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Nonradiative relaxation processes in molecular crystals

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Internal conversion is the dominant relaxation channel from higher lying excited states in molecular crystals and involves the transfer of energy from the electronic system to the lattice. In this work, we present results from simulations of the nonradiative relaxation process with an emphasis on both intra- and interband transitions. We find the internal conversion process to be strongly nonadiabatic and the associated relaxation time in the case of large energy excitations to be limited by the transitions made between states of different bands.

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1. Introduction

In recent years, impressive progress has been made within the field of organic optoelectronics with commercial applications already in the market. However, in order to fully explore the possibilities of the organic materials and to further improve device performance a fundamental understanding of the mechanisms that govern excitation dynamics and charge carrier transport is needed. Limiting further discussions to the first of these topics, this subject has been investigated in great detail in conventional semiconductors, in particular, in quantum-well structures [1,2], and to some extent also in π-conjugated polymers and molecular materials. Although practical devices are likely to be produced from disordered polycrystalline films, high purity crystals are required for studies of the intrinsic dynamics, since, otherwise, trapping of excitons to impurities can dominate the dynamical process. In particular, α-hexathiophene [3,4], rubrene [5], and pentacene [6,7] have been extensively studied and are considered to be representative model systems for π-conjugated molecular crystals. From such studies the dominant relaxation channel from higher lying excited states was identified to be internal conversion [3], i.e., the ultrafast nonradiative relaxation between molecular states of the same spin multiplicity [8]. This process is followed by a much slower decay of the (intra)molecular vibrations on the order of a few picoseconds [4].

As a complement to the experimental studies, there is a need for a theoretical description of the exciton dynamics involved in the relaxation process. Such a study should account for the exchange of energy between electrons and phonons as well as the dynamics of the phonon and electronic degrees of freedom. In a recent work, Miyamoto et al. [9] performed real-time simulations of excited state dynamics in carbon nanotubes. Their method is based on an *ab initio* treatment of the system with the ionic motion determined from direct integration with a force field obtained from density functional theory. The time evolution of the charge density is based on Ehrenfest dynamics which requires the potential energy surface (PES) to be associated with a particular excited state. In the case of the carbon nanotubes, it was shown that the influence of the particular excited state on the ion dynamics is negligible which can justify this approach. This is an effect of the rigidity of the cylindrical shaped carbon structures and the relatively weak electron–phonon interaction strength. For molecular crystals, though, the adiabatic picture breaks down as the coupling between electronic and nuclear degrees of freedom facilitates a transition in the region where the PES of the participating states approach one another energetically [10]. In studies of these kinds of materials there is therefore a need for a treatment which includes nonadiabatic effects [11].

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In this work, we perform simulations of nonradiative relaxation dynamics in molecular systems using single crystal pentacene as a model system. Our methodology relies on the simultaneous treatment of electron and ion dynamics, while still allowing for nonadiabatic transitions to occur. The essential idea is to solve the time-dependent Schrödinger equation for the electrons, together with an effective Newton's equation for the ions, such that the ionic forces are determined from the generalized Hellmann–Feynman theorem [11]. Due to the computational costs associated with these simulations we perform our calculations on finite sized systems. One drawback of this approach is that the particular size of the system affects the spacing between the intraband energy levels and since the rate of internal conversion between two excited states is expected to increase exponentially with decreasing difference between the energies of these states [8,12], a quantitative description of the dynamics of the nonradiative relaxation may therefore not be obtained. Nevertheless, qualitatively we are able to capture the major effects involved in the process and present a detailed picture of the process of internal conversion in molecular crystals.

2. Methodology

In our approach, we obtain the time dependence of the electronic degrees of freedom from the solutions to the time-dependent Schrödinger equation

$$i\hbar|\dot{\Psi}(t)\rangle = \hat{H}_{\mathrm{el}}|\Psi(t)\rangle \tag{1}$$

and determine the ionic motion in the evolving charge density distribution by simultaneously solving the lattice equation of motion within the potential field of the ions:

$$M_i\ddot{\mathbf{r}}_i = -\nabla_{\mathbf{r}_i}\langle\Psi(t)|\hat{H}|\Psi(t)\rangle - \lambda\dot{\mathrm{r}}_i. \tag{2}$$

Here, $\hat{H}(\hat{H}_{\mathrm{el}})$ is the (electronic) Hamiltonian of the system, $\mathbf{r}_i$ and M_i the position and mass of the ith ion, respectively, and λ a viscous damping constant appended to account for the dissipation of energy from the system.

Crucial for the efficiency of this method is the representation of the Hamiltonian. A simple yet powerful model for π-conjugated polymers was devised already in 1979 by Su et al. (SSH) [13]. In the SSH model the lattice is treated classically, i.e., the operators of the lattice displacements are replaced with their expectation values. This corresponds to expressing the electronic Hamiltonian in the mean-field approximation [14].

