A DISCRETE SELFTRAPPING EQUATION MODEL FOR SCHEIBE AGGREGATES

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Abstract. A discrete nonlinear model for the dynamics of Scheibe aggregates is proposed. The collapse of the collective excitations found by Möbius and Kuhn is described in the isotropic case as a shrinking ringwave which is eventually absorbed by an acceptor molecule.

1. Introduction

Recently, Huth et al. proposed a nonlinear continuum model for the energy transfer in Scheibe aggregates [1]. These are highly ordered molecular monolayers, which can be produced by Langmuir-Blodgett technique [2,3]. Oxycyanine dyes, e.g., are used as donor molecules and thiacyanine dyes as acceptor molecules. Even with a donor to acceptor ratio as low as 10^4, the aggregates exhibit highly efficient transfer of energy from impinging photons via excited host molecules to acceptor guests [4,5]. In Ref. [4] it is found that the coherent exciton picture provides an adequate description of the experimental results, which indicated a lifetime of the coherent exciton, t_{life}, before it is absorbed by an acceptor molecule, of about 10^{-10} s [5]. The exciton involves approximately 10^4 molecules. In Ref. [6] the isotropic continuum model proposed in [1] was used for a qualitative prediction of the lifetime. Here the dynamics of the ringwave solution to the cubic Schrödinger equation in two spatial dimensions [7] is essential.

In the present paper we introduce a discrete model of the Scheibe aggregate based on the discrete selftrapping equation (DST) [8]. The dynamics of the ringwave in this discrete case is investigated and results concerning absorption at the acceptor molecule are included in the isotropic case. Further ongoing work concerning the discrete model will be reported elsewhere [9,10].

2. Discretization of the continuum model

The continuum model proposed in [1] leads to the cubic Schrödinger equation for the wave function of the molecular excitation u(r,t)

$$iu_t + u_{rr} + r^{-1} u_r + 2|u|^2u = 0 \qquad (1)$$

in dimensionless variables [6] in the case of two spatial dimensions and circular symmetry. Here r is the radial coordinate and t is the time. The first conserved quantity becomes

$$I_1 = \int_0^\infty |u|^2 r dr = \alpha \ell / 2\pi \ , \tag{2}$$

where α is the anharmonicity parameter and ℓ is the molecular spacing in the Scheibe aggregate. For realistic values of the physical parameters $I_1 = 5.55$ [6]. Under certain conditions, an initial circular ringwave was found in [7] to shrink and collapse at the centre of the ring in a finite time, giving rise to blow-up of the excitation amplitude at the centre. With N_0 ($= 10^4$) molecules inside the ringwave the initial radius becomes $r_0 = 50.9$ [6] (yielding an initial amplitude of the ringwave $u_0 = I_1/2r_0 = 0.0545$). Furthermore, if the initial radial velocity $r_0' = 0$, the theory predicts a collapse time $t_{collapse} = 809$ [6]. In the following, we use the scaling invariance of Eq. (1) $t \to \beta t$, $r \to \beta^{1/2} r$, $u \to \beta^{-1/2} u$, $I_1 \to I_1$ with the constant $\beta = 1024$ yielding $r_0 = 1.59$, $u_0 = 1.74$, and $t_{collapse} = 0.790$.

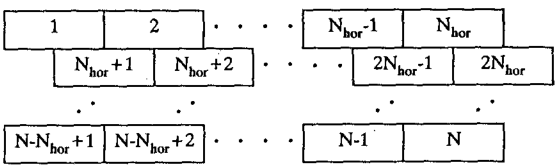

Figure 1. Position and numbering of the molecules in the brickstone work model of the Scheibe aggregate [5]. N is the total number of molecules and N_{hor} is the number of molecules in one horizontal row of the aggregate. Both N and N_{hor} are chosen to be odd.

