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Electron-Lattice Dynamics in π-Conjugated Systems

Magnus Hultell

Linköpings universitet
INSTITUTE OF TECHNOLOGY

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Department of Physics, Chemistry and Biology
Linköpings universitet, SE-581 83 Linköping, Sweden

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To Anna and Elliot

Abstract

In this thesis we explore in particular the dynamics of a special type of quasi-particle in π-conjugated materials termed polaron, the origin of which is intimately related to the strong interactions between the electronic and the vibrational degrees of freedom within these systems. In order to conduct such studies with the particular focus of each appended paper, we simultaneously solve the time-dependent Schrödinger equation and the lattice equation of motion with a three-dimensional extension of the famous Su–Schrieffer–Heeger (SSH) model Hamiltonian. In particular, we demonstrate in Paper I the applicability of the method to model transport dynamics in molecular crystals in a region were neither band theory nor perturbative treatments such as the Holstein model and extended Marcus theory apply. In Paper II we expand the model Hamiltonian to treat the revolution of phenylene rings around the σ-bonds and demonstrate the great impact of stochastic ring torsion on the intra-chain mobility in conjugated polymers using poly[phenylene vinylene] (PPV) as a model system. Finally, in Paper III we go beyond the original purpose of the methodology and utilize its great flexibility to study radiationless relaxations of hot excitons.

Preface

This thesis is a summary of the work that I have carried out in the Computational Physics group at Linköpings Universitet in-between the fall of 2003 and the fall of 2006. It consists of two parts, where the first part aims to provide the theoretical foundation for the scientific papers presented in the second part, having in mind a reader with a general knowledge of theoretical physics.

I am deeply thankful to my friends and colleagues, former and present, at the department. In particular, I would like to acknowledge Professor Sven Stafström, my advisor, for his distinguished guidance, Johan Henriksson for generous support on scientific and computer related problems, and Ingegärd Andersson for taking care of the administrative issues. Finally, I would like to thank my beloved wife Anna for moral support when patiently listening to my many scientific monologues.

Magnus Hultell Linköping, December 2006

Contents

CHAPTER

ONE

Introduction

For the past forty years the semiconductor industry has relied on innovative improvements of *inorganic* silicon and gallium arsenide based technologies to fuel its unparalleled market growth. In recent years, however, efforts have been made to incorporate also organic materials into these architectures. At first, they where utilized only as sacrificial stencils (photoresists) and passive insulators and took no active role in the electronic functioning of devices. Today, however, conjugated organic materials and nanocrystals are utilized as the active components in such promising fields as pixel-resolved full color organic light emitting diode (OLED) displays, organic field effect transistors (OFET) integrated circuits, and photovoltaic cells. At present the speed, heating, and power efficiency of these devices are all limited by the transportation of charge through the active organic layer(s)[22] and a detailed understanding of the basic properties that govern these processes is therefore essential for further material improvements.

1.1 Adiabaticity

In this thesis we will explore the microscopic physics of organic systems numerically with the aid of theoretical models. Since these usually rely on the non-relativistic time-(in)dependent Schrödinger equation, which is analytically solvable only for two body problems, several approximations are often required to obtain cost effective schemes for calculating the relevant molecular properties to within a reasonable level of accuracy. An important concept often invoked during these efforts is that of *adiabaticity*, which basically implies that there are two sets of variables which describe the system of interest and that the system can be well characterized by the eigenstates defined at each fixed value of one set of variables which changes slowly compared to the other set.[32] This slowly varying set of variables are called *adiabatic parameters* and if such parameters can be identified, it will greatly facilitate the description and understanding of both the static properties and the dynamical behavior of the system since the system then would stay mostly in the same so-called adiabatic (eigen)state. In the regions where the rapidly changing

variables cannot fully follow the changes of the adiabatic parameters, so-called *nonadiabatic transitions* among the adiabatic states are induced, and the dynamics becomes more complex.

