

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.

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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 mimic 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 ζ th site.