Electronic excited states in quasi-one-dimensional organic solids with strong coupling of Frenkel and charge-transfer excitons
Electronic excited states in quasi-one-dimensional organic solids with strong coupling of Frenkel and charge-transfer excitons

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Parts of this work have been published in the following articles and conference contributions

Articles


Conference contributions


Introduction

The seemingly infinite variety of organic materials represents an almost incomprehensible potential to create new or alternative approaches to realize highly customized functionalities. The high expectations invested into organic compounds are fueled by the experiences already made in the field of standard inorganic materials, in particular semiconductors such as silicon, germanium, GaAs, and others. The properties known for the bulk materials have been largely modified by utilizing the materials in artificial structures such as quantum wells [1], quantum wires and quantum dots [2]. The electronic states responsible for the bulk behavior are characterized by bands of weakly bound charge carriers, rather than by the localized states of the atoms. The initial bulk states have been altered by either combining different materials, e.g., by alternating layer-by-layer deposition in case of quantum wells [3], or by exploiting finite size effects emerging in tiny clusters used, e.g., as quantum dots [2].

In organic materials, much more degrees of freedom are available to tailor properties. The choice of the class of material determines which particular degree is eventually exploited. One degree of freedom is given by the molecule itself. The prototypical molecular crystal, such as anthracene, tetracene, and pentacene, consists of generously spaced and weakly bound molecules. Due to the very small overlap of the molecular wave functions, adjacent molecules hardly influence each other. Thus, the character of the low energy electronic states of the isolated molecule is preserved to a large degree in the condensed phase.

Another degree of freedom is given by the possibility to combine molecular units to larger molecules, such as polymers and proteins. The chemical bonding between the constituent units and their mutual steric alignment can significantly modify the electronic states of the individual components. As a third degree of freedom, successfully applied by nature, the three-dimensional spatial arrangement of largely extended molecules can provide or inhibit the formation of certain properties. The arrangement of protein spacer units carrying the chromophoric units in the photo-synthesis reaction center in purple bacteria (schematically sketched in Figure 1.4) may serve as an example.

Organic materials increasingly penetrate the technological areas dominated by conventional materials. Several well known devices, such as light-emitting diodes [4, 5, 6], solar-cells [7, 8], and field effect transistors [9, 10] designed entirely on the basis of organic materials have been successfully demonstrated. At a first glance, the functionality of these devices appears to be similar to their inorganic-based ancestors. However, the physical concepts applied are significantly different. Moreover, the potential provided by organic materials inspires the application of concepts never feasible with purely inorganic materials. As one of the first but ambitious ideas, scientists try to adopt functions known from biological systems.

The physics taking place in thin films needs be understood, in order to incorporate the organic substances in technologically relevant applications. In particular it is necessary to
be aware of effects connected to the geometrical arrangement of the molecules or effects attributable to the boundaries and interfaces present.

This work aims to contribute further insight into the optical properties of a special class of small molecule materials. Our interest focuses on materials which belong to a sub-group of the so-called quasi-one-dimensional molecular crystals. The crystals and related clusters can be considered as a first link between ‘traditional’ molecular crystals, such as anthracene, and polymers. We will investigate the formation of the lowest excited states depending on both the circumstances arising from given by a spatial arrangement of the molecules and the presence of boundaries.

To distinguish this group of materials from J-aggregates, assemblies which can be quasi-one-dimensional (rod-like) as well, we narrow the range of considered materials as follows: The crystals of the quasi-one-dimensional materials we are interested in consist of planar aromatic molecules which are arranged in face-to-face stacks providing a strong overlap of the molecular wavefunctions. The distance between molecules in this stacking direction is much smaller than in the others.

In a large number of PTC-derivatives (molecules sharing a perylene tetracarboxylic acid core), these conditions are met. Among them are the representatives 3,4,9,10-perylene-tetracarboxylic dianhydride (PTCDA) and N,N'-dimethyl-3,4,9,10- perylene-tetra carboximide (MePTCDI) [11, 12, 13] (Figure 1.1(a),(b)). In the crystal, sketched in Figure 1.1(c)-(f), the molecular planes within the stacks are separated by 3.40 Å in MePTCDI [11] and 3.37 Å in PTCDA [14, 15]. This separation is small in comparison with other lattice constants and also small in comparison with the size of the molecules. As a result, the interactions of the π-electron systems within the stacks is very strong, compared with the interaction in the other directions.

Another prominent class of pigments known to form columnar molecular crystals are phthalocyanines. Phthalocyanines (Pc), in particular metal phthalocyanines, condensate in various crystalline structures. A coordination with central atoms of the transition metal series (e.g. doubly ionized transition metals, Cu$^{2+}$, Zn$^{2+}$ [16]), or Mg$^{2+}$ [16], keep the ligand phthalocyanine rings almost planar and hence aromatic. In Figure 1.2(a), the chemical structure of the MgPc molecule is shown. Several crystal modifications of these complexes are quasi-one-dimensional, such as MgPc [17] and the α-and β-phase of ZnPc [18]. For MgPc, we depict the molecular arrangement of the molecules within the crystals in panels 1.2(b),1.2(d) of Figure 1.2. In the stacks (Figure 1.2(d)), the molecular planes are separated by 3.19 Å. This distance can be detuned by integration of solvent molecules into the crystal [19].

