ON EXCITATION TRANSFER AND RELAXATION MODELS IN LOW-TEMPERATURE SYSTEMS*

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Starting from Redfield's reduced density formalism, we derive the coupled relaxation equations and expressions for the rate constants applicable to excited dimer systems. In a comparative discussion the limitations are shown of relaxation models derived previously.

1. Introduction

In recent years the phenomenon of excitation transfer between molecules in condensed phases has been subject to numerous experimental and theoretical investigations. Among these, the study of excited molecular dimers embedded in a host crystal has been of considerable utility [1]. Theoretical models developed for such systems usually treat the crystal modes as a heat bath coupled to the dimer. In particular, theories which have assumed that the coupling between the electronic states and the bath degrees of freedom can be described in terms of (gaussian) random variables have been extensively used and greatly influential [2]. In the present note, we suggest limits of validity to such theories operative in particular at low temperatures.

The hamiltonian of these models is given by

$$\mathcal{H} = \mathcal{H}_{el} + \mathcal{H}_{B} + \delta \mathcal{H}_{s}$$

$$\mathcal{H}_{el} = \epsilon_1 |1\rangle\langle 1| + \epsilon_2 |2\rangle\langle 2| + J\{|1\rangle\langle 2| + |2\rangle\langle 1|\}, \quad \delta \mathcal{H} = \delta \epsilon_1 |1\rangle\langle 1| + \delta \epsilon_2 |2\rangle\langle 2| + \delta J\{|1\rangle\langle 2| + |2\rangle\langle 1|\}, \quad (1)$$

where \mathcal{H}_B is the hamiltonian of the bath, $\delta \mathcal{H}$ is the interaction energy operator between bath and electronic degrees of freedom, ϵ_i is the stationary energy of site state $|i\rangle$ and J is the stationary transfer matrix element. In contrast to ϵ_i and J, the interaction terms are variables in the bath coordinates, which will remain unspecified. With no loss of generality we can take the average of the interaction terms (over the bath density matrix) to be zero.

In the absence of interactions ($\delta \mathcal{H} = 0$), the electronic hamiltonian has eigenvalues and eigenstates given by:

$$E_{\pm} = \frac{1}{2} (\epsilon_1 + \epsilon_2) \pm [(\epsilon_2 - \epsilon_1)^2 / 4 + J^2]^{1/2}, \qquad (2)$$

$$|+\rangle = \cos(\theta/2)|1\rangle + \sin(\theta/2)|2\rangle, \quad |-\rangle = -\sin(\theta/2)|1\rangle + \cos(\theta/2)|2\rangle, \quad \tan \theta = -2J/(\epsilon_2 - \epsilon_1), \quad \epsilon_2 > \epsilon_1.$$
 (3)

In the limit $\epsilon_2 = \epsilon_1$, the eigenstates are the symmetric and antisymmetric combinations of the site states while for $|\epsilon_2 - \epsilon_1| \ge |J|$, the eigenstates are almost pure site states. In general, however, the eigenstates are as given in eqs. (3).

In the presence of interactions, $\delta \mathcal{H}$, the dimer subsystem is subject to relaxation mechanisms. The case in which the interactions are electron—phonon in origin has been discussed by Soules and Duke [3], Rackovsky and

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Silbey [4], and Abram and Silbey [5]. The case in which these interactions have been treated as classical random functions was treated by Sewell [6], Haken and Strobl [2,7], and by Reineker et al. [8].

The basic approximations and results of these treatments will be discussed below (sections 3 and 4), in comparison with our present findings (section 2), which are based upon the quantum mechanical version of Redfield's reduced density formalism [9].

2. Derivation of the coupled relaxation equations

The total density matrix, $\rho(t)$, of the system obeys the Liouville equation of motion

$$i\hbar\dot{\rho}(t) = [\mathcal{H}, \rho(t)] . \tag{4}$$

The dynamics of the dimer subsystem can be described by the equation of motion of the reduced density matrix $\sigma(t) = \text{Tr}_{\text{B}}\rho(t)$, where Tr_{B} denotes the trace over the bath degrees of freedom. There are a number of methods to derive this equation, and we will not repeat them here, but merely give the final result [9]. To second order in $\delta \mathcal{H}$, the equation for the matrix elements of $\sigma(t)$ (in the so-called dimer representation which diagonalizes \mathcal{H}_{el}) is

$$\dot{\sigma}_{NM}(t) = -i\omega_{NM}\sigma_{NM}(t) - \sum_{QP} R_{NMPQ}\sigma_{PQ}(t), \qquad (5)$$