One of the most well known examples of adiabatic approximations is the Born–Oppenheimer approximation. It relies on the fact that the lighter electrons very rapidly readjust their motions to match the motion of the much slower nuclei. The inter-nuclear coordinates, collectively denoted as R, can therefore be considered a very good adiabatic parameter. This enables a separation of electronic and nuclear coordinates in the instantaneous state of the molecule, where the electronic state only depends on R in a parametric sense. In most cases this is a good approximation and the adiabatic states generally describe the molecule well. In some regions of R, however, two or more of such so-called Born–Oppenheimer states might come close together. At these positions, a small amount of energy change is enough to induce a nonadiabatic transition between the adiabatic electronic states. The transition can actually be achieved rather easily by gaining that energy from the nuclear motion. Various molecular spectroscopic processes, molecular collisions, and chemical reactions can all be described by the concept of nonadiabatic transitions.

1.2 Outline of Research

The work presented in the papers in this thesis is implicitly yet intimately related to the concept of (non)adiabaticity. Explicitly, however, it is the excitation and conduction of charge that is the focus of my research. In an organic material these properties are strongly correlated to the geometrical configuration of the system as well as to the electronic interactions between its constituent parts; e.g., between molecules in a molecular solid. The stronger the interactions are, the more delocalized are the constituent charge carriers and the more adiabatic the system becomes (see Section 2.3). The microscopic physics of these and similar processes are explored in single crystal pentacene (Paper I) and poly[phenylene vinylene] molecules (Paper II), both of which belong to the special class of organic materials termed π-conjugated systems. In the case of the former system additional studies of excitation dynamics has been performed (Paper III).

1.3 Outline of Thesis

Following this brief introduction, the second chapter of the thesis is devoted to the unique charge carrying species of π-conjugated systems and specifically on how the dynamics of one of these, the polarons, relates to the concept of adiabaticity. In the third chapter, a model that enables the simultaneous study of electron-lattice dynamics and the associated adiabaticity in terms of the time-evolution of occupied eigenstates is developed. This constitutes the methodological framework for the three papers presented in the second part of the thesis, briefly introduced in the fourth and final chapter of the first part.

CHAPTER

TWO

Storage and Transport of Charge

The materials of relevance for this thesis belong to the special class of so-called π-conjugated hydrocarbon systems for which the valence electrons of constituent sp^2-hybridized carbon atoms display local σ- and π-orbital symmetry with respect to one inter-nuclear axis (as defined, e.g., in Ref. [4]). In particular, this means that three of the four valence electrons of carbon are involved in the covalent bonds that define the molecular backbone, while the remaining valence electron occupies the $2p_z$-orbital directed parallel to the local surface normal of the molecular plane. While the former electrons remain localized to the region of their associated bonds, the state of the later electrons may extend throughout the system due to the significant orbital overlap between neighboring $2p_z$-orbitals. These electrons, termed π-electrons due to the π-symmetry of the $2p_z$-orbital, will have energies much closer to the Fermi level than their σ counterparts for which the gap between the σ-bonding and anti-bonding states is large compared to phonon and charge carrier energies. Consequently, it is often sufficient to treat only the π-electrons when considering the electronic structure of these systems.

2.1 Electronic Structure of Conjugated Polymers

One of the simplest hydrocarbons known to display this type of electron structure is polyacetylene, $[\text{CH}]_n$. In its transoid form, assuming equal C-C bond lengths and a quasi one-dimensional structure, each unit of repetition would contribute one electron in a $2p_z$-orbital to the π-electron system. Since spin degeneracy allows for two electrons to occupy every $2p_z$-orbital this would render the π-band half filled and place the system in a metallic state. In reality, however, it turns out that intrinsic *trans*-polyacetylene (*t*-PA) display semiconductive properties. This is because the uniform one-dimensional chain of atoms is unstable against so-called Peierls-distortions[35] and thus lower its total energy by spontaneous dimerization. The band structure of the perfectly conjugated molecule as obtained, e.g., within the Su–Schrieffer–Heeger (SSH) model,[39] verify that a fully occupied band and a completely empty band, separated by an (Peierls) energy gap of 1.4 eV, is obtained.

