

Hermann Haken; G. Strobl

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Exact treatment of coherent and incoherent triplet exciton migration

H. HAKEN AND G. STROBL

Institut für theoretische und angewandte Physik der Technischen Hochschule, Stuttgart

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We set up an exactly solvable model by assuming that the excitation energy of an localized exciton at a lattice site as well as the transition matrix elements are random functions of the time (due to lattice vibrations). For the explicit example for triplet exciton motion in a linear chain we show that there is an abrupt change from coherent to incoherent motion depending on the fluctuating energies.

If the corresponding conditions is fulfilled after a sufficiently high time the motion becomes a diffusion process.

In the literature both coherent and incoherent migration of excitons has been treated theoretically. In our analysis we want to shed light on the question which parameters determine whether coherent and incoherent exciton migration takes place and if there is a continuous or discontinuous transition from one kind of migration to the other one. For this end we choose a model which allows for an exact solution and which contains the relevant parameters. In this paper we present the mathematical skeleton and refer the reader for the detailed discussion of the implications and particularly for connection with previous theoretical and experimental work on this subject to the detailed paper of the authors.

We assume that both the energy of an exciton at the lattice site n as well as its transition matrix element from a lattice site n to m is a random function of a time caused by lattice vibrations. We assume that one may neglect the reaction of the exciton on the lattice vibrations site so that the lattice acts as a thermal reservoir in the thermodynamic sense. This is a reasonable assumption for not too low temperatures. We assume that the single fluctuations of the transition matrix elements and of the excitation energy of the atoms at the lattice sites are due to many independent lattice modes with a broad spectrum. (Mathematically spoken: the fluctuating coefficients are supposed to be Gaussian and Markoffian). By means of this Hamiltonian we find equations for the averaged density matrix which can be solved by the method of Green's function exactly. We use second quantization denoting the electronic ground state by Φ_0 . The generation respectively

annihilation of exciton n is described by the operators b_n^+ resp. b_n . The Hamiltonian then reads

$$H = \hbar \left\{ \sum_n \bar{h}_{nn}(t) b_n^+ b_n + \sum_{n \neq n'} (H_{n-n'} + h_{nn'}(t)) b_n^+ b_{n'} \right\} \quad (1)$$

where the first sum describes the energy of an exciton at lattice sites n whereas the second term describes the transition of the exciton from lattice site n' to n . $H_{n-n'}$ is the time averaged part and $h_{nn'}$ describes the residual fluctuations. The Markoffian property is represented by

$$\langle h_{nn'}(t) h_{n''n'''}(t) \rangle = [\delta_{nn'} \delta_{n''n'''} + \delta_{nn''} \delta_{n'n'''} (1 - \delta_{nn'})] \cdot \gamma_{n'n} \cdot 2 \delta(t) \quad (2)$$

We may further assume

$$\langle h_{nn'}(t) \rangle = 0 \quad (3)$$

and

$$\gamma_m = \gamma_{-m} \quad (4)$$

The density matrix is determined by

$$\dot{\rho} = -\frac{i}{\hbar} [H, \rho] = -\frac{i}{\hbar} [\bar{H}, \rho] - [h(t), \rho] \quad (5)$$

In the following we are interested in the density matrix averaged over the fluctuations.

A detailed analysis shows that the averaged density matrix obeys the equation.

$$\begin{aligned} \langle \dot{\rho} \rangle_{nn'} = & -i [\bar{H}, \langle \rho \rangle]_{nn'} - 2 \Gamma \langle \rho \rangle_{nn'} + 2 \delta_{nn'} \sum_{\nu} \gamma_{n-\nu} \langle \rho \rangle_{\nu\nu} + \\ & + 2(1 - \delta_{nn'}) \gamma_{n-n'} \langle \rho \rangle_{n'n} \end{aligned} \quad (6)$$

where Γ is given by $\sum_m \gamma_m$.

