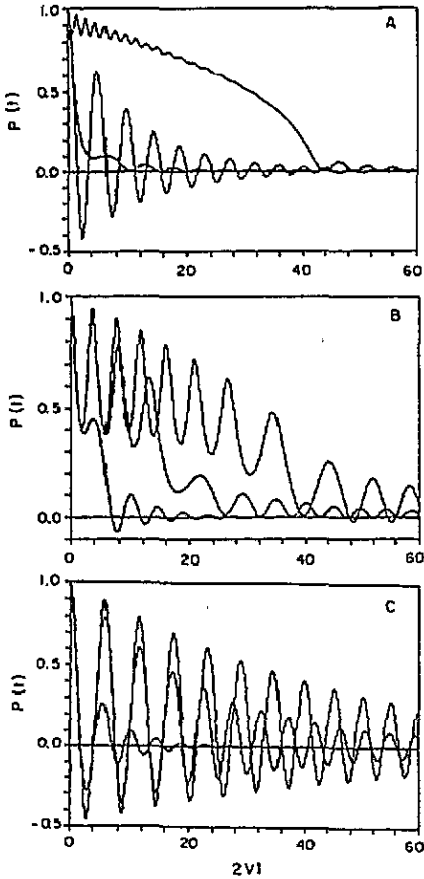
where

$$I_1 = -\frac{1}{3V} \int_0^t \dot{p}(t') \exp[-\alpha(t-t')] dt'$$

$$I_2 = -\frac{1}{3V} \int_0^t p(t') \dot{p}(t') \exp[-\alpha(t-t')] dt'$$

and  $r(0)$  and  $s(0)$  are the initial values of  $r(t)$  and  $s(t)$ . Insertion of  $r(t)$  and  $s(t)$  into (4b) and the subsequent substitution of the outcome into (4a) yield

$$\begin{aligned} \ddot{p}(t) + \alpha \dot{p}(t) = & -[6V^2 + 3\chi Vr(0) \exp(-\alpha t)]p(t) + [9V^3 + 3\chi V^2 p(t)]I_1 \\ & + [3V^2 \chi + 3\chi^2 V p(t)]I_2 + 3V^2 \exp(-\alpha t) [s(0) - r(0)]. \end{aligned} \quad (6)$$



**Figure 1.** Effects of the interplay of the dissipation with transport non-linearity. Predictions are based on the numerical solutions of the exact equation (equation (6)). (a) The rate of dissipation is kept fixed at  $\alpha/2V = 0.25$  and  $\chi/4V$  changes as  $-2.5$  (top),  $-1.51$  (middle) and  $-1.0$  (bottom). (b), (c) The effects of variation in the amount of dissipation ( $\alpha/2V = 0.05, 0.1$  and  $0.5$  from the top to the bottom) are shown (b) in the self-trapped ( $\chi/4V = -1.60$ ) and (c) in the free-particle ( $\chi/4V = -1.25$ ) dynamics regions.

Equation (6) is the closed integrodifferential equation which describes the dynamics of the excitations in our trimer in the simultaneous presence of non-linearity and dissipation.

### 3. Results and discussion

It has been repeatedly emphasized in the literature that there is an apparent connection between the integrability of ordinary non-linear differential equations and the Painlevé property [15, 16]. On the basis of the singular point analysis of Ablowitz, Ramani and Segur (ARS) [15], it has been concluded that equation (6), or equivalently equation (4), does not satisfy the necessary conditions to possess the Painlevé property (see appendix). Therefore, the behaviour predicted by (6) is analysed using the standard integration algorithms [17].

In all figures, the SOPD is drawn versus time in units of  $1/2V$ . The excitation is assumed to be initially localized ( $p(0) = 1$ ;  $r(0) = q(0) = s(0) = 0$ ) in one of the sites of the trimer which is chosen particularly to allow comparison with the dimer cases. The non-dissipative dynamics of our system have been described in several studies in the literature. Although it is possible to recover those results by letting  $\alpha = 0$ , we shall not repeat them but refer the reader to the appropriate articles

[5–7]. For the purposes of this study, it is sufficient to recall that one can distinguish between the two regimes of the parameter space:  $\chi/4V > 0$  and  $\chi/4V < 0$ . In both regimes, the formation of the self-trapped states is the rule provided that the non-linearity is strong enough.

The effects of the interplay of the dissipation with transport non-linearity predicted by (6) are shown in figure 1. First, the amount of dissipation is kept constant and the non-linearity parameter is changed (figure 1(a)). Then, the behaviour under different rates of dissipation for self-trapped and free-particle dynamics are displayed respectively, in figures 1(b) and 1(c). It is to be understood that the signature of the self-trapped states is the ‘incomplete’ oscillations on the positive side of the  $p(t)$  scale. In the absence of dissipation, transition from the free-particle to self-trapped dynamics takes place at  $\chi/4V = -1.5$  and  $0.5$  in the two regimes.