Besides crystals, also much smaller aggregates with a face-to-face stacking of the phthalocyanine rings are known, e.g., the dimers SnPc$_2$ [20], LuPc$_2$ [21], SiPc$_2$ [22], and the μ-oxo dimer (SiPc)$_2$O. In such a face-to-face arrangement, the rings which are linked by a metal atom (or a metal containing unit) are parallel, but rotated by certain angle against the shared rotation axis of the rings. We sketched the geometry of a trimer compound analogous to LuPc$_2$ [23, 24] in Figure 1.2(c). Adjacent rings in this Lu$_2$Pc$_3$ cluster are rotated against each other by 45$^\circ$ and separated by 2.9 Å.
Figure 1.1: Structural formula and crystal geometry of the PTC-derivatives PTCDA and MePTCDI. The chemical structure of the molecules is given in the upper part (a),(b). The lower parts show the crystal structure of the materials; according to Refs. [14, 15] for PTCDA and Ref. [11] for MePTCDI. The projections of the crystal structure onto the (010) plane reveal the columnar stacking along the a-axis (pictures (e),(f)). In the additional projections onto the (100) plane (pictures (c),(d)), the two molecules belonging to one unit cell are highlighted. It is obvious from these projections that the quasi-one-dimensional columns are well separated from each other.
The electronic and optical properties of these compounds are strongly determined by the interaction between the molecules. The close stacking ensures a rather small interplanar distance. All members of one family of materials share an identical carbon(-nitrogen) backbone. The different spatial extension of particular substituents cause different sterical alignments of the molecules in the crystal [26] and in clusters. Within the stacks, the molecular planes are parallel to each other, their bulky side groups determine the interplanar separation and force adjacent molecules to arrange shifted with certain offsets against each other (Figure 1.3). Owing to the offsets, the molecules appear tilted against the stacking axis. It can be clearly seen from Figures 1.1(f), 1.1(e), and 1.2(d) that the tilting is specific for each modification.

The specific molecular arrangement motivates to consider the solid to be composed of weakly interacting stacks. The crucial effects determining the composition of the electronic states of the entire solid are expected to occur within the stacks, whereas the influence of surrounding molecules belonging to other stacks are expected to be minor corrections. Hence,
we idealize the crystal by considering the isolated stack. The description of such stacks relies on the investigation of finite, and in the case of crystals, infinite linear molecular chains.

Due to the small overlap typically present between the molecular wave functions, the lowest excited states in non-quasi-one-dimensional molecular crystals, to which we will refer as excitons throughout this work, are essentially composed of molecular excitations. In the case of quasi-one-dimensional materials, the excited states are expected to be of larger complexity. The overlap between molecular wave functions of close-by nearest neighbors in the stack can become considerably large, although still being small in comparison with the overlap between covalently bound partners. Under this precondition, the energy of localized nearest neighbor charge-transfer (CT) excitations, i.e., excitations which involve two molecules simultaneously, might become small enough to appear energetically close to the molecular excitations. Hence, the CT excitations can play an important role in the formation of the lowest energy excitons.

The inclusion of charge-transfer states has an important consequence. If a coupling between molecular excitation and localized CT excitations is possible, two different possibilities to transport excitation energy through the aggregate are opened: A molecular excitation, localized at one site, can be transferred as a whole to another site. However, a non-vanishing charge transfer integral allows in a first step the dissociation of a molecular excitation into a CT excitation where either an electron or a hole, respectively, are transferred to another - preferably nearest neighbor - site. In a second step, the counter charge, i.e., the hole or the electron, respectively, is transferred to the second site by forming there a molecular excitation again.

In biological systems, aggregates of chromophores, located as functional sub-groups on large macro-molecules, are potential candidates for such a description. The spectroscopic properties of photosynthetic reaction centers in the purple bacterium *Rhodopseudomonas viridis*, consisting of closely spaced bacteriachlorophylls, are determined by a considerable mixing of molecular and CT excitations [28, 29]. Another part of the photosynthetic unit, the light harvesting antenna complex, consists of similar chromophores. To understand the energy transfer from the antenna to the reaction centers, the electronic structure of the antenna must be available. The light harvesting antenna complex LH2 of the purple bacteria *Rhodopseudomonas molischianum* [30] and *Rhodopseudomonas acidophila* [31] is formed by a (chain like) circular aggregate of bacteriachlorophylls (Figure 1.4). The presence of relatively closely spaced chlorophyll units demands the investigation of the role and potential admixture of intermolecular CT excitations [30, 31].
Figure 1.4: Schematical illustration of the photosynthetic unit of the bacterium *Rhodobacter sphaeroides*. Shown is the arrangement of light harvesting (LH) complexes and the reaction center (RC). Clearly seen are the cyclic aggregates formed of the chromophores, the bacteriochlorophylls (B). Particularly closely arranged are the chromophores B850, B875, $P_A$, and $P_B$. Adapted from Refs. [32, 33].