2.2 Charge Storage in Conjugated Polymers

In conjugated polymers it is the strong electron(hole)-lattice interactions that is responsible for the dimerization of the molecular backbone. These interactions are also responsible for the existence of unusual self-trapped charge carrier species that manifest themselves upon doping or electrical charging as self-localized electronic states with energy levels within the otherwise forbidden band gap.[1] It is instructive to introduce these through successive doping of a finite sized *trans*-polyacetylene chain. In its ground state both chain ends are terminated by double bonds.[38] The stable configuration of such a system when extending over an odd number of CH-units must therefore contain a region across which the bond length alternation is changed. Situated in the middle of the chain, the single energy level localized by the corresponding misfit potential must, due to charge conjugation symmetry, reside in the middle of the band gap. This topological defect between two degenerate ground state phases in *trans*-polyacetylene is called a *soliton*.

Due to spin degeneracy the first electron (hole) injected into this system will occupy the mid-gap level, thus forming a negatively (positively) charged soliton. The addition of a second electron to the system of a negatively charged soliton will, however, induce lattice distortions and cause an occupied state in the valence band and an unoccupied state in the conduction band to migrate into the band gap to form two new localized states. The combination of the localized charge and the lattice deformation is called a *polaron*. Yet again, when a third electron is added to the system the polaron will relax to a *soliton–antisoliton pair* with energy levels in the middle of the band gap since the relaxation energy is less than the increase in energy required to create either an extra polaron or a *bipolaron*, the later in which case the third electron simply enters the empty polaron state.

Note that for degenerate ground state molecules with an even number of bonds, as well as for nondegenerate ground state molecules, the polaron is the stable state for single charge injection. Further injection of also a second identical charge will lead to the formation of a soliton–antisoliton pair in the former case and a bipolaron in the later.

2.3 (Non-)Adiabatic Polarons

The research presented in Papers I and II in this thesis deals exclusively with the field induced dynamics in singly charged *non*degenerate ground state molecules, i.e., with the dynamics of polarons. Originally, the term polaron referred to a self-trapped electronic carrier in an ionic (*polar*) material. For these systems the energy of the charge carrier depends on the positions of a solid's ions through long-range electron-lattice Coulomb interactions (sometimes referred to as Frölich interactions). However, while retaining the term polaron, models of self-interaction also consider the short range interactions between electrons and atoms associated with

[1] The notion of self-trapped carriers was introduced by Landau in 1933 for otherwise free charge carriers being bound within potential wells produced by the displacements of atoms from their carrier-free equilibrium positions.[24]

covalent bonding.[15] In what follows, we will consider only these later interactions since they are the dominant ones in most π-conjugated systems.

Studies of self-trapping within a short-range interaction are often based on the Holstein molecular crystal model (MCM).[19] In particular, a tight-binding electron moving through a one-dimensional lattice of diatomic molecular sites is envisioned, which interacts with the local vibrational mode of deviation in each sites internuclear separation from equilibrium. The corresponding model Hamiltonian read

$$H = -t_M \sum_{i,j} c_i^\dagger c_j - g \sum_i c_i^\dagger c^i (a_i + a_i^\dagger) + \omega_0 \sum_i a_i^\dagger a_i, \tag{2.1}$$

where c_i ($c_i^\dagger$) and a_i ($a_i^\dagger$) are, respectively, destruction (creation) operators for fermions and for local vibrations of frequency ω_0 for the internuclear separation distance on site i, t_M is the electron inter-site resonance integral, and g is an electron-phonon (e-ph) coupling constant.

Within this model, the setting in of a polaronic regime is directly related to the magnitude of two parameters which are often introduced in this field: $\lambda \equiv g^2/(2t_M\omega_0)$, which measures the energetic convenience to form a bound state, and $\alpha \equiv g/\omega_0$, which controls the number of excited phonons to which the charge couple. For polarons to form both conditions $\lambda > 1$ and $\alpha > 1$ have to be satisfied, corresponding to (1) a lattice deformation energy gain, $E_p = -g^2/\omega_0$, larger than the loss of bare kinetic energy (of the order of half the bandwidth, $\sim -2t_M$) *and* (2) a strong reduction of the effective hopping matrix element due to a sizeable local displacement of the nuclear positions. However, from the definitions of λ and α one can immediately recognize that since $\lambda = (\alpha^2/2) \cdot (\omega_0/t_M)$, a crucial role is played by the adiabatic ratio ω_0/t_M. In essence, this ratio tells us weather it is the electrons ($\omega_0 \ll t_M$) or the phonons ($\omega_0 \gg t_M$) that constitutes the faster subsystem of the two. When $\omega_0 \ll t_{\mathrm{M}}$ the electrons very rapidly readjust their motions to match the motion of the much slower nuclei and the adiabatic approximation (see Section 1.1) may be used to describe the self-trapped states. In this case the condition for a large λ is more difficult to realize than $\alpha > 1$ and polaron formation will therefore be determined by the more restrictive $\lambda > 1$ condition. The opposite is true when the system is in the nonadiabatic regime, i.e., when $\omega_0 \gg t_{\mathrm{M}}$.

