Quenching of excitations in an impure molecular crystal

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Abstract. The rate of quenching of excitons in a one-dimensional molecular crystal by an impurity is quantum-mechanically calculated.

1. Introduction

There are two basic mechanisms of quenching of an exciton in a molecular crystal, viz (i) the exciton-phonon coupling and (ii) the coupling of the electronic (vibronic) excitations of an impurity with the electronic excitations of the rest of the crystal. Various authors (Kenkre and Reineker 1982) have discussed the first mechanism. The second process has been described by a generalized master equation (Lakatos-Lindenberg et al 1972; Pearlstein 1972; Huber 1979, 1981; Ghosh and Huber 1980; Klafter and Silbey 1980, 1981; Kenkre and Wong 1981; Scher and Wu 1981). Incidentally, the Schrödinger equation for one-electron moving in an impure crystal has been solved by Koster and Slater (1954). Although the work of Koster and Slater is for a localized carrier in a semiconductor, the final working equations are algebraically similar to the equations of motion describing a site excitation in the tight binding limit. Therefore, from the algebraic point of view, excitonic solutions will mimick the electronic ones. Koster and Slater derived the electronic solutions by applying periodic boundary conditions and basing their argument on the symmetry of the chain. In the present work we point out that these solutions are obtained simply from the structure of the Hamiltonian matrix ($H_{ij} = H_{ji}$) rather than the detailed symmetry of the Hamiltonian. As any calculation (diagonalization of the Hamiltonian matrix) would reveal, the so-called 'localized' solution (found by Koster and Slater) is wrong. Instead, we find a solution which is always spread over a few sites around the impurity and which looks like a localized solution only when the chain is sufficiently large. Finally, we discuss a quantum-mechanical formulation of the simplest trapping model (which is a familiar model for the generalized master equation approach to exciton trapping).

2. Excitons in an impure molecular crystal

We consider a one-dimensional crystal with ε_e and $\varepsilon_{e\zeta}$ as excitation energies of the normal species and the impurity respectively. The impurity occupies the ζth site.

Excited electronic states are

$$\psi_{ek} = \sum_j^{\text{sites}} C_j \phi_{ej},$$

where ϕ_{ej} is the many-electron function describing the crystal when the jth molecule is excited to the eth level and the others are unexcited. The coefficients C_j's are determined from the secular equation:

$$\varepsilon_e^k C_j = \varepsilon_e C_j + \Omega(C_{j+1} + C_{j-1}) \quad \text{for } j \neq \zeta, \zeta \pm 1, \tag{1a}$$

$$\varepsilon_e^k C_{\zeta \pm 1} = \varepsilon_e C_{\zeta \pm 1} + \Omega C_{\zeta \pm 2} + \Omega'_{\mp} C_\zeta, \tag{1b}$$

and

$$\varepsilon_e^k C_\zeta = \varepsilon_{e\zeta} C_\zeta + \Omega'_+ C_{\zeta+1} + \Omega'_- C_{\zeta-1}, \tag{1c}$$

where Ω, Ω'_+, and Ω'_- are the corresponding elements of the Hamiltonian matrix H. The eigenvalues of (1) are

$$\varepsilon_e^k = \varepsilon_e + 2\Omega \cos kr, \tag{2}$$

where r is the lattice constant. These values are associated with the solutions

$$C_j = a \exp[i(j+\delta_+)kr] + b \exp[-i(j+\delta_+)kr] \quad (j > \zeta), \tag{3a}$$

and

$$C_j = A \exp[i(j+\delta_-)kr] + B \exp[-i(j+\delta_-)kr] \quad (j < \zeta). \tag{3b}$$

The phases δ_+ and δ_- and the coefficients a, b, A and B are still unknown. Since the Hamiltonian is hermitian, H may be written as a real symmetric matrix by making an appropriate choice of the functions ϕ_{ej}. [With usual Hamiltonians, this is achieved by choosing ϕ_{ej}'s as real functions]. If H is a real symmetric matrix, the coefficients can be chosen as purely real or purely imaginary functions. Thus there are three types of solutions: the 'cosine' type, the 'sine' type and a single eigenvector which is quasi-localized. The last solution will be henceforth called the 'singleton'.