The model which we will develop in this work allows us to investigate the formation of the lowest electronically excited states dependent on the degree of CT admixture. We organize this work as follows: The starting Chapter 2 briefly reviews possible methods to obtain the excited states and the corresponding electronic spectra in finite linear aggregates. In particular, the essential idea of the small radius exciton theory is worked out. In Chapter 3, we establish the small radius exciton description of the electronically excited states in linear finite chains. We shall explicitly formulate the model Hamiltonian for strong coupling of Frenkel and charge transfer excitons. All parameters characterizing the Hamiltonian are initially left unassigned in order to study all possible constellations arising from different molecular alignment in general. Motivated by strategies applied within systems with periodic boundary conditions, we will develop a partly analytical procedure to obtain the eigenstates of the Hamiltonian, which are the electronic excited states. The whole set of eigenstates obtained in a finite chain possesses a larger variety than the eigenstates known from the pure Frenkel case. The properties of these excitons and their relation to special features of each system given are analyzed in Chapter 4. As a further key point we are interested in the impact of the chain length on the electronic spectrum. Throughout Chapter 5, we discuss quantitatively the size dependent behavior of the excitonic states and quantum confinement. In the last Chapter 6, we return to the materials which triggered the investigations presented in this work. For the representatives MePTCDI and PTCDA, which served as model compounds of many experimental and theoretical investigations before, we will extract the model Hamiltonian of all compatible model proposals available and demonstrate the consequences which arise from the finite chain description.
Treatment of finite linear molecular chains: A survey

The description of finite linear molecular chains involves several strategies. It is natural to expect that different strategies are utilized since finite chains include very small chains, containing two or three molecules, as well as largely extended chains. For each range of chain lengths, a certain concept turns out as the most accurate. Moreover, the methods must also contain either the limiting case of a single isolated molecule or of the infinite chain, e.g., by applying periodic boundary conditions.

In this chapter we briefly survey two approaches: The first concept to find the electronic excited states of an arbitrary cluster or chain utilizes quantum chemical methods. Methods typically applied start out from the pure many electron problem where the motion of the atomic nuclei has already been separated in Born-Oppenheimer approximation. The procedure does not regard the binding status of an atom, all necessary information is given by the position of the atoms in real space and their type. Hence, no distinction between intra- and inter-molecular interactions is made.

An alternative framework is provided by the small exciton theory. Small radius excitons are used to describe elementary collective electronic excitations of molecular crystals that consist of weakly interacting molecules. This standard tool to investigate excited states in organic molecular crystals \cite{34} initially distinguishes between intra- and intermolecular properties.

Figure 2.1 may serve us as a guide to correlate the methods which have been most relevant for this work with its application range.

2.1 The quantum chemical approach

The pool of quantum chemical methods encompasses a huge range of possible application fields. The demand to describe a high material diversity starting exclusively from their atomic composition, but with reasonable effort leads to highly specialized quantum mechanical algorithms. Down to the present day, the calculation of the lowest excited states in larger aromatic molecules and molecular clusters, or chains, respectively, is predominantly carried out using semi-empirical, self consistent HARTREE-FOCK (SCF-HF) methods with Configuration Interaction (CI).
Figure 2.1: Overview on the treatment of finite molecular chains. The displayed methods span a large range of possible chain lengths $N$. The special quantum chemical method abbreviated with ZINDO/S + CIS is introduced in Section 2.1.1.

number of molecules $N$

- Infinite chain
- Finite chain
- Single molecule

- Quantum chemistry
- Conjugation analysis
- ZINDO/S + CIS
- Quantum chemistry
- Small cluster calculations
- Idealized boundary conditions
- Quantum chemical treatment
- Exclusion theory
- On-site shell of boundaries
- Inclusion of vibronic states
- Diagonalization
- Diagonalization
- Partially analytical treatment
- Quantum-momentum $k$
- Idealized boundary conditions
- Periodic boundary conditions
- Exclusion theory
- Quantum-momentum $k$
- Quantum-momentum $k$
- Quantum-momentum $k$

$N = \infty, 80, 81, 22, 21, 20, 8, 7, 6, 5, 4, 3, 2, 1$
2.1 The quantum chemical approach

We will briefly sketch the typical steps and approximations made to obtain the solutions of the general \( n \) electron problem\(^1\). Our focus is laid on essential ideas, sometimes of merely technical nature, which allow us later to recognize relationships to the small radius exciton description.