The Holstein model was originally proposed as a conceptual aid to describe a type of small polaron that may be formed when a carrier is confined to a transition-metal ion of a transition-metal oxide. Self-trapped carriers in molecular solids are, however, frequently much larger than those envisioned by the MCM and often encompasses many atoms. In particular, rather than being confined to a point, a carrier on a real molecule generally sloshes amongst its atoms in response to their motions.[14] This property can be captured with the previously mentioned Su–Schrieffer–Heeger (SSH) model in which the e-ph coupling is due to the dependence of the resonance integral on the relative distance between two adjacent ions.[39] Within this picture, λ still determines the energetic advantage in deforming the lattice and losing kinetic energy, but α was shown by Capone *et al.*[11] to be directly related to λ regardless of the value of the adiabatic ratio ω_0/t_M. The value of λ therefore simultaneously determines how well both conditions (1) and (2) are

satisfied, and it will be the relevant parameter for the description of the system for any value of ω_0/t_M.

In terms of λ, or rather E_p/J, where $J \equiv -2t_M$, three carrier type "regimes" may be identified for molecular solids. On the one hand we have the systems with weak intermolecular interactions ($J \ll E_p$) for which the small Holstein polaron localized to a single molecule is stable, and on the other hand we have the systems with strong intermolecular interactions ($J \gg E_p$) for which the energy gain of self-trapping is negligible and localized carrier states therefore unstable. For systems in the intermediate regime ($J \sim E_p$) the polaron is delocalized over several molecular units and the electron probability density can sample an even larger region in space. The transition region in particular is sampled in Paper I using modulated values of J for intrinsic single crystal pentacene.

Note that similar conditions as (1) and (2) apply also to the case of *intra*-molecular self-trapping for which the atomic resolved SSH model is even better suited. However, since the inter-atomic bare hopping, t, within a molecule is quite strong, the adiabatic approxmation do, in general, apply. Polarons formed within these type of systems are therefore often strongly delocalized; e.g., in t-PA the polaron extends over 40 sites.[8] However, in the case when there is revolution of molecular segments around individual bonds, the hopping reduce to such levels that there might be a transition into the nonadiabatic regime (see Paper II).

2.4 (Non-)Adiabatic Polaron Transport

There are distinctly different mechanisms involved in the transport of a nonadiabatic, highly localized small polaron as compared to the conduction of the adiabatic extended state free carrier and although we are interested in the dynamics of polarons in the intermediate regime, a brief review is in order. In the later case the process may be described by standard textbook band transport theory,[23] while in the former case hopping theory applies, the fundamental mechanism of which involve phonon-assisted tunneling of carriers from occupied to unoccupied localized donor states. This process is well described by extended Marcus theory,[6] but due to its simplicity the transfer rates derived by Miller and Abrahams[27] for impurity conduction in disordered semiconductors are often used in models of electronic hopping transport. For example, the pioneering study by Bässler[5] of the hopping mobility (μ) in disordered organic solids with a Gaussian distributed density of states (DOS) relies on Miller–Abrahams transfer rates for inter-state hopping with which a fairly good agreement with observed temperature and field dependencies on μ was retrieved. However, analyzing the carrier concentration dependence in semiconducting materials within the framework of six existing semianalythical models,[3,5,26,28,37,40] a much more general, as well as accurate, description of the hopping mobility in the zero field limit was recently given by Coehorn *et al.*[12] Combining Eq. (30) in Ref [12] with Eq. (6) in Ref. [34], the later of which expresses the field dependence in terms of a field-dependent multiplication factor, a very compact description for the mobility up to intermediate field strengths is obtained for organic solids with a Gassian DOS.