We write the cosine solution as

$$\begin{aligned} C_j &= 2a \cos(j+\delta_+)kr \quad (j > \zeta), \\ C_j &= 2A \cos(j+\delta_-)kr \quad (j < \zeta), \end{aligned} \tag{3c}$$

and

$$C_\zeta = (\Omega/\Omega'_+) \, 2a \cos(\zeta+\delta_+)kr = (\Omega/\Omega'_-) 2A \cos(\zeta+\delta_-)kr$$

the sine solutions as

$$\begin{aligned} C_j &= 2ia \sin(j+\delta_+)kr \quad (j > \zeta), \\ C_j &= 2iA \sin(j+\delta_-)kr \quad (j < \zeta), \end{aligned} \tag{3d}$$

and

$$C_\zeta = (\Omega/\Omega'_+) \, 2ia \sin(\zeta+\delta_+)kr = (\Omega/\Omega'_-) 2iA \sin(\zeta+\delta_-)kr$$

and the singleton as

$$C_{\zeta+p} = a\exp(-\gamma rp) + b\exp(\gamma rp),$$
$$C_{\zeta-p} = A\exp(-\gamma rp) + B\exp(\gamma rp),$$

(3e)

where $\gamma = ik$ and a, b, A and B are coefficients which will be determined from the (periodic) boundary conditions. The singleton is associated with the eigenvalue

$$\varepsilon_e^\gamma = \varepsilon_e + 2\Omega\cosh(\gamma r).$$

Solutions of the cosine and sine type and their corresponding eigenvalues resemble those derived by Koster and Slater (1954) from a consideration of symmetry of the single-particle states where the impurity is assumed to occupy the zeroth site (that is, $\zeta = 0$). The results of the above consideration, however, follow the assumption that H is a real symmetric matrix and the location of the impurity is not the deciding factor.

The localized solution discussed by Koster and Slater (1954) (and which corresponds to the singleton) is not truly orthogonal to the 'symmetric' (cosine) solutions. The constraint of orthogonality requires that both $\exp(-\gamma rp)$ and $\exp(+\gamma rp)$ have to be linearly combined (equation (3e)). Because of the exponentially increasing part, the singleton is not really localized around the impurity, but spread over a few sites. However, as the chain length increases, it seems that the singleton is localized around the impurity.

3. Cyclic boundary conditions

We use the cyclic boundary conditions

$$C_{N/2+1} = C_{-N/2}$$

and

$$C_{N/2} = C_{-N/2-1}$$

in order to determine the phases $\delta_\pm$. There are $(N+1)$ unit species in the crystal.

The cosine solutions have phases $\delta_\pm = \delta_0 \mp (N+1)/2$ where $\delta_0 = 2m\pi/kr - \zeta$, m being a real positive integer. The boundary condition at the impurity site requires that $a\Omega'_- = A\Omega'_+$. Therefore, these solutions are quasi-symmetric on both sides of the impurity,

$$C_{\zeta\pm p} = \frac{\Omega'_\pm}{\Omega}\cos\left(p - \frac{N+1}{2}\right)kr$$

(4a)

with

$$C_\zeta = \cos\left(\frac{N+1}{2}\right)kr.$$

The wave vector (k) is found from

$$(\varepsilon_e - \varepsilon_{e\zeta}) = \left(\frac{\Omega_+'^2 + \Omega_-'^2}{\Omega} - 2\Omega\right)\cos kr + \frac{(\Omega_+'^2 + \Omega_-'^2)}{\Omega}\sin kr \tan\left(\frac{N+1}{2}\right)kr. \quad (4b)$$

The sine solutions are quasi-antisymmetric,

$$C_{\zeta \pm p} = \pm\frac{\Omega_\mp'}{\Omega}\sin\left(p - \frac{N+1}{2}\right)kr \quad (5a)$$

with

$$C_\zeta = 0.$$

The wavevector (k) is given by

$$k = 2\pi m/(N+1)r, \quad (5b)$$

where $m = 1, 2 \ldots, N/2$ if N is even or $m = 1, 2 \ldots, (N-1)/2$ if N is odd.