Figure 1 shows Kuhn and Möbius' brickstone work model of the Scheibe aggregate [5]. Each donor and acceptor molecule is a dipole which is represented as a brickstone. Clearly, the molecular monolayer is anisotropic. However, assuming that the length is twice the width of each brickstone and taking only the dipole-dipole interactions between a molecule and its four nearest neighbours into account, the resulting model agrees with a direct discretization of Eq. (1). Thus replacing $u_{rr} + r^{-1}u_r = u_{xx} + u_{yy}$ by the central difference

$$\left(\sum_1^4 A_{\text{nearest neighbours}} - 4\,A\right) / \lambda^2$$

we get the discrete selftrapping equation (DST)

$$i\dot{\underline{A}} + i\,\mathrm{diag}(\underline{\alpha})\underline{A} + \gamma\,\mathrm{diag}(|\underline{A}|^2)\underline{A} + \epsilon \underline{\underline{M}}\underline{A} = 0 \ . \tag{3}$$

Here $u(n_x\lambda, n_y\lambda, t) \to A_n(t)$, A_n denoting the excitation of molecule number n, placed at $(x,y) = (n_x\lambda, n_y\lambda)$, n_x and n_y being integers and λ the distance between neighbouring molecules. $\underline{A}$ is the column vector $(A_1, A_2, \cdots, A_N)$, $N = N_{hor} \times (2N_{hor} - 1)$ being the total number of molecules and N_{hor} the number of molecules in each row in Fig.1.

In the DST-model each dipole molecule is described as a nonlinear oscillator, the nonlinearity entering into Eq. (3) via the diagonal $N \times N$ matrix (zero elements not shown)

$$\gamma \, \mathrm{diag}(|\underline{A}|^2) = \gamma \begin{bmatrix} |A_1|^2 & & & \\ & |A_2|^2 & & \\ & & \ddots & \\ & & & |A_N|^2 \end{bmatrix} \tag{3a}$$

γ being the nonlinearity parameter ($\gamma = 2$ when Eq. (3) is a discretization of Eq. (1)). The nonlinear oscillators are coupled via the symmetrical $N \times N$ matrix (zero elements not shown)

$$\varepsilon \underline{\underline{M}} = \varepsilon \left[\begin{array}{ccccccccccccccccccccc}
&&N_{hor}&&&&&N_{hor}&&&&&N_{hor}&&&&&&N_{hor}&& \\
&&&&&1 \\
&&&&&1&1 \\
&&&&&&\ddots&\ddots \\
&&&&&&&1&1 \\
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1&1&&&&&&&&&1&1 \\
&1&\ddots&&&&&&&&&1&1 \\
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&&&&&&&&&&&1&1 \\
&&&&&&&&&&&&1&\ddots \\
&&&&&&&&&&&&&\ddots&1 \\
&&&&&&&&&&&&&&1&1
\end{array} \right] , \tag{3b}$$

ε being the dispersion parameter ($\varepsilon = 1/\lambda^2$. Diagonal terms, -4, have been removed from Eq. (3b) by a gauge transformation). Losses, not included in Eq. (1), enter via the term $i \, \mathrm{diag}(\underline{\alpha})\underline{A}$, where

$$\mathrm{diag}(\underline{\alpha}) = \begin{bmatrix} \alpha_1 & & & \\ & \alpha_2 & & \\ & & \ddots & \\ & & & \alpha_N \end{bmatrix} . \tag{3c}$$

Here,

$$\alpha_i = \begin{cases} \alpha_{acc} & \text{for } i = (N+1)/2 \\ \alpha_{don} & \text{for } i \neq (N+1)/2 \quad , \end{cases} \tag{3d}$$

where α_{acc} is the loss coefficient for the oscillator placed at site $n = (N+1)/2$, modelling the absorption at the acceptor molecule (at the centre of the ringwave). Radiative losses, represented by damping at the donor molecules, are neglected ($\alpha_{don} = 0$).

Initial data for the numerical solution of the DST equation, presented in the following section, are obtained by sampling the initial ringwave with radius $r_0 = \lambda\sqrt{N_0/\pi}$.

3. Numerical results

Figure 2 shows the time evolution of the ring wave in the DST model without losses corresponding to the continuum model of the actual Scheibe

