MODEL CALCULATIONS IN THE THEORY OF EXCITATION TRANSFER ☆

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Received 16 October 1974

Memory functions appearing in the generalized-master-equation theory of excitation transfer are calculated in the context of the standard model of linearly interacting excitons and phonons, and their relation to other memory functions, calculated by Grover and Silbey, is established. The calculations confirm the prescription given by Kenkre and Knox for obtaining the memory functions from optical spectra.

In spite of several recent attempts [1–3] at the description of the coupled coherent (wave-like) and incoherent (diffusive) motion of excitons in molecular aggregates, a unified picture has not yet emerged. In this letter we apply the formalism of generalized master equations (GME) developed in some of these papers [3] to a specific model used in some others [2], and obtain the explicit form of the GME memory function.

The model is described [2] by the Hamiltonian

$$H = H_{\rm ex} + H_{\rm ph} + H_{\rm int}, \qquad H_{\rm ex} = \epsilon \sum_m a_m^\dagger a_m + \sum_{m \neq n} J_{mn} a_m^\dagger a_n,$$
$$H_{\rm ph} = \sum_q \omega_q b_q^\dagger b_q, \qquad H_{\rm int} = \sum_{m,q} \omega_q X_q^m (b_q + b_{-q}^\dagger) a_m^\dagger a_m, \tag{1}$$

which, in terms of transformed operators, may be rewritten [2] as

$$H = \tilde{H}_{\rm ex} + H_{\rm ph}, \qquad \tilde{H}_{\rm ex} = \sum_m \tilde{\epsilon}_m A_m^\dagger A_m + \sum_{m \neq n} J_{mn} \exp(\alpha_m^\dagger) \exp(\alpha_n) A_m^\dagger A_n,$$
$$\tilde{\epsilon}_m = \epsilon - \sum_q |X_q^m|^2 \omega_q, \qquad A_m = a_m \exp(\alpha_m^\dagger), \qquad \alpha_m = \sum_q X_q^m (b_q - b_q^\dagger). \tag{2}$$

In eqs. (1) and (2) $b_q^\dagger$, $a_m^\dagger$ and $A_m^\dagger$ create respectively a phonon of wavevector q, a "bare" exciton at site m, and a "clothed" exciton at site m. The theory developed in ref. [3] describes the evolution of $P_m(t)$, the probability of occupation of site m by an exciton, through the GME

$$\frac{\partial P_m(t)}{\partial t} = \int_0^t {\rm d}s \sum_m [\mathcal{W}_{mn}(t-s) P_n(s) - \mathcal{W}_{nm}(t-s) P_m(s)] \tag{3}$$

where the expression for $\mathcal{W}_{mn}(t)$ contains suitably defined projection operators. The earlier calculations [3] of $\mathcal{W}_{mn}(t)$ constituted an extension of the Förster theory [4] and led to an expression for $\mathcal{W}_{mn}(t)$ in terms of optical spectra. The projection operator defined earlier thus contained an explicit summation over both variables as well as over phonon states. However, to facilitate comparison with refs. [1, 2], we shall redefine the projection operator ‡ in a manner compatible with those treatments. The operator now diagonalizes (as before) in the repre-

☆ Work partially supported by the National Science Foundation under grant no. DID71-04010-A02.

‡ This definition of the projection operator has also been given recently [5] in the different contexts of polaron motion where memory expressions, agreeing with ours, have been obtained. However, the questions asked in ref. [5] and the conclusions drawn are quite different from ours.

sentation of the eigenstates of $(\Sigma_m \tilde{\epsilon}_m A_m^\dagger A_m + H_{ph})$ and performs a weighted sum (with thermalization factors) over the phonon states. This leads to

$$\mathcal{W}_{mn}(t) = \mathrm{Re}\,\{(\mathrm{Tr}\exp(-\beta H_{ph}))^{-1}\mathrm{Tr}\,(\exp(-\beta H_{ph})\exp(itH_{ph})V_{mn}\exp(-itH_{ph})V_{nm})\}$$
$$\equiv \mathrm{Re}\,\langle V_{mn}(t)V_{nm}\rangle \tag{4}$$