For the singleton the boundary condition $C_{\zeta - p} = C_{\zeta + (N+1-p)}$ yields

$$b = -\frac{\Omega_-' - \Omega_+'\exp[-\gamma r(N+1)]}{\Omega_-' - \Omega_+'\exp[-\gamma r(N+1)]}a \quad (6a)$$

such that the wave vector γ satisfies the relation

$$\varepsilon_e - \varepsilon_{e\zeta} = \frac{(\Omega_+' + \Omega_-')^2}{\Omega}\frac{\sinh \gamma r}{\sinh[\gamma r(N+1)]} + \frac{(\Omega_+'^2 + \Omega_-'^2)}{\Omega}\frac{\sinh \gamma r(N-1)/2}{\sinh \gamma r(N+1)/2}$$

$$- 2\Omega\cosh\gamma r. \quad (6b)$$

We note that for $\Omega_+' = \Omega_-' = \Omega$ these coefficients and eigenvalues are not identical with those derived by Koster and Slater (1954). Secondly, for a molecular crystal Ω_+' need not necessarily equal Ω_-'.

4. Lifetime of excitations

The quenching process implies a redistribution of the excitation energy among different electronic levels and vibrational modes (VI) of the impurity. In other words these vibronic states (VI) are coupled with the excited levels (EX) of the host crystal. The projected amplitude of excitation will change in time according to an effective Hamiltonian, $\hat{H}_{eff}$. Similar considerations in the context of unimolecular fragmentation have led Nordholm and Rice (1975) to suggest a dissipative part $-i\hat{H}_D$ of the effective Hamiltonian,

$$\hat{H}_{eff} = \hat{H} - i\hat{H}_D.$$

The Markoffian approximation will be justified in the present case if the time spent in the transition EX→VI is very short on the time scale of the excitonic motion, and if the escape from the transition zone to the EX modes is irreversible. Similar models have been used earlier (Mies and Krauss 1966; Mies 1969) to describe radiative deactivation.

We assume that the dissipative part gives rise to an imaginary term in $\varepsilon_{e\zeta}$ only, $\varepsilon_{e\zeta} = \varepsilon^r_{e\zeta} + i\varepsilon^i_{e\zeta}$, such that the off-diagonal matrix elements are still arranged in a real symmetric form (although because of the ζth diagonal element the Hamiltonian matrix of (1) is no longer hermitian). In general, eigenvalues and the coefficients (C's) will be complex. However, translational symmetry of the host molecule part of the crystal remains unaltered giving a constant ratio of coefficients C_{j+1}: C_j, ($j \neq \zeta$, $\zeta - 1$) and indicating that if the sine type of solutions exist, these will be accompanied by the cosine type of solutions. Now, the sine solutions remain unaffected by $\varepsilon_{e\zeta}$; hence these remain valid. Therefore, the cosine type of solutions (and the singleton) still holds. Eigenvalues and coefficients corresponding to the cosine type of solutions (and the singleton) are found by a straightforward substitution of k by $k' + ik''$ (γ by $\gamma' + i\gamma''$).

Eigenvalues for the cosine solutions are given by

$$\varepsilon^k_e = \varepsilon_e + 2\Omega \left(\cos k'r \cosh k''r - i \sin k'r \sinh k''r \right),$$

where k' and k'' are found by solving the two equations

$$\varepsilon_e - \varepsilon^r_{e\zeta} = \left(\frac{\Omega'^2_+ + \Omega'^2_-}{\Omega} - 2\Omega \right) \cos k'r \cosh k''r$$

$$+ \frac{(\Omega'^2_+ + \Omega'^2_-)}{\Omega} (\alpha \sin k'r \cosh k''r - \beta \cos k'r \sinh k''r)$$

and

$$\varepsilon^i_{e\zeta} = \left(\frac{\Omega'^2_+ + \Omega'^2_-}{\Omega} - 2\Omega \right) \sin k'r \sinh k''r$$

$$- \frac{(\Omega'^2_+ + \Omega'^2_-)}{\Omega} (\alpha \cos k'r \sinh k''r + \beta \sin k'r \sinh k''r)$$

in a self-consistent manner. Here α and β are given by

$$\alpha = \tan\left(\frac{N+1}{2} \right)k'r \bigg/ \left[\cosh^2\left(\frac{N+1}{2} \right)k''r \right.$$

$$\left. + \tan^2\left(\frac{N+1}{2} \right)k'r \sinh^2\left(\frac{N+1}{2} \right)k''r \right]$$

and

$$\beta = \tanh\left(\frac{N+1}{2} \right)k''r \bigg/ \left[\left(\cos^2\left(\frac{N+1}{2} \right)k'r \right) \right.$$

$$\left. + \sin^2\left(\frac{N+1}{2} \right)k'r \tanh^2\left(\frac{N+1}{2} \right)k''r \right].$$

The eigenvalue corresponding to the singleton is

$$\varepsilon_{e\gamma} = \varepsilon_e + 2\Omega(\cosh \gamma'r \cos \gamma''r + i \sinh \gamma'r \sin \gamma''r)$$

where γ' and γ'' are similarly determined by a self-consistent procedure.