The persistence time of the self-trapped states becomes longer, the higher the non-linearity parameter and/or the lower the rate of dissipation. Nevertheless, irrespective of the character of the dynamics, the dissipation causes the trimer eventually to reach equilibrium. Although we do not provide the results of the numerical experiments for  $\chi/4V > 0$ , the rule is again the same: dissipation drives the system to the equilibrium state in which the probability distribution is completely delocalized.

Next, the behaviour of equation (6) in the limit  $\exp(-\alpha t) \simeq 1$  is examined in order to relate it to the results of Banacky and Zajac which conflict with both those of Tsironis *et al* and those presented above. In the limit  $\exp(-\alpha t) \simeq 1$ , the integrals  $I_1$  and  $I_2$  (see equation (5)) reduce to

$$I_1 = -(1/3V)[p(t) - p(0)] \quad I_2 = -(1/6V)[p(t)^2 - p(0)^2].$$

Consequently, the dynamics are characterized by an ordinary second-order inhomogeneous non-linear differential equation

$$\ddot{p}(t) + \alpha \dot{p}(t) = Ap(t)^3 + Bp(t)^2 + Cp(t) + D \quad (7)$$

where

$$A = -0.5\chi^2$$

$$B = -1.5\chi V$$

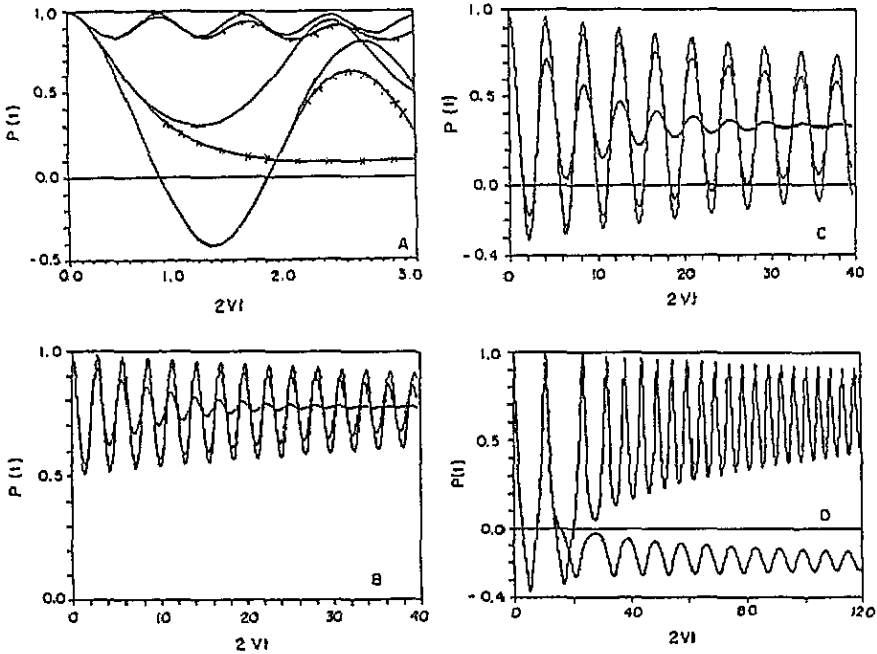
$$C = -9V^2 + 0.5\chi^2 p(0)^2 + \chi V[p(0) - 3r(0)]$$

$$D = 3V^2 p(0) + 0.5\chi V p(0)^2 + 3V^2[s(0) - r(0)].$$

The simulations of the non-linear dissipative dynamics resulting from equation (7) are shown in figure 2.

The message of figure 2 is that equation (7) is a good approximation for  $\exp(-\alpha t) \simeq 1$ , a condition which is obviously valid at times shorter than  $1/\alpha$ . However, the non-linear nature of the equation makes this validity very strict in the sense that, at times that do not satisfy  $\exp(-\alpha t) \simeq 1$ , not only is it a poor approximation but also it may completely fail to describe (even the qualitative features of) the dynamical behaviour inferred by the exact equation.

It is now possible to resolve the conflict by combining the results given in figure 2 with the following facts.



**Figure 2.** Simulations of the dissipative non-linear dynamics resulting from the 'approximate' equation (equation (7)). (a) A comparison between the numerical solutions of (7) (—) and of (6) (—x—) for several values of  $\chi/4V = -2.5$  (top),  $-1.51$  (middle) and  $-1.0$  (bottom) at  $\alpha/2V = 0.25$ . (b)–(d) Simulations for various values of the non-linearity parameter and for several values of the dissipation rate are displayed: (b)  $\chi/4V = 1.0$  and  $\alpha/2V$  changes as 0.05, 0.1 and 0.5; (c)  $\chi/4V = 0.0001$  and  $\alpha/2V$  changes as 0.05, 0.1 and 0.5; (d)  $\chi/4V = -1.48$  and  $\alpha/2V = 0.02$  (top) and  $\chi/4V = -1.48$  and  $\alpha/2V = 0.03$  (bottom).

(i) The conclusion of Banacky and Zajac [11] is based on the numerical simulations of the dimer counterpart of equation (7) which incidentally assumes the same form in both the site and the symmetry-adapted representations. In any case, any physical quantity, if calculated on the basis of the same transport tool, must assume values independent of the representation used [12, 13].