2.1.1 Calculation of excited states with standard Hartree-Fock methods

a) Molecular spin orbitals and Slater determinants
In Born-Oppenheimer approximation, we search for the electronic wave functions \(|\Phi\rangle\) with the atomic nuclei fixed; formally expressed by the stationary Schrödinger equation:

\[
\hat{H}|\Phi(x_1, \ldots, x_n)\rangle = E|\Phi(x_1, \ldots, x_n)\rangle .
\]

(2.1)

Any solution \(|\Phi\rangle\) depends on the general coordinates \(x\) of all electrons. The coordinate \(x = (r, \sigma)\) combines both the spatial coordinates \(r\) and the spin coordinates \(\sigma\) of an electron. Each solution has to obey the Pauli-principle, hence \(|\Phi\rangle\) is an element of the \(n\)-particle antisymmetric Hilbert sub-space. To prepare the ground for further approximations, a convenient basis set \(\{\Psi_j\}\) has to be chosen to expand the states \(|\Phi\rangle\) in the form

\[
|\Phi(x_1, \ldots, x_n)\rangle = \sum_j C_j^j|\Psi_j\rangle .
\]

(2.2)

Usually, Slater determinants are used as basis-functions. They are antisymmetrized product states composed of single particle wave functions \(|a\rangle\), the so-called spin orbitals:

\[
|\Psi_j\rangle = \frac{1}{\sqrt{n!}} \begin{vmatrix}
 a_1(x_1) & a_2(x_1) & \cdots & a_n(x_1) \\
 a_1(x_2) & a_2(x_2) & \cdots & a_n(x_2) \\
 \vdots & \vdots & \ddots & \vdots \\
 a_1(x_n) & a_2(x_n) & \cdots & a_n(x_n)
\end{vmatrix} \equiv |a_1 a_2 \ldots a_n\rangle^{(-)} .
\]

(2.3)

The antisymmetrization of the product state which ensures the fulfillment of the Pauli-principle, shall be emphasized by the superscript \((-)\) at the Dirac brackets. Each spin orbital consists of a spatial wave function \(a(r)\) and an independent spin wave function \(\alpha(\sigma)\):

\[
a_i(x) = a_i(r, \sigma) = a_i(r) \alpha(\sigma) .
\]

(2.4)

When the total number of considered electrons is even, i.e., all electrons are expected to be paired in the ground state, always two spin orbitals can be approximated by spatial orbitals which share the same spatial function but vary in the spin adjustment:

\[
a_i(x) = a_i(r, \sigma) = \begin{cases} a_i(r) \alpha(\sigma) = a_i(r) \\ a_i(r) \beta(\sigma) = \bar{a}_i(r) \end{cases} .
\]

(2.5)

This closed shell approximation is used in the so-called Restricted Closed Shell Hartree Fock method.

If the single-particle wave functions form a complete set in the one-particle Hilbert space, the set \(\{\Psi_j\}\) of all Slater determinants forms a complete set in the \(n\)-electron space. This

---

\(^1\)Typically, the number of electrons or particles, respectively, is denoted with a capital \(N\). Since the symbol \(N\) will be assigned otherwise later in this work, we use instead \(n\).
correspondence between one-particle and \( n \)-particle Hilbert space is of vital importance for the consideration and further analysis of excited states. For technical reasons during real calculations, the completeness of the basis set can be kept neither in the one-, nor in the \( n \)-particle space. However, the necessarily truncated sets are still inevitably connected by relationship (2.3).

b) The Hartree Fock method

The HARTREE-FOCK approximation represents the ground state \( |\Phi_0\rangle \) with the simplest possible antisymmetric wave function, with one Slater determinant. According to the Ritz variational principle, the ground state \( |\Phi_0\rangle \) corresponds to the wave function which minimizes the expectation value \( E_0 \) of the electronic Hamiltonian with respect to \( |\Phi_0\rangle \):

\[
E_0 \langle \Phi_0 | \Phi_0 \rangle = \langle \Phi_0 | \hat{H} | \Phi_0 \rangle \rightarrow \text{Min}.
\]  

(2.6)

With the restriction to one \( |\Psi\rangle \), correlation effects are neglected, i.e., in Hartree Fock approximation the motion of electrons with opposite spin is not correlated.

The variational step which is carried out with respect to the spin orbitals leads to the HARTREE-FOCK equations; a set of equations which determines the optimal set of spin orbitals \( |a_i\rangle \). Each equation has the form of an eigenvalue problem:

\[
\hat{f}_i |a_i\rangle = \varepsilon_i |a_i\rangle \quad \forall i,
\]

(2.7)

where \( \hat{f}_i \) is an effective one-electron operator (FOCK operator), in which the electron-electron repulsion is considered as the average potential experienced by electron \( i \) due to the presence of the other electrons. Hence, the Fock operator \( \hat{f}_i \) depends on the eigenfunctions of the other electrons. Correspondingly, the equations (2.7) are nonlinear and have to be solved in a self-consistent way and yield a complete, infinite, and orthonormal set of HARTREE FOCK orbitals which form is by no means initially determined. In practice, however, the solving procedure SCF (self-consistent field) method calculates the HF orbitals as superposition of a finite set of functions \( |\mu\rangle \):

\[
|a_i\rangle = \sum c^{\mu}_{i} |\mu\rangle.
\]

(2.8)

The more basis functions the set \( |\mu\rangle \) contains, the more flexibly the spin orbitals (2.4) can be represented and the lower the expectation value (2.6) becomes. In a typical approach, the LCAO method (linear combination of atomic orbitals), the MO are expanded into so-called atomic orbitals \( |\mu\rangle \) which are hydrogen-like functions.