CHAPTER

THREE

Model and Method

When the dynamics of π-conjugated systems was discussed in terms of extended state adiabatic transport and localized state nonadiabatic transport in Section 2.4, no theory for the intermediate transition region between these two limiting cases was suggested. That is because, to the best of our knowledge, there is no single model capable of covering this broad regime. To explore the microscopic physics of the transport processes within this regime as well as the transition from adiabatic to nonadiabatic dynamics, which is the main focus of Paper I, we have extended the methodology used by Johanson and Stafström[21] and precedingly by Block and Streitwolf.[7] Due to its great flexibility it has also been applied to the cases of intramolecular transport dynamics in Paper II and excitation dynamics in Paper III.

3.1 General Considerations

The methodology relies on the simultaneous numerical solution of the time-dependent Schrödinger equation,

$$i\hbar|\dot{\Psi}(t)\rangle = \hat{H}_{\mathrm{el}}|\Psi(t)\rangle, \tag{3.1}$$

and the lattice equation of motion,

$$M_i\ddot{\mathbf{r}}_i = -\nabla_{\mathbf{r}_i}\langle\Psi|\hat{H}|\Psi\rangle - \lambda\dot{\mathbf{r}}_i. \tag{3.2}$$

Here, $\hat{H}$ ($\hat{H}_{\mathrm{el}}$) is the (electronic) molecular Hamiltonian, $\mathbf{r}_i$ and M_i the position and mass of the i:th atom, respectively, and λ a viscous damping constant appended to allow for heat to dissipate from the system. These calculations may be performed using state of the art numerical differential equation solvers, provided that the wave function $|\Psi\rangle$ is expanded as a linear combination of known basis functions. However, the evaluation and handling of the large number of two-electron integrals that would arise from a fully quantum mechanical treatment of $\hat{H}_{\mathrm{el}}$ even for small basis sets of moderately sized systems exclude *ab initio* treatments of most realistic systems. Instead, we are restricted to work with more cost efficient approximative treatments of $\hat{H}$.

3.2 Model Hamiltonian

For the π-conjugated materials, the gap between σ bonding and anti-bonding states is large compared to that of the π-states. We therefore assume that the σ-electrons can be treated classically and that the stretching, bending, and twisting of bonds from the undimerized state only contribute to the lattice energy part of the Hamiltonian, $\hat{H}_{\text{latt}}$. Since these geometrical changes are expected to be small we expand the σ-bonding energies to second order around the undimerized reference state. The lattice Hamiltonian then read

$$\hat{H}_{\text{latt}} = \frac{K_1}{2}{\sum_{i>j}}'(r_{ij}-a)^2 + \frac{K_2}{2}{\sum_{i>j>k}}'(\phi_j-\phi_0)^2 + \frac{K_3}{2}{\sum_{i>j>k>l}}'(\theta_k-\theta_0)^2, \quad (3.3)$$

where K_1, K_2 and K_3 are harmonic force-constants for the stretching, bending, and twisting of bond lengths r_{ij}, bond angles ϕ_j, and dihedral angles θ_k, respectively, when compared to the reference values a, ϕ_0 and θ_0 of the undimerized reference system. The primes indicate that all summations run over nearest neighbors only.

So far we have not discussed the π-electrons of the carbon valence $2p_z$-orbitals. The bonding and anti-bonding states associated with these electrons appear much closer to the band gap and are hence the likely participants in phonon, exciton, and polaron formation. Their contribution to the Hamiltonian, $\hat{H}_\pi$, must therefore be included quantum mechanically. Treating the resonance integrals, β_{ij}, in the Mulliken approximation,[29] i.e., as proportional to the overlap integrals, S_{ij}, by a constant k, the energy contribution from the π-electron system then read

$$\hat{H}_\pi = -k{\sum_{i>j}}'S_{ij}[\hat{c}_j^\dagger\hat{c}_i + \hat{c}_i^\dagger\hat{c}_j], \quad (3.4)$$