(ii) The initial conditions chosen restrict trajectories of the trimer to those of the dimer. Such trajectories are a set of zero measure in phase space of the trimer [5–7].

Consequently, in [11], saturation of  $p(t)$  to certain non-zero values at long times following the free and/or self-trapped oscillations are mistakenly interpreted as offering rich and very interesting possibilities for quasi-particle transport.

The apparent dissipation-assisted self-trapping transition (see especially figure 2(d)) which had been interpreted as the long-time settling of the system into the non-dissipative stationary states of the corresponding non-adiabatic dimer [18, 19] is simply an artefact that arises as a result of the inadequacy of (7) or its dimer counterpart in describing the dynamics for times longer than that required to satisfy  $\exp(-\alpha t) \simeq 1$ .

In concluding, we would like to point out that the tools developed here for understanding the dissipative non-linear dynamics in a trimer should be considered a step forward towards understanding more extended systems. The development has

been useful for the resolution of the conflict as to whether the net effect of dissipation is to destroy the self-trapped states if one waits for a sufficiently long time.

### Appendix. Painlevé analysis

The method of ARS [15] has been employed to examine the Painlevé property of equation (6) or its equivalent form (4).

An ordinary non-linear differential equation (ODE) is said to have the Painlevé property (or to be of  $p$  type) if none of its solutions, viewed as a function of a complex variable, has movable critical points. A critical point (a branch point or an essential singularity) is termed movable if its location in the complex plane depends on the initial conditions. It is known that, if an ODE is of  $p$  type, it can be reduced to a standard form that can be solved in terms of elementary functions, elliptic functions and Painlevé transcendents [16].

To simplify the notation, the variables of the system ( $n = 4$ ) of first-order ODEs (4) are renamed as  $w_1 = p$ ,  $w_2 = q$ ,  $w_3 = r$ ,  $w_4 = s$ , and  $z$  is chosen as the complex variable of the problem. The system (4) satisfies the basic assumption of ARS:  $w_i = F_i(z, w_1, \dots, w_4)$ ,  $i = 1, \dots, 4$ , where each  $F_i$  is analytic in  $z$  and rational (here algebraic) in  $w_i$ . Moreover the dominant behaviour of the solution in the sufficiently small neighbourhood of the (movable) singularity is algebraic. Because of this assumption, ARS do not identify essential singularities. Therefore it can only provide necessary conditions for an ODE to be of  $p$  type.

There are basically three steps to the Painlevé test.

(1) To find the dominant behaviour around some possible singularity  $z_0$ , one looks for a solution of the ODE in the form of

$$w_i \simeq \alpha_i (z - z_0)^{p_i} \quad i = 1, \dots, 4 \quad (\text{A1})$$

where  $\text{Re}(p_i) < 0$ . From the behaviour of the leading terms, the following  $(\alpha_i, p_i)$  pairs are obtained:

$$(\pm 2i/\chi, -1) \quad (\pm 2i/3V\chi, -2) \quad (-2/3V\chi, -2) \quad (\mp 4i/3\chi, -1). \quad (\text{A2})$$

Since each  $p_i$  is an integer, one can proceed to the algorithm.

(2) To find the resonances, for each  $(\alpha_i, p_i)$ , one constructs a simplified equation that retains only the leading terms of the original equation and substitutes

$$w_i = \alpha_i (z - z_0)^{p_i} + \beta_i (z - z_0)^{p_i+r} \quad i = 1, \dots, 4 \quad (\text{A3})$$

in the simplified equation. To leading order in  $\beta$ , one obtains

$$\mathbf{Q}(r)\beta = 0 \quad (\text{A4})$$

where  $\mathbf{Q}(r)$  is a  $4 \times 4$  matrix. The resonances are the non-negative roots of the indicial equation which is obtained by setting  $\det[\mathbf{Q}(r)] = 0$ . Consequently, the resonances are found as  $r = -1, 1, 2, 4$ . The resonance  $r = -1$  represents the arbitrariness of  $z_0$ . There is no zero root since none of the  $\alpha_i$  is arbitrary in the first step. All the resonances, other than  $r = -1$ , are positive real integers. Furthermore, all possible



$p_i$ -values are integers. Therefore, there are no algebraic branch points. The fact that all the resonances are distinct is necessary, but not sufficient, to state that there are no logarithmic branch points.

(3) If the system satisfies the conditions to be of p type, then one can in principle evaluate all the terms in the series

$$w_i = \alpha_i(z - z_0)^{p_i} + \sum_{j=1}^{r_s} a_{ij}(z - z_0)^{p_i+j} \quad (\text{A5})$$

where  $r_s$  is the largest resonance. The last step to conclude whether the system (4) passes the test is to substitute (A5) into the original equation and to check whether the recursion relations obtained from this substitution are consistent to yield  $n - 1$  (i.e. three) integration constants, and to determine all the coefficients. On the basis of the statement above, it is found that the sequential solutions of the recursion relations lead to inconsistency right at  $r = 1$ , which indicates the existence of movable logarithmic branch points.

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