We have expanded the SSH Hamiltonian to encompass for the higher dimensionality of molecular crystals [15]. In this approach only the π-electrons are treated explicitly within a tight-binding model of the form

$$\hat{H}_{\mathrm{el}} = -\sum_{\substack{i,j=1\\ i>j}}^{N}{}' \beta_{ij}(t)(\hat{c}_i^{\dagger}\hat{c}_j + \hat{c}_j^{\dagger}\hat{c}_i) \tag{3}$$

with resonance integrals

$$\beta_{ij}(t) = \begin{cases} \beta_0 - \alpha\Delta r_{ij}(t) & \text{intramolecular,} \\ kS_{ij}(0) & \text{intermolecular.} \end{cases} \tag{4}$$

Here, the intramolecular expression involves a first-order expansion of deviations in bond lengths, Δr_{ij}, between sites i and j from that of the undimerized state with uniform bond lengths a. The intermolecular resonance integrals are obtained within the Mulliken approximation [16]. The overlap integrals S_{ij} are derived analytically from the scheme presented in Ref. [17] for the initial state of the system, whereas the parameter values for the reference resonance integral β_0 and the electron-phonon coupling constant α are taken directly from Ref. [15]. The prime in Eq. (3) indicates that the summation runs over nearest neighbors only.

For the molecular dynamics we adopt a classical description of the σ-bond energy. This contribution is expanded to second order around the undimerized reference state. Supplemented with the constraint of fixed molecular length [18], we obtain

$$\hat{H}_{\mathrm{latt}} = \frac{K_1}{2}\sum_{\substack{i,j=1\\ i>j}}^{N}{}' \left(\Delta r_{ij} - \frac{2\alpha}{K_1}\langle\rho_{i'j'}\rangle\right)^2 + \frac{K_2}{2}\sum_{b=1}^{\mathrm{uni.ba.}}{}' (\Delta\theta_b)^2, \tag{5}$$

where only the deviations in bond lengths and bond angles are accounted for owing to the negligible contributions from the torsional degrees of freedom of the systems discussed in this work. Here, K_1 and K_2 are harmonic force-constants and $\langle\rho_{i'j'}\rangle$ denotes the mean electron density. All summations in Eq. (5) involve unique geometrical variables Δr_{ij} and $\Delta\theta_b$ corresponding to alternations in bond lengths and bond angles, respectively, from the undimerized reference state. Also taking into account the kinetic energy of ionic motion, $E_{\mathrm{kin}} = (1/2)\sum_{i=1}^{N} M_i\dot{r}_i^2$, the system Hamiltonian then reads

$$\hat{H} = \hat{H}_{\mathrm{el}} + \hat{H}_{\mathrm{latt}} + \frac{1}{2}\sum_{i=1}^{N} M_i\hat{\dot{r}}_i^2. \tag{6}$$

Eqs. (1), (2), and (6) form a closed system within the mean-field approximation inherent in the SSH model. We now make the ansatz $\rho_{nn'}(t) = \sum_{p=1}^{N} C_{np}^{*}(t) f_p C_{n'p}(t)$ for the density matrix, where f_p is the initial and further on time-independent occupation number of the pth molecular orbital (MO) and $C_{np}(t)$ are the time-dependent expansion coefficients of linear combinations of orthonormal atomic orbitals of the form

$$|\psi_p(t)\rangle = \sum_{n=1}^{N} C_{np}(t)|\phi_n\rangle. \tag{7}$$

$C_{ip}(t)$ are then normalized solutions of the following equation (see Appendix A.1):

$$i\hbar\dot{C}_{ip}(t) = -\sum_{j=1}^{N}{}' \beta_{ij}(t)C_{jp}(t). \tag{8}$$

Using the Hellmann–Feynman theorem for the ionic forces, Eq. (2) then reads (see Appendix A.2)

$$M_i\ddot{\mathbf{r}}_i = -\sum_{p=1}^{N} f_p \sum_{n,n'=1}^{N} C_{np}^{*}(t)\langle\phi_n|\nabla_{\mathbf{r}_i}\hat{H}|\phi_{n'}\rangle C_{n'p}(t) - \lambda\dot{\mathrm{r}}_i. \tag{9}$$

For the later analysis of the electronic relaxation dynamics it is useful to express the normalized time-dependent molecular orbitals, $|\psi_p(t)\rangle$, in a basis of instantaneous eigenfunctions, $|\varphi_q\rangle$ [19]. Expanding $|\varphi_q\rangle$ in the same basis as the time-dependent solutions (see Eq. (7))

$$|\varphi_q\rangle = \sum_{n''=1}^{N} B_{n''q}|\phi_{n''}\rangle \tag{10}$$

with expansion coefficients, $B_{n''q}$, obtained from the time-independent Schrödinger equation $-\sum_{j=1}^{\prime N}\beta_{ij}(t)B_{jq} = \varepsilon_q B_{iq}$ (see Appendix A.3), we obtain, at each time step t, a relationship between the two sets of expansion coefficients in Eqs. (7) and (10) (see Appendix A.4):

$$C_{n'p}(t) = \sum_{q=1}^{N} B_{n'q}\alpha_{qp}(t), \tag{11}$$

where the elements $\alpha_{qp}(t) = \langle\varphi_q|\psi_p(t)\rangle$ can be used to define the time-dependent occupation number of the instantaneous

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