where Tr denotes a trace over the phonons, $\beta = 1/kT$, and $V_{mn} = J_{mn}\exp(\alpha_m^\dagger)\exp(\alpha_n)$. For simplicity of notation we shall restrict our analysis to a two-molecule system, although the extension to a larger system is quite trivial. Then m,n take values 1 and 2, and we shall write $J_{12} = J_{21} = J$. Invoking the identity $\exp(itH)\exp(O) \times \exp(-itH) = \exp(\exp(itH)O\exp(-itH))$ and exploiting the fact that H_{ph} contains only harmonic terms, we have

$$\langle V_{12}(t)V_{21}\rangle = J^2\langle\exp(-\alpha_1(t))\exp(\alpha_2(t))\exp(-\alpha_2)\exp(\alpha_1)\rangle \equiv J^2\exp(-h(t)+h(0)) \tag{5a}$$

$$h(t) = \langle\alpha_1(t)\alpha_1\rangle + \langle\alpha_2(t)\alpha_2\rangle - \langle\alpha_1(t)\alpha_2\rangle - \langle\alpha_2(t)\alpha_1\rangle. \tag{5b}$$

A straightforward calculation then yields an expression for the memory in (3):

$$\mathcal{W}_{12}(t) = J^2\exp\left[-\sum_q(|X_q^1|^2 + |X_q^2|^2 - X_q^1X_q^2 - X_q^2X_q^1)\{\coth(\beta\omega_q/2) - (2N_q\cos\omega_q t + \exp(-i\omega_q t))\}\right] \tag{6a}$$

$$N_q = (\exp(\beta\omega_q) - 1)^{-1}. \tag{6b}$$

One can establish [6] the connection of this expression to the well-known optical-spectrum calculations of Lax [7] when the Förster assumption [4] of the absence of correlations between phonons on different molecules (leading, eq. (5b) above, to $\langle\alpha_1(t)\alpha_2\rangle = \langle\alpha_2(t)\alpha_1\rangle = 0$) is made. This confirms the prescription given by Kenkre and Knox [3] for calculating the memory function from optical spectra.

Grover and Silbey [2] have separated V_{mn} into $\langle V_{mn}\rangle$ and $(V_{mn} - \langle V_{mn}\rangle)$ and a memory function pertinent to the latter appears in their analysis. The correlation function corresponding to this "fluctuating" interaction is

$$\eta_{mn}(t) = \langle V_{mn}(t)V_{nm}\rangle - \langle V_{mn}\rangle\langle V_{nm}\rangle \tag{7}$$

which equals, from eq. (6) above,

$$\eta_{mn}(t) = \tilde{J}^2\left[\exp\left\{\sum_q(|X_q^1|^2 + |X_q^2|^2 - X_q^1X_{-q}^2 - X_q^2X_{-q}^1)(2N_q\cos\omega_q t + \exp(-i\omega_q t))\right\} - 1\right] \tag{8a}$$

$$\tilde{J}^2 = J^2\exp\left[-\sum_q(|X_q^1|^2 + |X_q^2|^2 - X_q^1X_q^2 - X_q^2X_q^1)\coth(\beta\omega_q/2)\right]. \tag{8b}$$

This is indeed identical to $\tilde{J}^2\{g_{mnnm}(t) - 1\}$ of Grover and Silbey [2].

The most important aspect of the memory $\mathcal{W}_{mn}(t)$ above is the absence of a decay to zero. It begins at J^2 which represents initial coherent transfer with interaction J and, when irreversibility assumptions are made leading to line broadening (allowing the replacement of sums by integrals), eventually decays to $\tilde{J}^2$ which represents final *coherent* transfer with interaction $\tilde{J}$. With a non-zero $\tilde{J}$, approach to equilibrium and eventual incoherent transfer are thus impossible in this model unless further irreversibility assumptions are made. Only these can lead to a decay of the constant $\tilde{J}^2$ component. Through the connection mentioned earlier, the above statements concerning exciton transport can be shown to correspond to definite characteristics of the optical spectra. Clarifications concerning the nature of excitation transfer in general and the relations among the various theories [1–3] in particular are possible [6] on the basis of the above calculation.

The authors acknowledge helpful conversations with Professor R.S. Knox.

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