where $\hat{c}_i^\dagger$ ($\hat{c}_i$) creates (anhilates) an electron on site i and, assuming a tight-binding approach, the summation run over nearest neighbors only. Analytical formulas for S_{ij} between $2p$ Slater type atomic orbitals $\mathbf{p}_{\pi,i}$ and $\mathbf{p}_{\pi,j}$ on sites i and j (arbitrary directions) have been obtained by Hansson and Stafström[17] from the master formulas of Mulliken *et al.*[30] Expanded to first order around the undimerized state, it is easy to show that for systems where all $2p$ Slater type atomic orbitals are orthogonal to the bond plane

$$S_{ij} = k^{-1}\cos(\Phi_{ij})[t_0 - \alpha(r_{ij}-a)], \quad (3.5)$$

where $\Phi_{ij} = \arccos(\mathbf{p}_{\pi,i}\cdot\mathbf{p}_{\pi,j}/|\mathbf{p}_{\pi,i}||\mathbf{p}_{\pi,j}|)$ is the angle between $\mathbf{p}_{\pi,j}$ and the projection of $\mathbf{p}_{\pi,i}$ with respect to revolution around the bond axis, and

$$t_0 = k\cdot f(a) = A\cdot(15+15a\zeta+6(a\zeta)^2+(a\zeta)^3), \quad (3.6)$$

$$\alpha = k\cdot f'(a) = A\cdot a\zeta^2(3+3a\zeta+(a\zeta)^2), \quad (3.7)$$

with $\zeta = 3.07$ Å^{-1} for the $2p$ orbitals of carbon and $A = k\cdot(e^{-a\zeta}/15)$. Equations 3.4–3.7 are the relevant formulas for the π-electrons in the systems treated in this thesis. Note though that if the orthogonality condition is not satisfied by all $\mathbf{p}_\pi$ vectors, π-electrons will mix with the σ-bonding system which would hence require an exact treatment also of this part of the Hamiltonian.

3.3 Statics

The starting point for further calculations is to retrieve the ground state conformation of constituent molecules. By definition this is the state of minimum total energy, E_{tot}, with respect to variations in $\{r_{ij}\}$ and may consequently be obtained from the condition

$$\frac{\partial E_{\mathrm{tot}}}{\partial r_{ij}} = \frac{\partial \langle \Psi_0 | \hat{H}_\pi + \hat{H}_{\mathrm{latt}} | \Psi_0 \rangle}{\partial r_{ij}} = 0, \tag{3.8}$$

where $|\Psi_0\rangle$ is the ground state determinant. In order to keep the molecular size of the system we also include the constraint that the total bond length change should be zero, i.e. $\sum'_{i>j}(r_{ij} - a) = 0$. Using the method of Lagrangian multipliers, it is easy to show that this constraint may be incorporated into the model by simply subtracting a constant term in the "distance spring part" of Eq. (3.3) such that,

$$\frac{K_1}{2}\sum_{i>j}{}' \left(r_{ij} - a - \frac{2\alpha}{K_1}\langle \rho \rangle \right)^2, \tag{3.9}$$

where $\langle \rho \rangle$ is the mean charge density. Incorporated into the lattice Hamiltonian, Eq. (3.8) is then solved in a self-consistent way using, e.g., the resilient propagation method RPROP,[10,36] so as to retrieve the geometrical configuration of the ground state.

At this point it is important to stress that the configurations obtained are for a specific set of parameters that must be optimized to reproduce the conformation, the charge distribution, the relevant part of the phonon spectrum etc., as retrieved by experiments and/or by *ab initio* calculations. This is a multi-objective optimization task to which evolutionary algorithms may be applied since the only requirement placed by the method is that one can evaluate an objective (cost) function f for a given set of input parameters $\mathbf{x}$. If, for example, our primary interest lies in reproducing the geometry (i.e., the molecular bondlengths r_{ij}) and bandgap energy E_g of a molecule, we define, e.g., a scalar valued molecular cost function

$$f(\mathbf{x}) = |E_{g,\,ab} - E_{g,\,og}(\mathbf{x})| + \sum_{i>j}{}' |r_{ij,\,ab} - r_{ij,\,og}(\mathbf{x})|, \tag{3.10}$$