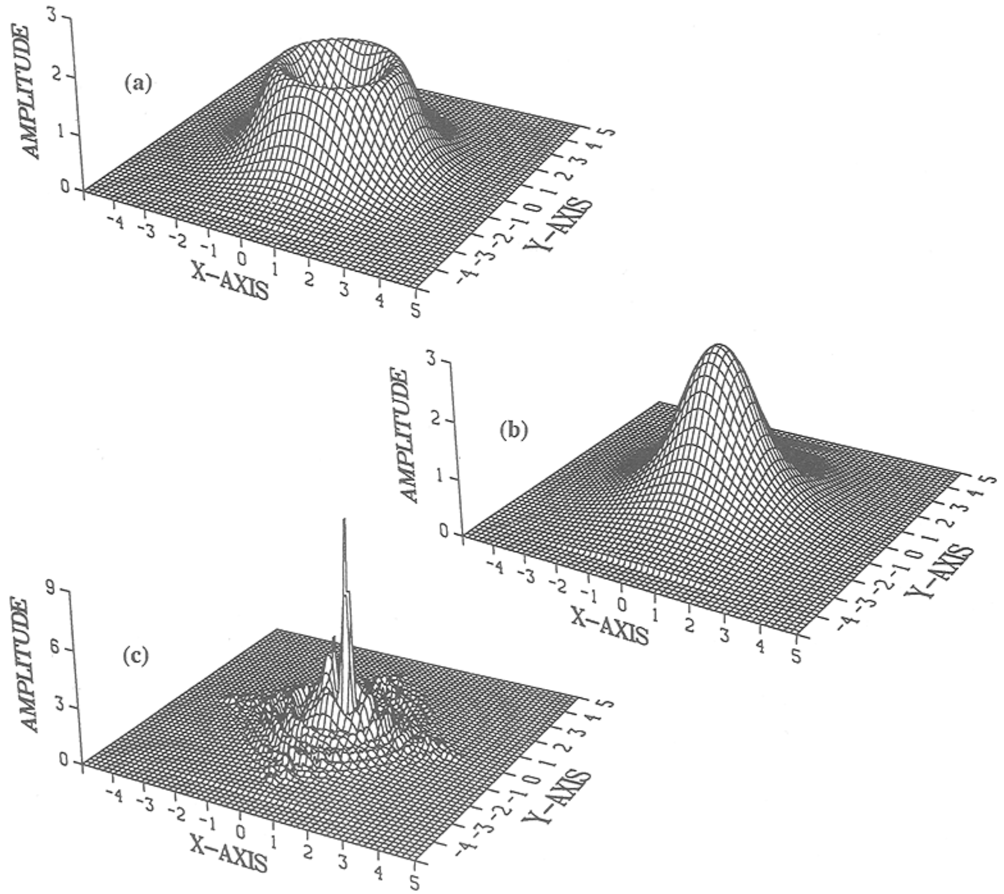

Figure 2. Evolution of ringwave in DST model. $\varepsilon = 314.4$, $\gamma = 2$, $r_0 = 1.59$, $I_1 = 5.55$, $N_0 = 10^4/4$, $\alpha_{acc} = 0$. t = (a) 0, (b) 0.6, (c) 0.75.

aggregate [6] with the particular scaling described in Section 2. For computational reasons, N_0 was reduced from 10^4 till $10^4/4$. It was checked that the time evolution does not depend critically on the choice of N_0. (Thus a further reduction of N_0 till $10^4/12$ did not produce any significant change in the computational results.)

Initially (Fig. 2a-b), the ringwave is seen to contract as predicted by the isotropic continuum model [7]. However, no matter how fine the grid may be, the amplitude of the shrinking ringwave in the centre area will eventually reach such a magnitude that the resolution of the grid becomes insufficient. As a consequence, the discrete model cannot reproduce the blow-up any further and dispersive radiation among the coupled oscillators results (Fig. 2c). In the scaled continuum model of the Scheibe aggregate the collapse time is 0.790 while the time needed for maximal excitation at the centre was found to be 0.59 in the corresponding DST-model. One reason for this difference is the fact that the requirement for the validity of the continuum perturbation theory [7], $I_1 >> 4$, is barely fulfilled ($I_1 = 5.55$). In Figure 3, we compare the radius of the

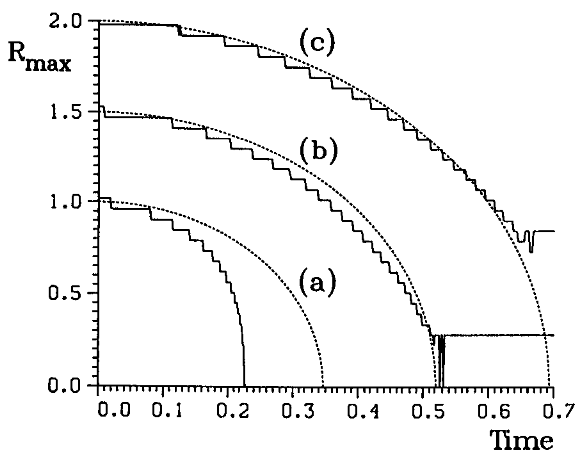

Figure 3. Ringwave radius, R_{max}, as a function of time. Dotted curves: continuum model. Full curves: DST model (ε = 312.5, γ = 2, u_0 = 2.5, α_{acc} = 0). (a) I_1 = 5.0, (b) I_1 = 7.5, (c) I_1 = 10.0.