Imaginary parts of the eigenvalue give the characteristic lifetime for the quasi-symmetric excitations, that is, they are the velocity constants for quenching of these

excitons. A positive value of $\text{Im}(\varepsilon_e^k)$ is unacceptable on physical grounds. In practice, one may not encounter this difficulty if the impurity causes a small perturbation only, that is, effects of $\varepsilon_{e\zeta}^i$ are evaluated by the lowest orders in perturbation theory (or else one has to modify (1) so that mixing of different bands is taken into account). Using (1) in their present form, a small negative value of $\varepsilon_{e\zeta}^i$ suffices to yield physically acceptable solutions.

5. Discussion

Pearlstein (1972) discussed the quenching of fully coherent, Frenkel, excitons by an ad-hoc linear differential equation. The latter gives a time-dependent description of the
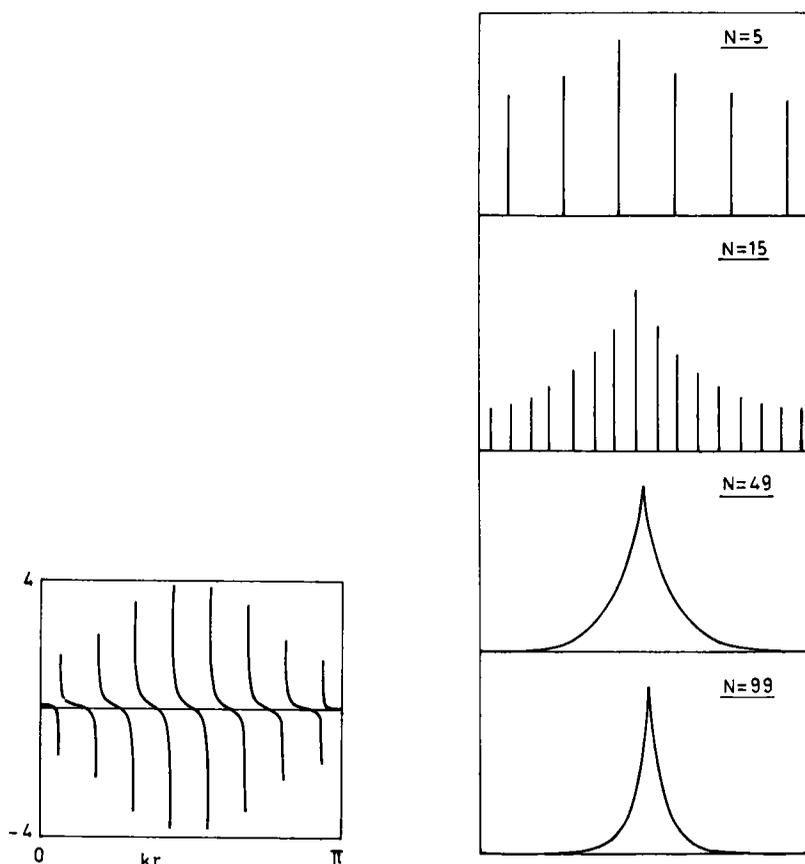

Figure 1a. Right hand side of equation (4b) vs kr.

Figure 1b. Coefficients of linear combination for the singleton vs the length of the crystal. For $N = 5$ and $N = 15$ these coefficients are shown as line spectra spread over different sites. For larger values of N ($N = 49$ and 99) a continuous line is drawn.

motion of a Frenkel exciton packet in a given band and has complex eigenvalues. According to Pearlstein this equation is not strictly derivable from the Schrödinger equation. Our analysis, based on single excitons and a projected Hamiltonian (Nordholm and Rice 1975), yields the difference equation for each eigenvector.

In figure 1(a), the right hand side of (4b) is plotted against kr. Points where these plots intersect the $y = \varepsilon_e - \varepsilon_{e\zeta}$ axis give eigenvalues for the cosine excitations. The least eigenvalue is found with the singleton. For a pure crystal, the singleton represents the lowest energy cosine excitation.

