

COUPLED WAVE-LIKE AND DIFFUSIVE MOTION OF EXCITONS*

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Using a new formalism for exciton transport, equations for the time evolution of the average of the square of the displacement of the exciton are presented and results obtained earlier by other authors are shown to emerge as particular cases of these equations.

The transfer of energy by means of the motion of excitons is of relevance in diverse fields of study as sensitized luminescence and photosynthesis. A unified description of the wave-like (coherent) and the diffusive (incoherent) nature of exciton transport presents an intriguing problem and several attempts have recently appeared in the literature. For instance, Haken and collaborators [1] have presented a formalism based on a stochastic treatment of the incoherent part of the Hamiltonian, Grover and Silbey [2] have published an approach proceeding from the microscopic equations through dynamics, and Kenkre and Knox [3] have developed a theory based on generalized master equations (GME). Some results concerning the "moments of the excitonic motion", based on the approach of ref. [1] have appeared [4] earlier in this journal. In this note results concerning this aspect of exciton transport, which are based on the theory of ref. [3], are presented and it is shown that they reduce to the expression of refs. [2, 4] in particular cases.

The theory of exciton transport developed in ref. [3] may be briefly stated as follows. From the basic Liouville equation for the density matrix the following equation is derived [5] for P_m the probability of occupation of the exciton state m :

$$\partial P_m(t)/\partial t = \int_0^t ds \sum_n \{W_{mn}(t-s)P_n(s) - W_{nm}(t-s)P_m(s)\} + J_m(t) \quad (1)$$

which differs from the ordinary Master equation (and therefore from the traditional theory of exciton transport) primarily through the non-Markofficity of the gain-loss terms, i.e. the existence of the memory in W_{mn} , and secondarily through the term J_m which arises out of the initial off-diagonal density-matrix. For comparison with the results of ref. [1, 2, 4] we now let m, n , etc., stand for the molecular sites in a simple model of a linear chain. It can be shown [3] that eq. (1) can then be written as

$$\partial P_m(t)/\partial t = \int_0^t ds \phi(t-s) \sum_n \{F_{mn}P_n(s) - F_{nm}P_m(s)\} + J_m(t) \quad (2)$$

where F_{mn} are the familiar transition rates appearing in the usual Master equation and where the memory ϕ can be easily obtained [3] from the optical spectra of the substance under study and is thus a given property of the system.

As in refs. [2, 4] we seek an equation describing the time evolution of the second moment of the motion i.e. of the average of the square of the displacement $\overline{m^2}(t) = \sum_m m^2 P_m(t)$. From eq. (2) one obtains

$$\frac{d\overline{m^2}(t)}{dt} = \phi * \sum_{m,n} F_{mn} (m^2 - n^2) P_n + J(t) \quad (3)$$

where an obvious notation has been used for the convolution and $J(t) = \sum_m m^2 J_m(t)$. There are several instances wherein the term $J(t)$ can be dropped for physical reasons and there are others when it can be incor-

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porated in the memory ϕ . In such cases eq. (3) takes the form

$$\frac{dm^2(t)}{dt} = \left(\frac{dm^2}{dt} \right)_{t=0} + \phi * \sum_n A_n P_n \quad (4)$$

where $A_n = \sum_m F_{mn}(m^2 - n^2)$ is a given property of the system. In many instances homogeneity applies i.e. $F_{mn} = F_{m-n} = F_l$. This represents the absence of preferred sites and implies

$$A_n = \sum_l F_l l^2 + 2n \sum_l F_l l \equiv \langle l^2 \rangle + 2n \langle l \rangle \quad (5)$$

the angular brackets denoting averages w.r.t. the rates F_l . Eq. (4) then yields

$$\frac{dm^2(t)}{dt} = \left(\frac{dm^2}{dt} \right)_{t=0} + \langle m^2 \rangle \int_0^t ds \phi(s) + 2 \langle m \rangle \int_0^t ds \phi(t-s) \bar{m}(s). \quad (6)$$

Most situations of physical interest possess no bias i.e. the "forward" rate F_m equals the "backward" rate F_m . The factor $\langle m \rangle$ and consequently the last term in eq. (6) then drop out completely, resulting in a simple proportionality between the time derivative of m^2 and the tegral of the memory ϕ . If the rates F_m are assumed to have a cut off for $m > k$ say, the proportionality constant $\langle m^2 \rangle$ has the expression

$$\langle m^2 \rangle = 2F_1 + 2 \cdot 4F_2 + \dots + 2 \cdot r^2 F_r + \dots + 2k^2 F_k. \quad (7)$$

In particular, for the nearest-neighbor approximation made in refs. [2, 4] eq. (6) reduces to

$$\frac{dm^2(t)}{dt} = C + 2F_1 \int_0^t ds \phi(s) \quad (8)$$

where C is the value of dm^2/dt at $t=0$.

We shall now show how the general result (8) can be made to yield the expressions (eq. (42) of ref. [2], and eqs. (10) and (9) respectively of refs. [4]) obtained earlier for $m^2(t)$. The curve for $\phi(t)$ is obtained from optical spectra and therefore, possesses structure appropriate to the system under study. However, if one approximates it by an exponential

$$\phi(t) = \alpha \exp(-\alpha t) \quad (9)$$

one obtains (with $m^2(0) = 0$)

$$\bar{m}^2(t) = (C + 2F_1)t + \frac{2F_1}{\alpha} [\exp(-\alpha t) - 1] \quad (10)$$

which contains the results obtained in refs. [2, 4] as particular cases. With the correspondence $\alpha \rightarrow 2(\Gamma + \gamma_1)$, $F_1 \rightarrow H_1^2/(\Gamma + \gamma_1)$, eq. (10) is seen to be identical to eqs. (10) and (9) of the refs. [4] when C , the initial value of dm^2/dt is taken to be $4\gamma_1$. This initial value is also assumed by Reineker and by Schwarzer and Haken in the ref. [4] and it is of interest to remark that the condition $\rho_{nn'}(t=0) = \delta_{n0}\delta_{n'0}$ assumed by them to obtain their respective eqs. (10) and (9) imply the "initial random phase" condition which in turn makes the dropping of $J_m(t)$ in eq. (3) above an *exact* operation. By making the same approximation (9) above for ϕ and choosing a different value for C the results of ref. [2] can be recovered. In view of the fact that the actual form of the memory ϕ , available from optical spectra, depends upon the particular system and is only *approximated* by an exponential, and that the value of dm^2/dt at $t=0$ depends in general upon the process of absorption, the results obtained earlier concerning $m^2(t)$ are seen to be particular cases of the formalism in ref. [3].

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- [5] The derivation is based on projection techniques and such an equation was first obtained by R.W. Zwanzig, for instance in *Lect. in Theor. Phys.* (Interscience, Boulder 1961) Vol. III. Also a non-Markoffian equation (without the term $\mathcal{D}_m(t)$) appears to have been written down for the first time in the context of exciton motion by G. Paillotin in *J. Th. Biol.* **36** (1972) 223.