c) Excited states and Configuration Interaction

The calculation of excited states and the consideration of correlation effects is realized in the framework of Configuration Interaction (CI). It is obvious that the HARTREE FOCK ground state is only one basis element of the set which spans the entire \( n \)-particle space. However, with the help of the scheme of molecular orbitals obtained from the SCF calculation, the other basis elements \( |\Psi_{j>0}\rangle \) can be constructed which are necessary to correctly characterize any arbitrary many-particle state in the form (2.2). Starting from the HF ground state determinant \( |\Psi_0\rangle \) as reference, further determinants \( |\Psi_j\rangle \), so-called configurations, are generated by redistributing electrons from occupied to formerly unoccupied orbitals (see Figure 2.2).
2.1 The quantum chemical approach

The method with which the excited states in the basis of configurations are calculated is called Configuration Interaction (CI).

Calculations which focus on transition energies between ground and excited states typically restrict the expansion (2.2) to singly excited configurations

\[ |S_k⟩ = \sum C_{k}^{rs}|a_r \rightarrow a_s⟩ \] (2.9)

which are, as shall be demonstrated here for the closed shell approximation, generated by the promotion of one electron from an orbital \( r \) to an orbital \( s \) [35]. We further permit no change of the total spin upon excitation. Then, still in the framework of closed shells, the ground and all considered excited states are singlets. With this restriction, the singly excited configurations introduced in (2.9) are defined as singlets:

\[ |a_r \rightarrow a_s⟩ = \frac{1}{\sqrt{2}} \left( |a_1 \bar{a}_1 \ldots a_r \bar{a}_s \ldots⟩^{(-)} + |a_1 \bar{a}_1 \ldots \bar{a}_r a_s \ldots⟩^{(-)} \right) \] (2.10)

The final excited states \( |S_k⟩ \) are calculated by solving the equation

\[ \hat{H}|S_k⟩ = E_k|S_k⟩ \] (2.11)

which takes after inserting the ansatz (2.9) for \( |S_k⟩ \) the form of an eigenvalue problem in the coefficient matrix \( C_{k}^{rs} \). The ground state \( |Ψ_0⟩ \) obtained from RHF calculations cannot be improved anymore, since according to the theorem of BRILLOUIN [36] the ground state does not mix with excited configurations anymore.

\[ ^{2}\text{This formalism is abbreviated as CIS.} \]
d) Semi-empirical methods

For molecules containing 30 atoms (preferably carbon, oxygen, and nitrogen) and more, the calculation of the ground state and the excited states is very demanding, let alone of clusters containing more than one of these molecules. Up to the current day, first-principles HF calculations of the electronic properties of the kind of molecules we introduced in Chapter 1 are still rare. Exemplarily, the ab-initio treatment of an MgPc molecule presented in reference [37] has never been extended to dimers so far. To cope with such large systems, the calculation scheme has been simplified. In the so-called semi-empirical methods, two essential approximations are made.

The first approximation restricts the number of considered atomic orbitals necessary for the LCAO ansatz. The basis set consists of the $s$-, $p$-, and, in case metal atoms are present, $d$-type orbitals of the valence electrons. Further, the hydrogen-like wave functions are approximated by Slater-type orbitals which have been proven to describe the properties of covalently linked atoms conveniently.

The second essential simplification affects the calculation of matrix elements in AO representation. Since any matrix element incorporating many-particle states can be reduced to integrals over MO and hence to integrals over AO, the consequences of this approximation are felt in any step of the calculation, both in the SCF calculation and in the final CI.

In the course of the calculation, several matrix elements are either neglected completely or substituted by simpler expressions which often contain adjustable parameters. All NDO (Neglect of Differential Overlap) methods, such as CNDO, MNDO, PM3, AM1, INDO, or ZINDO, are based on the Zero Differential Overlap (ZDO) approximation. In this approximation, any overlap between the orbitals of different atoms is neglected, and hence all matrix elements involving AO which are located at different atoms are forced to be exactly zero. Once applied, the relationships between the atomic orbitals take the simple form of the corresponding relationships between orthonormal orbitals. Since thereby the existing inter-atomic interactions would have been dramatically reduced, several interactions are reintroduced. In particular, the ZINDO method (Zerner’s Intermediate Neglect of Differential Overlap) [38, 39, 40] sets the one-electron integrals proportional to the overlap of the incorporated AO’s. Two-electron repulsion integrals appear as one single parameter if all AO are located at one atom (one-center integrals). Alternatively, if the incorporated AO’s are located at two different atoms $A$ and $B$, all matrix elements of the Coulomb type

$$
\langle \mu A | \frac{1}{|r_1 - r_2|} | \nu B \rangle = \int \int d^3r_1 d^3r_2 \mu^*(r_1)\nu^*(r_2) \frac{1}{|r_1 - r_2|} \mu(r_1)\nu(r_2), \quad (2.12)
$$

are set dependent on the separation of the two atoms $A$ and $B$. Besides these parameterizations which are typical for all INDO methods, ZINDO provides two empirical factors $F_\pi$ and $F_\sigma$. Developed to describe the properties of large aromatic molecules which are governed by the $\pi$-electron system, the recommended factors $F_\pi = 0.585$ and $F_\sigma = 1.267$ [41] are adjusted to support the leading role of $p_\pi$-interactions even more.