The first term on the right hand side of equation (6) describes the completely coherent motion. The solution of this equation would be the usual Frenkel exciton. The remaining part alone would represent a master equation describing a random walk problem. The crux of the problem therefore consists to determine the interplay between these two parts and to decide which one is dominant. An obvious way to treat such a problem would be to start of the assumption that one part is dominant over the other so that the equation is first solved for this part alone and then the other part is taken into account as a perturbation. We have done this but we do not represent the results here because they don't give an answer about the transition region. We rather want to solve eq. (6) exactly. For this end we first eliminate the time dependence by $\rho_{nn'}(t) = \rho_{nn'} \exp(Rt)$ and use the internal translational symmetry of the averaged equation (6) by the ansatz

$$\rho_{nn'} = \exp(i K n) \cdot N^{-1/2} \cdot \rho_{n-n'}^K \quad (7)$$

With $n-n' = m$ we find for the new variables $\rho_{n-n'}$ the following set of equations

$$\begin{aligned} R^{(K)} \rho_m^K = & -i \sum_{m'} H_{m-m'} [\exp(-i K (m - m')) - 1] \rho_m^K - 2 \Gamma \rho_m^K + \\ & + 2(1 - \delta_{m0}) \gamma_m \exp(-i K m) \rho_{-m}^K + 2 \delta_{m0} \gamma_K \rho_0^K \end{aligned} \quad (8)$$

where

$$\gamma_K = \sum_{\lambda} \gamma_{\lambda} \exp(i K \lambda) \quad (9)$$

In the following we drop the index K where it is not necessary and write

$$(\varrho_m^K) = \varrho$$

Equation (8) takes the form of a matrix equation:

$$r\varrho = D_1\varrho + D_2\varrho \quad (10)$$

where

$$r = R + 2I; D_{1; m, m'} = -i H_{m-m'} [\exp(iK(m-m')) - 1]$$

and

$$D_{2(m, m')} = \delta_{mm'} 2\delta_{m0}\gamma_K + \delta_{m, -m'} 2(1 - \delta_{m0})\gamma_m \exp(-iK m)$$

Equation (10) is solved by the Green's function method where the Green's function is defined by

$$G_r = (D_1 - r)^{-1} \quad (11)$$

Thus (10) is reduced to a new eigenvalue problem

$$\varrho = -G_r D_2 \varrho \quad (12)$$

As is known from the problem of determining wave function of impurities in solids the Green's function formulation as expressed by (12) has the advantage that due to the shortrange character of D_2 equation (12) is of very low rank. We have solved equation (12) explicitly for triplet excitons in a linear chain assuming

$$\begin{aligned} H_m &= H_1 (\delta_{m,1} + \delta_{m,-1}) \\ \gamma_m &= \gamma_1 (\delta_{m,1} + \delta_{m,-1}) + \gamma_0 \delta_{m0}; \gamma_0 \gg \gamma_1 \end{aligned}$$

where δ is the usual Kronecker symbol. If we assume

$$\gamma_1 \ll \gamma_0 \ll \gamma_K \quad (13)$$

it turns out that D_2 contains only one matrix element so that the secular equation reduces to

$$1 + 2\gamma_K G_{00,r} = 0 \quad (14)$$

The Green's function for the problem (11) is given by

$$G_{00} = - \frac{\cot \frac{N}{2} Z}{i c \cos \left(Z + K \frac{a}{2} \right)} \quad (15)$$

where

$$i c \sin \left(Z + K \frac{a}{2} \right) = r; \quad \text{Im } Z \geq 0$$

has to hold.

Equation (14) is thus an equation for c and therefore an equation for the decay constant r . A detailed discussion of the equation (14) yields the following result: If the fluctuation constant γ_0 for the excitonic excitation energy is bigger than two times the transition matrix element h_1 (that is

$$\gamma_K \approx \gamma_0 > 2 H_1), \quad (16)$$

holds. Then after a sufficiently long time the excitonic motion is described by a diffusion process. If (16) does not hold the diffusion character does not show up. The characteristic time after which the exciton motion becomes a diffusion process is given by

$$t \gg \{(2\gamma_0)^2 - (4H_1)^2\}^{-1/2} \quad (17)$$

If (16) and (17) hold the mean square deviation of the exciton obeys the equation

$$\langle n^2(+) \rangle \equiv \sum n^2 \rho_{nn}(t) \equiv 2tD + \langle n^2(o) \rangle \quad (18)$$

As a second example we have treated energy transfer within a two atomic molecule assuming both a fluctuating energy for the transition as well as for the excitation energy which represents an extension of Sewell's calculations [1].

References

- [1] G. SEWELL, Phys. Rev. 129, 597 (1963).