In figure 1(b), we show the singleton eigenvector for different values of N. This excitation is always spread over a few sites. When N is large enough, it looks like an excitation localized on a small fraction of the chain length around the impurity.

An imaginary term in $\varepsilon_{e\zeta}$ will change some of the eigenvalues. Such changes for $N = 15$ (a chain of 16 unit species) are shown in table 1. In general, the singleton excitation shows the fastest decay (particularly if N is large), a consequence of its localization in the neighbourhood of the quencher. Time dependence of the probability of finding the crystal in different quasi-symmetric excited states is shown in figure 2.

Our analysis predicts that the longest wavelength excitation will spread over a few lattice sites around the impurity and will be quenched quickly. Theoretical computations and time-resolved experiments on the excited states of heteronuclear aromatic organic molecules (although not directly comparable to molecular crystals) support these results. These conclusions, with appropriate quantitative modifications, can be directly extended to the case of a three-dimensional doped molecular crystal. However, experimental results will be greatly influenced by three factors, viz (i) scattering by other excitons (Haken and Strobl 1973; Reinecker 1979), (ii) scattering by phonons (Soules and Duke 1971) and (iii) disorder in the lattice, which is a common occurrence in molecular crystals.
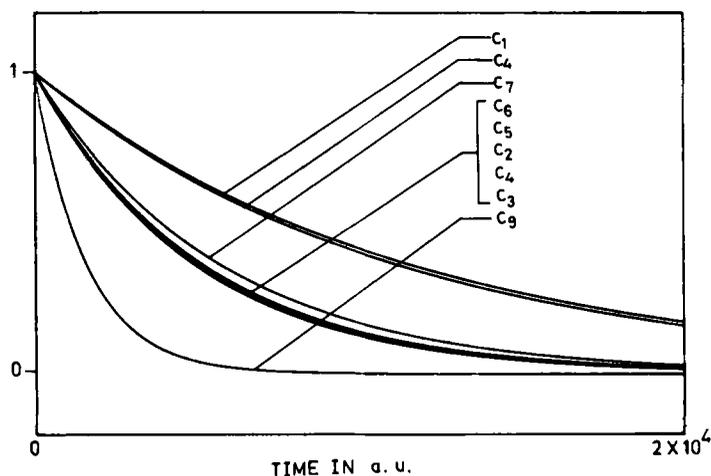

Figure 2. Time dependence of the probability of finding the crystal in different quasi-symmetric excited states. Eigenvalues are listed in table 1.

Table 1. Eigenvalues for $N = 15$ (Number of unit species $= 16$).

	Pure crystal, (a)	Crystal with impurity, (b)	Crystal with impurity, (c)	Crystal with impurity as a quencher (d)	
	ε_e^k	ε_e^k	ε_e^k	Re ε_e^k	Im $\varepsilon_e^k \times 10^{-4}$
C_1	-0.300	-0.302	-0.301	-0.300	-0.044
C_2	-0.315	-0.320	-0.316	-0.310	-0.101
C_3	-0.358	-0.364	-0.361	-0.361	-0.108
C_4	-0.423	-0.429	-0.427	-0.427	-0.102
C_5	-0.500	-0.506	-0.505	-0.505	-0.101
C_6	-0.576	-0.583	-0.583	-0.583	-0.098
C_7	-0.641	-0.647	-0.649	-0.649	-0.089
C_8	-0.685	-0.691	-0.692	-0.692	-0.046
C_9	-0.700	-0.706	-0.715	-0.715	-0.318

(a) $\varepsilon_e = \varepsilon_{e\zeta} = -0.500$ a.u., $\Omega = \Omega'_+ = \Omega'_- = -0.1$ a.u.

(a) $\varepsilon_e = -0.500$ a.u., $\varepsilon_{e\zeta} = -0.550$ a.u., $\Omega = \Omega'_+ = \Omega'_- = -0.1$ a.u.

(c) $\varepsilon_e = -0.500$ a.u., $\varepsilon_{e\zeta} = -0.550$ a.u., $\Omega = -0.1$ a.u., $\Omega'_+ = \Omega'_- = -0.11$ a.u.

(d) $\varepsilon_e = -0.500$ a.u., $\varepsilon_{e\zeta}^r = -0.550$ a.u., $\varepsilon_{e\zeta}^i = -0.001$ a.u., $\Omega = -0.1$ a.u., $\Omega'_+ = \Omega'_- = -0.11$ a.u.

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