For PTC-derivatives [42, 43] and for phthalocyanines (viewed as porphyrine-derivatives in the most general sense) [16, 19, 25, 44], extensive studies using INDO methods are available. In comparison to the standard INDO or ZINDO, respectively, the special methods INDO/S and ZINDO/S [38, 39, 40] have been used which feature especially modified parameters to calculate UV-VIS spectra accurately.

These calculations confirm that the low energy part of the UV-VIS spectrum of PTC-derivatives is governed by one relevant molecular transition polarized along the long molecular axis [43, 45] (for more details see Chapter 6.1). Single phthalocyanine molecules exhibit
2.1 The quantum chemical approach

Figure 2.3: Correspondence of localized (left) and ‘supermolecular’ orbitals of a trimer (right). Shown are the highest occupied (HOMO) and lowest unoccupied molecular orbitals (LUMO) of the single molecules and their relationship with the highest occupied and lowest unoccupied MO of the entire cluster. Adapted from Ref. [47].

two degenerate, dipole-allowed transitions which are energetically well separated from higher-energy transitions [21, 46]. The corresponding transition dipole moments are perpendicular to each other and polarized within the molecular plane.

2.1.2 Supermolecular approaches and localization

a) Calculation of clusters as supermolecules

The most obvious and accurate way to get the electronic structure of clusters containing more than one molecule is, of course, to calculate the entire cluster at once. These calculations start out from the spatial distribution of all atoms. Thus, no artificial distinction between intra- and inter-molecular interactions is made.

The HF-SCF calculations yield the ground state of the whole composite (see Figure 2.3 right). Each orbital is allowed to spread over the whole aggregate. Hence, also the configurations necessary to construct the excited states in the CI reflect the geometrical symmetry of the whole cluster.

As already mentioned, the computational effort to perform first-principle HF calculations
on clusters still exceeds acceptable expenses. Hence, semi-empirical methods are the tool of choice. However, most of the available methods do not treat intra- and inter-molecular interactions in exactly the same fashion: Many of such numerical methods contain parameter modifications which have been optimized to describe polyaromatic molecules with a high accuracy. In particular, the interactions of the $p_z$-orbitals in $\pi$-alignment (see Figure 2.4 left) have been favored. In principle, such adjustments are not desirable as soon as interplanar interactions between $\pi$-systems come into play. The schematical illustration in Figure 2.4 shows for stacked ethylene molecules the shortcomings of a $\pi$-favoring parameterization.

The interplanar $\pi-\pi$ interaction is important for the formation of band structures in large stacking systems with semiconducting properties. The term $\pi-\pi$ interaction itself indicates by no means its actual origin in terms of interacting atomic orbitals; it is used to address the non-covalent interactions between the molecular $\pi$-systems, as proposed in reference [27]. With the co-facial stacking, the alignment of $p_z$-orbitals of one molecule with respect to $p_z$-orbitals of an adjacent molecule corresponds neither to an arrangement with $\pi$-symmetry nor to $\sigma$-symmetry; both ideal alignments are shown in the center panel of Figure 2.4. In reality, the interaction of $p_z$-orbitals contains contributions of both $\pi$- and $\sigma$-character (Figure 2.4, right). Normally, the modifications of the semi-empirical parameterizations remain unchanged for the stacking situation. One way to account for the stacking is offered by the empirical factors of ZINDO/S with which the $\pi$ and $\sigma$-type interactions can be balanced. In references [48, 49], the ZINDO/S method adjusted with $F_{\pi} = 0.585$ and $F_{\sigma} = 1.000$ has been successfully applied to face-to-face dimers of several polycyclic aromatic molecules.

In the present state, semi-empirical calculations can provide the exited states of clusters containing up to 10 molecules of PTC-derivatives or clusters with even less phthalocyanine molecules with acceptable effort and accuracy. Hence, supermolecular calculations cover only a tiny range of cluster sizes (cf. Figure 2.1).

b) Advanced Composite-Molecule and Configuration Analysis

Of course, it is desirable to relate the obtained excited states to the properties of the molecular sub-units.

A very intuitive approach to get information about the contribution of the individual
2.1 The quantum chemical approach

molecular excitation

$$|\text{ME}_B \rangle = |a^B_H \rightarrow a^B_L \rangle$$

charge-transfer excitation

$$|\text{CT}_{B \rightarrow A} \rangle = |a^B_H \rightarrow a^A_L \rangle$$

Figure 2.5: Assignment of singly excited configurations constructed from a localized orbital set.