where

$$R_{NMPQ} = -\int_{0}^{\infty} d\tau \bigg[\langle \delta \mathcal{H}_{QM} \delta \mathcal{H}_{NP}(\tau) \rangle \exp(-i\omega_{QM}\tau) + \langle \delta \mathcal{H}_{QM}(\tau) \delta \mathcal{H}_{NP} \rangle \exp(-i\omega_{NP}\tau) \\ - \delta_{QM} \sum_{S} \langle \delta \mathcal{H}_{NS}(\tau) \delta \mathcal{H}_{SP} \rangle \exp(-i\omega_{SP}\tau) - \delta_{PN} \sum_{S} \langle \delta \mathcal{H}_{QS} \delta \mathcal{H}_{SM}(\tau) \rangle \exp(-i\omega_{QS}\tau) \bigg].$$
(6)

Here, $\omega_{NM} = (E_N - E_M)/\hbar$, $\delta \mathcal{H}_{RS}$ is the matrix element of $\delta \mathcal{H}$ in the eigenstates of \mathcal{H}_{el} , and the brackets represent the average over the density matrix of the bath.

In deriving this equation we have assumed that the initial density matrix was factorized $\rho(0) = \rho_B \sigma(0)$ and that the bath modes equilibrate fast in comparison with the dimer modes (negligible memory effects). The relaxation matrix elements are in general complex, the imaginary part representing (dispersive) frequency shifts of the electronic states due to the interaction with the bath, and the real part representing relaxation constants. We will neglect the frequency shift in what follows, and, in addition, we will assume that the bath density matrix is given by that for the canonical ensemble. The validity of all these approximations will be discussed in a forthcoming article.

By neglecting the frequency shift, we may now write the integral in eq. (6) as 1/2 the integral from $-\infty$ to $+\infty$. Then by using the detailed balance relation, eq. (13) below, we have in the $|\pm\rangle$ representation

$$R = \begin{pmatrix} ++ & -- & +- & -+ \\ A\Gamma & -\Gamma & \psi(0) & \psi(0) \\ -A\Gamma & \Gamma & -\psi(0) & -\psi(0) \\ +- & A\psi(\omega_{-+}) & -\psi(\omega_{-+}) & \Gamma_{PD} + (1+A)\Gamma/2 \\ -+ & A\psi(\omega_{-+}) & -\psi(\omega_{-+}) & -(1+A)\Gamma/2 & \Gamma_{PD} + (1+A)\Gamma/2 \\ \end{pmatrix},$$
(7)

where

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$$\Gamma = \frac{1}{\hbar^2} \int_{-\infty}^{\infty} d\tau \, e^{i\omega_{-+}\tau} \langle \delta \mathcal{H}_{-+}(\tau) \delta \mathcal{H}_{+-} \rangle , \qquad (8)$$

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$$\Gamma_{\rm PD} = \frac{1}{2\hbar^2} \int_{-\infty}^{\infty} d\tau \langle [\delta \mathcal{H}_{--}(\tau) - \delta \mathcal{H}_{++}(\tau)] (\delta \mathcal{H}_{--} - \delta \mathcal{H}_{++}) \rangle, \qquad (9)$$

$$\psi(\omega) = \frac{1}{2\hbar^2} \int_{-\infty}^{\infty} d\tau \, e^{i\omega\tau} \langle \delta \mathcal{H}_{-+}(\tau) (\delta \mathcal{H}_{--} - \delta \mathcal{H}_{++}) \rangle, \qquad (10)$$

$$A = A(T) = \exp(-\hbar\omega_{-+}/k_{\rm B}T).$$
⁽¹¹⁾

In deriving eq. (7) we have assumed $\delta \mathcal{H}_{+-}$ to be hermitean for convenience.

The pure dephasing rate, Γ_{PD} , which describes spectral diffusion, and the population relaxation rate, Γ , represent autocorrelations (at specific frequencies) of the coupling energy fluctuations; Γ_{PD} is given in terms of the static transition frequency fluctuations, and Γ in terms of the state-to-state scattering fluctuations as mismatch frequency ω_{-+} , the stationary transition frequency, ψ represents cross correlation terms.