ringwave, as a function of time, in the continuum model and the DST-model for different values of I_1. The larger I_1, the better agreement between the two models and the larger the radius at which the ringwave begins to disperse.

In the continuum model [6] the absorption by the acceptor molecule was neglected. In the present DST-model where the discreteness prevents completion of the collapse we now add loss at the acceptor site. Figure 4 shows the amplitude at this site as a function of time in the lossfree

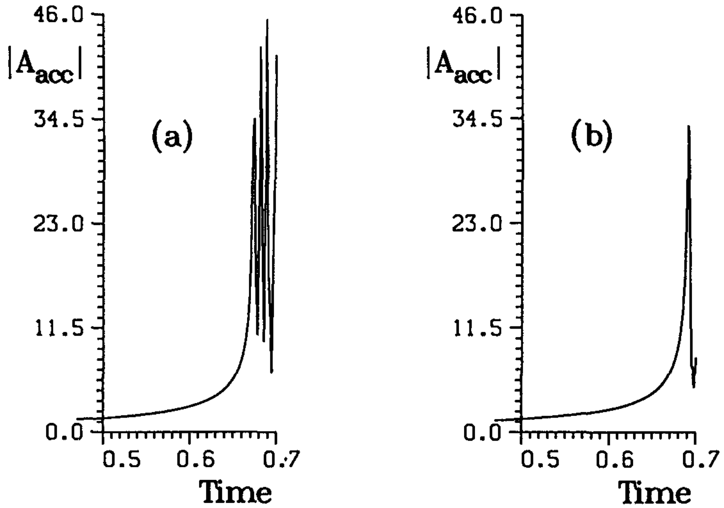

Figure 4. Centre amplitude, $|A_{acc}|$, as a function of time. DST-model (ε = 314.4, γ = 2, u_0 = 1.72, I_1 = 5.5). (a) α_{acc} = 0, (b) α_{acc} = 10^2.

case (a) and for (b) α_{acc} = 10^2. The introduction of attenuation is seen to compete with the dispersion due to the discreteness of the model, and wins the competition, eventually. In this manner, a substantial part of the ringwave excitation is transmitted to the acceptor molecule. A delay in the shrinking of the ringwave due to the acceptor loss is also observed.

Conclusion

In the continuum model of the Scheibe aggregate the coherent excitations collapse at the centre of the ringwave in finite time. The molecular structure of the aggregate leads to a discrete model in which the collapse cannot be completed because of dispersion. Addition of absorption at the acceptor molecule collects the excitation at this site. A detailed study of the competition between dispersion and dissipation will be presented elsewhere.

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References

[1] G.C. Huth, F. Gutmann, and G. Vitiello, Phys. Lett. A 140 (1989) 339.

[2] L.M. Blinov, Russ. Chem. 52 (1983) 173.

[3] M. Sugi, J. Mol. Electron. 1 (1985) 3.

[4] D. Möbius and H. Kuhn, Israel J. Chem. 18 (1979) 375.

[5] D. Möbius and H. Kuhn, J. Appl. Phys. 64 (1988) 5138.

[6] P.L. Christiansen, S. Pagano, and G. Vitiello, Phys. Lett. A 154 (1991) 381.

[7] P.S. Lomdahl, O.H. Olsen, and P.L. Christiansen, Phys. Lett. A 78 (1980) 125.

[8] J.C. Eilbeck, P.S. Lomdahl, and A.C. Scott, Physica 16 D (1985) 318.

[9] P.L. Christiansen, O. Bang, S. Pagano, and G. Vitiello, "The Lifetime of Coherent Excitations in Continuous and Discrete Models of Scheibe Aggregates", Nanobiology (to appear).

10] O. Bang and P.L. Christiansen, "A Discrete Non-Linear Model of Collective Excitations of Langmuir-Blodgett Scheibe Aggregates" (to appear).