ab being an index for *ab initio* values and *og* an index for values of the *optimized geometry* retrieved from the solutions to Eq. (3.8), and minimize f with respect to $\mathbf{x}$ using a genetic algorithm that repeatedly modifies a population of individual solutions $\{\mathbf{x_i}\}$ over a predefined number of generations n_g. At each step, the algorithm generates n_e children that are exact copies of the three individuals with the best fitness values, n_m children that are uniformly selected individuals with random numbers of normal distribution appended to each vector element, and n_c children that are weighted arithmetic means of two parents chosen through roulette selection within the current population. For a continuous population size of 20 individuals evolving over n_g=100 generations with n_e=3, n_m=6, and n_c=11, an optimal parameter set that minimizes f is typically found within 30 to 40 generations.

3.4 Dynamics

Nontrivial dynamics may now be obtained if the ground state of the system is perturbed by an external force. In this thesis, we focus mainly on field induced charge carrier dynamics, but also excitation dynamics has been studied. Since the later does not add to the methodological description of the former, we shall here focus on the incorporation of the electric field $\mathbf{E}(t)$ into $\hat{H}$.

In our approach we take the field into account in the Coulomb gauge, i.e., by a scalar potential. Since periodic boundary conditions are not applicable in the Coulomb gauge, this will restrict us to use only finite sized systems. We further assume that the electric field is uniform in space and constant in time after a smooth turn on described by a half Gaussian function of width t_w centered at t_c. The external electric-field contribution to the Hamiltonian then read $\hat{H}_E(t) = |e| \sum_i \mathbf{r}_i \mathbf{E}(t)(\hat{c}_i^\dagger \hat{c}_i - 1)$, with the electric field in the $\hat{e}$-direction defined such that $\mathbf{E}(t)$=$E_0 \exp[-(t-t_c)^2/t_w^2]\hat{e}$ for $t < t_c$, and $E_0\hat{e}$ otherwise. Incorporated into $\hat{H}$, we arrive at the following expression for the total system Hamiltonian

$$\hat{H} = \hat{H}_\pi + \hat{H}_E + \hat{H}_{\text{latt}} = \sum_{i,j}{}' \hat{c}_i^\dagger h_{ij} \hat{c}_j - |e| \sum_i \mathbf{r}_i \mathbf{E}(t) + \hat{H}_{\text{latt}}, \tag{3.11}$$

the first term in the right hand part being the previously introduced $\hat{H}_{\text{el}}$.

With the aid of $\hat{H}$ we may now unravel the interdependence between Eqs. (3.1) and (3.2) through the time-dependent density matrix elements $\rho_{ij}(t)$. If in mean-field approximation we make the anzats that $\rho_{ij}(t) = \sum_p \psi_{ip}^\dagger(t) f_p \psi_{jp}(t)$, where $f_p \in [0, 1, 2]$ is the time-independent occupation number of the pth molecular orbital, then $\psi_{ip}(t)$ will be solutions to the time-dependent Schrödinger equation

$$i\hbar\dot{\psi}_{ip}(t) = \sum_j h_{ij}(t)\psi_{jp}(t), \tag{3.12}$$

and Eq. (3.2) resolves into the generalized Hellmann-Feynman theorem[1] for the ionic forces

$$M\ddot{\mathbf{r}}_i = -\sum_p f_p \, \psi_{ip}^\dagger(t) \langle \frac{\partial H}{\partial \mathbf{r}_i} \rangle \psi_{jp}(t) - \lambda \dot{\mathrm{r}}_i. \tag{3.13}$$

Expanding the time-dependent molecular orbitals $\psi_{ip}(t)$ in a basis of instantaneous eigenfunctions[7]

$$\psi_{ip}(t) = \sum_{p'} \varphi_{ip'}(t)\alpha_{p'p}(t), \tag{3.14}$$

defined by $\sum_j h_{ij}(t)\varphi_{jp}(t)$=$\varphi_{ip}(t)\epsilon_p(t)$, we obtain, additionally, the time-dependent occupation number of the eigenstate as

$$n_p(t) = \sum_{p'} f_{p'} |\alpha_{pp'}(t)|^2. \tag{3.15}$$

Since we expect that eigenstates will come close to each other in energy and nonadiabatic transitions therefore to occur, we rather solve Eq. (3.12) and Eq. (3.13) simultaneously, allowing for a time-dependent occupation of instantaneous eigenstates.