The relaxation constants satisfy detailed balance relations [note the Arrhenius factor A(T), eq. (11)] according to

$$2\gamma_{ab}(-\omega) = \int_{-\infty}^{\infty} d\tau \, e^{i\omega\tau} \langle a^+ b(\tau) \rangle = \exp(-\hbar\omega/k_{\rm B}T) \int_{-\infty}^{\infty} d\tau \, e^{i\omega\tau} \langle b(\tau)a^+ \rangle \,. \tag{12}$$

We mention that the secular matrix associated with the differential equation (5) is singular of rank 3. This corresponds to the fact that the sum of the population variables, $\sigma_{++} + \sigma_{--}$, is a conserved quantity in the present model. The set of four equations breaks eventually into two sets of two; one set of (linearity dependent) population variables, σ_{++} and σ_{--} , and one for the transition (or polarization) variables σ_{+-} and σ_{-+} . Such an approximate decoupling may occur for different reasons: (i) The presence of the frequencies $\pm \omega_{-+}$ in the secular matrix associated with (5) can be already sufficient that the modes do not couple strongly (i.e. $|\omega_{-+}| \ge \Gamma$, Γ_{PD}). (ii) At high temperatures we expect the spectral densities $g(\omega_{-+})$ and g(0) do not differ very much as long as $|\omega_{-+}|$ is small compared to the Debye frequency. Now, if $\Gamma_{PD} \ge \Gamma$ (or vice versa) then $|\psi(0)\psi(\omega_{-+})| \ll (\Gamma^2 + \Gamma_{PD}^2)$ and consequently the coupling between the two sets is small. (ii) At low temperature $k_{\rm B}T \ll \hbar \omega_{-+}$, we expect that the spectral densities available for *quasi-elastic* processes becomes very small (i.e. $\psi(0)$, $\Gamma_{PD} \rightarrow 0$ as $T \rightarrow 0$) so that eventually $\Gamma^2 \ge |\psi(0)\psi(\omega_{-+})|$ and Γ_{PD}^2 ; hence, the sets are decoupled once more. In general, however, no statement can be made about the decoupling of population and relaxation variables unless microscopic arguments are taken into account.

3. The Haken-Strobl model

In the Haken–Strobl (HS) model the correlations between site fluctuations are approximated as

$$\langle \delta \epsilon_i(t) \delta \epsilon_j(0) \rangle = \langle \delta \epsilon_i(0) \delta \epsilon_j(t) \rangle = 2\gamma_0 \delta_{ij} \delta(t), \quad \langle \delta \epsilon_i(t) \delta J(0) \rangle = \langle \delta J(0) \delta \epsilon_i(t) \rangle = 0,$$

$$\langle \delta J(t) \delta J(0) \rangle = \langle \delta J(0) \delta J(t) \rangle = 2\gamma_1 \delta(t)$$
(13)

and it is assumed that the fluctuations are gaussian. This corresponds to a classical stochastic description in which the cross correlations between the fluctuations in site energies ($\delta \epsilon_1$, and $\delta \epsilon_2$) and between site energies and transfer matrix elements are neglected. These assumptions are sensible at high temperature, for well separated molecules, when the thermal fluctuations at different sites in the crystal may be quite independent of one another. However, for neighboring molecules this approach will be inadequate, especially for low temperatures.

If we use the HS assumptions in the definition of R, we find the following relaxation parameters (where the tilde refers to the HS model).

$$\widetilde{\Gamma} = s^2 \gamma_0 + 2c^2 \gamma_1, \quad \widetilde{\Gamma}_{\text{PD}} = 2c^2 \gamma_0 + 4s^2 \gamma_1, \quad \widetilde{\psi}(\omega_{-+}) = \psi'(0) = sc(\gamma_0 - 2\gamma_1),$$

$$\widetilde{A} = 1 \text{ (i.e. } |\hbar\omega_{-+}| \leqslant k_B T), \quad s = \sin \theta, \quad c = \cos \theta.$$
(14)

In the limit $\epsilon_1 = \epsilon_2$, $\theta = \pi/2$ and so $\tilde{\Gamma} = \gamma_0$, $\tilde{\Gamma}_{PD} = 4\gamma_1$ and $\tilde{\psi} = 0$. In the opposite case, when $|\epsilon_1 - \epsilon_2| \ge |J|$, $\theta \approx 0$ one obtains $\tilde{\Gamma} = 2\gamma_1$, $\tilde{\Gamma}_{PD} = 2\gamma_0$ and again $\tilde{\psi} = 0$. This shows how the fluctuations in site space change their meaning as $|(\epsilon_1 - \epsilon_2)|/J|$ goes from 0 to ∞ .