molecules to the electronic states of the entire structure is called Advanced Composite-Molecule method [50], also known as molecule-in-molecule method [51]. The essential idea is to split the calculation into two steps. Firstly, the ground state of the isolated molecule (molecule A in Figure 2.3)

$$|0^A \rangle = |a^A_1 \bar{a}^A_1 \ldots a^A_H \bar{a}^A_H \rangle$$

is calculated as accurately as possible\(^3\). With the orbital scheme combined from all isolated molecules we can formally construct the ground state of the entire aggregate. For the example shown in Figure 2.3 (left), the corresponding ground state reads:

$$|0 \rangle = |0^A \ldots a^B_H \bar{a}^B_H a^B_C \bar{a}^C_C \rangle$$

Starting out from the aggregate ground state, singly excited configurations can be generated within the combined orbital scheme: A configuration indicated in Figure 2.5 is formed as follows:

$$|a^B_H \rightarrow a^B_L \rangle \equiv |\text{ME}_B \rangle$$

$$= \frac{1}{\sqrt{2}} \left( |0^A \ldots a^B_H a^B_H a^C_C \rangle \right).$$

Any generated singlet configuration can be interpreted immediately: If in such a configuration the electron has been promoted between orbitals of one molecule, the configuration represents a molecular excitation $|\text{ME} \rangle$ (Figure 2.5 left). If, on the other hand, the electron is transferred between orbitals localized on different molecules, the configuration corresponds to a charge transfer excitation $|\text{CT} \rangle$ (Figure 2.5 right). In the second step, the matrix elements between these configurations are evaluated with the same approximations which have been used during the HF-SCF calculations of the single molecules [50, 51]. Such methods neglect several inter-molecular interactions already at the SCF-level. However, the electronic states, albeit less accurate, are initially given in terms of molecular and CT excitations (cf. Figure

---

\(^3\)The subscript H indicates the highest occupied molecular orbital (HOMO), in all following equations the subscript L addresses the lowest unoccupied molecular orbital (LUMO).
2.3 and Figure 2.5), in our example in Figure 2.3 we would arrive at a linear decomposition:

\[
|a_{H} \rightarrow a_{L+1}\rangle = u_{1}|ME_{A}\rangle + u_{2}|ME_{B}\rangle + u_{3}|ME_{C}\rangle + \\
+ v_{1,+1}|CT_{A\rightarrow B}\rangle + v_{2,+1}|CT_{B\rightarrow C}\rangle \\
+ v_{2,-1}|CT_{B\rightarrow A}\rangle + v_{3,-1}|CT_{C\rightarrow B}\rangle.
\]

(2.16)

Moreover, the numerical effort is reduced significantly with respect to full cluster calculations and therefore permits the treatment of larger structures, demonstrated, e.g., for porphyrine dimers in references [28, 29].

A more extensive method to obtain the electronic states in terms of localized excitations starts from the idea that the ground state is invariant under unitary transformations of the full set of molecular orbitals. It is a supermolecular method in the sense introduced in the preceding section. The essential difference is that instead of using the basis initially calculated by the SCF-HF method (which we will abbreviate as SCMO basis below), the basis set is alternatively formed of localized orbitals. That means that each orbital wave function is mainly located at one molecule. Therefore, it is necessary to determine a basis transformation which mediates between the SCMO basis set (indicated in the right part of Figure 2.3) and a set of localized orbitals (left part of Figure 2.3, respectively). The unitary transformation is derived from so-called localization criteria [21, 52]. It can be found from demanding, e.g., an extremal population (either minimum or maximum, respectively) on the given sub-units, in our case molecules [21, 24]. Once the ground state is expressed with such localized orbitals (LO), the singly excited configurations constructed within the corresponding orbital scheme automatically have the meaning of molecular or CT excitations. In other words, the transformation within the orbital set automatically provides the unitary transformation which maps the SCMO-based configurations into the localized configurations, and vice versa. The result of a CI carried out in the basis of molecular and CT configurations is fully equivalent to the result obtained after CI with the SCMO-based configurations. Without losing information about intermolecular interactions at the SCF-level, the chosen local basis set allows us immediately to identify the composition of the excited states in terms of molecular and CT excitations.

With the basis transformation available, also the reverse process, the so-called Configuration Analysis (for a comprehensive overview, cf. reference [51]) can be applied. Here, the excited states are calculated from a CI using a basis set most convenient for numerical calculations, e.g., the SCMO basis. In the following step, the actual analysis, the configurations are reformulated into linear superpositions of localized configurations. This back-transformation automatically yields the excited states in terms of molecular and CT excitations.

For several reasons, e.g., numerical applicability, the unitary back-transformation might not be available. Nevertheless, a configuration analysis can be approximately carried out by implementing a small conceptual variation: If the orbitals of the whole cluster can be decomposed into the orbitals of the isolated molecules with satisfying accuracy, the orbitals of the single molecules can substitute the exact set of localized orbitals. Now, a projection of the states resulting from the full CI onto the approximate singlet configurations yields the decomposition of the excited states into the desired molecule-related excitations [45, 46]. As always, any projection gives rise to a loss of accuracy. For small clusters (up to three molecules), the loss is small; however, the full equivalence between the local and the non-local formulation has been violated.