CHAPTER

FOUR

Comments on Papers

Having detailed the theoretical framework of which I have been a part of developing, the purpose of this chapter is to give a brief introduction to the papers included in this thesis and highlight the main results that were obtained. In this context I would like to point out that although I have performed all calculations and written most of the text in these papers, I have been firmly supervised by my coauthor Professor Sven Stafström.

4.1 Paper I

In the first paper we study polaron dynamics in highly ordered molecular crystals and in particular the transition from adiabatic to nonadiabatic transport across the region of intermediate intermolecular interaction strength, J, where neither band theory nor perturbative treatments like the Holstein model[20] or extended Marcus theory apply.[6] For this purpose we rely on the methodological framework presented in Chapter 3 and use the time evolution of the occupation number $n_p(t)$ in Eq. (3.15) as a signature of the adiabaticity at hand. As a model system we use single crystal pentacene, but the value of J is varied to simulate different types of molecular crystals. This allows us to demonstrate the capability of our model to study carrier dynamics in the desired region of intermolecular interaction strength. The constraint of time-independence in intermolecular overlap introduced in order to enable this study can in principle be lifted with a second set of parameters to account for the dynamics of the inter-atomic interactions in-between the molecules.

4.2 Paper II

The second paper concerns the impact of phenylene ring torsions on the intra-chain mobility in conjugated polymers. For this purpouse we expand the SSH-model fully into three dimensions such that the modulation of hopping integrals caused by the torsion of rings around σ-bonds may be incorporated. Note though

that the distribution in torsion angles is treated within a static picture since the dynamics of polaron transport occurs at a timescale which is considerably faster than the dynamics of phenylene ring torsion.[9] Within this treatment we show that variations in ring torsion angles along a conjugated polymer chain have a strong effect on intra-chain charge carrier mobility. Variation in ring torsion along the polymer chain can cause electron localization and thus change the type of transport from adiabatic polaron drift to nonadiabatic polaron hopping. In particular, we show the sensitivity for such a transition in the case of random variations in the ring torsion angles along a PPV chain. The effective energy barrier associated with the change in torsion angle also depends on the applied electric field strength and by increasing the field strength a transition back to adiabatic transport can be obtained.

4.3 Paper III (in manuscript form)

Finally, in the third paper we study relaxation dynamics in molecular crystals following the initial excitation of an electron from an occupied to an unoccupied level well above the bandgap energy. Due to the strong electron-phonon coupling in the π-conjugated systems of interest here, the change in the electron density associated with the excitation will induce vibrational modes, or phonons, into the lattice. The processes by which the electron and the hole then relax towards lower lying states can involve, e.g., direct radiative recombination of the exciton, nonradiative relaxation between molecular states of the same spin multiplicity (termed internal conversion),[25] or even exciton dissociation into an electron-hole pair.[2] From experimental studies on α-hexathiophene,[13,16] rubrene,[31] and pentacene,[18,33] however, the dominant relaxation channel in π-conjugated molecular crystals from upper excited states has been identified to be internal conversion, wherefore the focus of the article is on nonradiative relaxation dynamics.

As a model system for molecular crystals we use single crystal pentacene and employ the procedure in Section 3.4 to monitor the coupled electron-phonon dynamics of the system. In particular, for a 10 molecule large system, we have studied the nonradiative relaxation process of excitons towards the first excited state, i.e., with the hole in the highest occupied molecular orbital (HOMO) and the electron in the lowest unoccupied molecular orbital (LUMO), both within and in-between bands of narrow spaced eigenstate energies. For intra-band transport we observe internal conversion stimulated by the transfer of energy from the electronic to the vibrational degrees of freedom followed by the decay of the phonon occupation number, which is in qualitative agreement with experimental results. Since the relaxation which we consider is entirely nonradiative we also observe the evolution of a stable polaron-exciton with corresponding eigenstate energies well within the band gap. For the situation when also inter-band transitions are considered we observe internal conversion processes much slower than what has been reported from experiments. We belive that this is because in real systems disorder and other irregularities limit the symmetry conditions for interband transitions imposed by an intrinsic system.

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