In order to compare the HS relaxation parameters, eqs. (14), with those obtained from the Redfield equations, we give the more general relations between Γ , Γ_{PD} and ψ , eqs. (8)–(10), and the fluctuations in site representation.

$$\Gamma_{\rm PD} = c^2 \gamma_{\epsilon\epsilon}(\omega=0) - 2sc[\gamma_{\epsilon J}(\omega=0) + \gamma_{J\epsilon}(\omega=0)] + 4s^2 \gamma_{JJ}(\omega=0), \qquad (15a)$$

$$\Gamma = \frac{1}{2} s^2 \gamma_{ee}(\omega_{-+}) + sc \left[\gamma_{eJ}(\omega_{-+}) + \gamma_{Je}(\omega_{-+})\right] + 2c^2 \gamma_{JJ}(\omega_{-+}), \qquad (15b)$$

$$\psi(\omega) = \frac{1}{2} sc \gamma_{ee}(\omega) - s^2 \gamma_{e,I}(\omega) + c^2 \gamma_{Je}(\omega) - 2sc \gamma_{J,I}(\omega), \qquad (15c)$$

$$A = \exp(-\hbar\omega_{-+}/k_{\rm B}T) \tag{15d}$$

and the correlation functions $\gamma(\omega)$ are given by the Fourier transform of

$$\gamma_{ee}(t) = \frac{1}{2} \langle [\delta \epsilon_2(t) - \delta \epsilon_1(t)] [\delta \epsilon_2(0) - \delta \epsilon_1(0)] \rangle, \quad \gamma_{eJ}(t) = \frac{1}{2} \langle [\delta \epsilon_2(t) - \delta \epsilon_1(t)] \delta J(0) \rangle,$$

$$\gamma_{Je}(t) = \frac{1}{2} \langle \delta J(t) [\delta \epsilon_2(t) - \delta \epsilon_1(t)] \rangle, \quad \gamma_{JJ}(t) = \frac{1}{2} \langle \delta J(t) \delta J(0) \rangle.$$
(16)

Note that $\gamma_{ee}(\omega) \rightarrow 2\gamma_0$, $\gamma_{JJ} \rightarrow \gamma_1$ and $\gamma_{eJ} = \gamma_{Je} = 0$ if the HS assumptions are applied.

4. Discussion

Haken and Strobl developed their original model for the high-temperature regime, where most of the underlying approximations are valid. Much of the subsequent experimental work, however, has been done in the lowtemperature regime where the HS model does not apply. Its limits of validity will be substantiated in the following discussion by comparing the results given here with those of the HS model.

First, the assumptions of eqs. (13) lead to a failure of the detailed balance relations, (12). The assumption of white spectra for the correlations can only be used if $|\hbar\omega_{-+}| \ll k_B T$ [upon the assumption that the frequency dependence of the correlations $\gamma(\omega)$ is much weaker than those of the reduced density matrix $\sigma(\omega)$]. For naph-thalene dimers of neighboring molecules at 1.4-2.8 K, $\omega_{-+} \approx 1-2 \text{ cm}^{-1}$, so that the HS model will be inapplicable at these temperatures. This has been pointed out before: the equilibrium solutions of eq. (5) with the HS assumptions lead to equal populations in the $|+\rangle$ and $|-\rangle$ states contrary to the expectations of Boltzmann statistics [1,10]. Correspondingly, the thermal activation of the $|+\rangle \rightarrow |-\rangle$ population relaxation, which is governed by the Arrhenius factor A(T), eq. (11), is lost in the HS model.

Secondly, at low temperatures for *neighboring* molecules, the energies $\delta \epsilon_1$ and $\delta \epsilon_2$, and also the transfer matrix element δJ , should experience fluctuations due to the same phonons and vibrational modes, and there is no a priori reason, therefore, to neglect the cross correlations between these fluctuations. Comparison of eqs. (14) and (15) shows that the HS model will assign an inappropriate combination of site fluctuations to the relaxation parameters Γ , $\Gamma_{\rm PD}$, $\psi(\omega_{-+})$ and $\psi(\omega = 0)$ if cross correlations are significant. This is in particular true if the site energy fluctuations $\delta \epsilon_2 - \delta \epsilon_1$ show destructive interference.

Thirdly, the HS model does not take into account the fact that the relaxation terms can depend sensitively on the frequencies, which occur in the Kubo integrals, e.g. (8)–(10). For example Γ_{PD} results from quasi-elastic processes ($\omega = 0$), while Γ originates with inelastic transitions ($\omega = \omega_{-+}$). We expect, at low temperatures, that the spectral density at ω_{-+} is much larger than it is at $\omega = 0$, so that Γ_{PD} becomes eventually negligible as $T \to 0$.

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This is in agreement with model calculations for homogeneous relaxation processes [11], and also indicated by experimental observations on naphthalene dimers: although the transition frequencies ω_{-+} for pairs of *translationally* equivalent and inequivalent molecules differ only by a factor ≈ 1.5 , the ratio between the population relaxation rates from these two systems is of the order 100 [12]. A particular sensitive point in relation to this is that $\psi(0)$ and $\psi(\omega)$ may be very different at low temperatures, a fact not discerned in the HS model.

In order to examine these results in some more detail, let us first look at the general case where $\tan \theta$ is of order unity. In this case, the HS model will ascribe certain temperature dependences to γ_0 and γ_1 which will imply the *T* behavior of Γ and Γ_{PD} . According to our last argument, the temperature dependence of Γ and Γ_{PD} should be very different in the low- and intermediate-temperature regime, and even if detailed balance would be fixed up in an ad hoc manner, this will result in misinterpretations of the temperature dependence of the HS parameters γ_0 and γ_1 . In addition, for $\gamma_0 - 2\gamma_1$ comparable to or greater than ω_{-+} , the HS model would predict a dynamic coupling of population and transition variables (for e.g. $\tan \theta \approx 1$) even at low temperatures when we do not expect it, since $\psi(0) \to 0$ as $T \to 0$.

We now consider the case $\theta = 0$, which corresponds to $J/(\epsilon_1 - \epsilon_2) \approx 0$. This occurs either for very small J (well separated molecules) or for very different molecules ($|\epsilon_1 - \epsilon_2|$ large). From (15) we have $\Gamma \propto \gamma_{JJ}(\omega_{-+})$, $\Gamma_{PD} \propto \gamma_{ee}(\omega = 0)$ and $\psi(\omega)$ is insignificant as long as $|\omega_{-+}| \ge |\psi(\omega_{-+})|$. Hence, the HS model can be applied in this case, provided that detailed balance is fixed up and that γ_1, γ_0 are interpreted as $\gamma_{JJ}(\omega_{-+}), \gamma_{ee}(\omega = 0)$.

The case $\theta = \pi/2$ is of particular interest because it corresponds to equivalent molecules: most experiments have been done on dimers consisting of neighboring molecules, and if this case in which the HS model has been applied most. Eqs. (14) and (15) show that $\Gamma_{PD} = 4\gamma_{IJ}(\omega=0) \rightarrow \gamma_1$, $\Gamma = \frac{1}{2}\gamma_{ee}(\omega) \rightarrow \gamma_0$ and $\psi(\omega) = -\gamma_{Je}$, $\tilde{\psi}(\omega) = 0$ as $\theta = \pi/2$; that is the HS model is only applicable as long as $|\hbar\omega_{-+1}| \ll k_BT$, and $\psi(\omega_{-+})$, $\psi(0)$ are negligible for any one of the reasons discussed in section 2. For temperatures comparable to or smaller than $\hbar\omega_{-+}$ detailed balance has to be taken into account; as to the interpretation of the parameters γ_0 and γ_1 one should be aware of the fact that γ_{ee} includes cross correlations between δe_2 and δe_1 and that $\gamma_{IJ}(\omega = 0)$ will be subject to a comparatively strong temperature dependence arising from the variation in the spectral *density* at zero frequency.

Finally, we would like to give a brief comment on Reineker's treatment of the EPR spectra in (naphthalene) dimers as presented in ref. [8]. The model developed there is essentially based on the HS model: the spin relaxation is described in terms only of the two very same orbital fluctuation parameters, γ_1 and γ_0 , which affect the spin modes via spin—orbit coupling. Thus the model by Reineker is subject to the same criticism as the HS model itself. Among our objections it is in particular the argument about the mismatch-frequency dependence of the different relaxation parameters, which applies here. This is so, because there are six rather than two states in the dimer triplet system, and the order of magnitudes between orbital- and EPR-transition frequencies differ by one order of magnitude, typically. We doubt therefore that all the relaxation rates between these levels can be described in terms of just two independent parameters, as T becomes comparable to ω_{-4}/k_B . This will be discussed in more detail in a forthcoming article [13] (there we will include hyperfine interactions which dominate the EPR dephasing of naphthalene dimers at least in the liquid helium temperature regime) [14].

To conclude, the Haken-Strobl model has its limitations of applicability, despite of its utility and attractive conceptual simplicity. In particular, at low temperatures one must take care in its use for dimer systems.

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