The reformulation of the eigenstates of the system in terms of localized excitations immediately permits the construction of an effective Hamiltonian. In the local representation,
the matrix elements of the Hamiltonian contain the on-site energies and the interactions between both molecular and CT excitations. As shown in reference [45], and refined in [53, 54], the effective Hamiltonian constructed after Configuration Analysis using the aforementioned projection approximation provides semi-quantitative insight on the most essential inter-molecular interactions.

For dimers taken from the crystals of MePTCDI and PTCDA (PTC-derivates) and magnesium phthalocyanine, the analysis points out two major facts as far as nearest stack neighbors are concerned [45, 46]: a) In the energetical range responsible for the low energy absorption, always a significant contribution of charge transfer excitations is observed. b) The charge transfer excitation can appear strongly mixed with the molecular excitations of consistent symmetry, i.e., the matrix element of the effective Hamiltonian responsible for the coupling of both elementary excitations does not vanish. In case of the PTC-derivatives, especially the states with large oscillator strength exhibit a strong admixture of CT excitations.

By applying periodic boundary conditions, the method can be extended to infinite crystals. The perturbative approach presented in reference [55] yield effective Hamiltonian matrices for separate subspaces of the total space of AO’s. It also provides us an interpretation of the obtained states by means of standard solid state theory.

The advantage of the supermolecular approach is that initially the knowledge in which way an atom is correlated to a particular sub-unit is completely neglected. The method does not artificially distinguish between single molecular properties and the intermolecular interactions. Hence, the method can be flexibly applied to materials of very different composition. The major disadvantage, mainly inherited from current computational possibilities, is clearly the inaccuracy which becomes more severe with increasing system size. Up to now, a sophisticated analysis can be performed only for very limited cluster sizes.

However, the terminology of molecular and CT-type excitations developed throughout this section bridges the gap to the second approach used to describe quasi-one-dimensional aggregates, the small radius exciton theory (Section 2.2).

2.1.3 Density functional methods

Density functional calculations may offer an alternative to Hartree Fock based methods. With the traditional density functional theory (DFT) the electronic ground state of the system is determined. It yields the total energy of the system and the electronic charge density. The restriction to the particle density abandons a large number of degrees of freedom which are otherwise introduced when many-particle wave functions are considered. Therefore, largely extended systems can be described very accurately. However, they can give only a first approximation of the electronic wave functions and the resulting transition energies. With an extension of the DFT, the time dependent DFT (TDDFT) [56], the energies of the ground state and excited states as well as the oscillator strength of corresponding transitions can be determined [57, 58]. The results for large molecules such as ZnPc [57, 59] or perylene radicals [60], are promising.

A different philosophy is applied in infinitely extend systems. The concepts to determine the electronic excited states in crystals, in particular the excitonic states, are reviewed in reference [61]. In this TDDFT derived method, a single particle band description beyond the effective mass approximation can be combined with the accurate calculation of electron and hole interactions [62, 63]: On the basis of the ground state properties, the quasi-particle excitations are obtained. Such excitations correspond to processes where one electron is added to or removed from the system. The quasi-particle excitations define the electronic
band structure of the system. These states form the basis for the coupled electron-hole excitations. To determine the electron - hole interaction between relevant electron and hole states, a BETHE-SALPETER equation of motion for the excited states must be solved [63]. The excited states, obtained in KOHN-SHAM (KS) representation, can be clearly classified as molecular or CT excitations. The authors of references [59, 64] claim that KS orbitals offer a direct connection to LCAO treatments. Although this technique is rather demanding, it provides already a significant quantitative improvement compared to HF-based CIS methods at equivalent computational cost.

2.2 Small radius exciton theory

The other main approach is provided by small radius exciton theory. Here, the properties of the single molecule and the existing intermolecular interactions must be available quantitatively in advance. This information is a necessary input parameter for the exciton models, which must be provided from independent sources. If not available from experiments, quantum chemical calculations are the tool of choice to determine the input quantities.

Small radius excitons [65] are used to describe elementary collective electronic excitations of molecular crystals that consist of weakly interacting molecules, e.g., for J-aggregates [66] and polyacenes [67]: Like in the context of the tight binding approximation, cf. e.g. references [68] and [69], the small radius exciton theory starts out from the wave function of an isolated site. Besides the wave function of each neutral molecular excited state $|\phi_{i,n}^{*}\rangle$, also its on-site energy $E_{i}^{F}(n)$ and further properties of the molecule located at the isolated site $n$ are known. With the effects of neighboring sites $n' \neq n$ considered as small perturbations, the changes in the properties as well as in the wave functions of adjacent sites are predicted when the sites are brought together. The wave functions $|\phi_{n}^{*}\rangle$ enter together with the molecular ground state functions $|\phi_{n',\neq n}^{0}\rangle$ the principal many-electron basis functions $|\text{ME}_{n}^{i}\rangle$ from which the collective excited states (excitons) are formed as superpositions of the basis functions. To emphasize the correspondence between the neutral molecular excitations and the excitonic states of a crystal, the collective excitations are also called molecular excitons or FRENKEL excitons.

A broad discussion on the nature and on the applicability of the FRENKEL exciton theory in perfectly ordered crystals can be found, e.g., in the book of DAVYDOV [34]. In solids whose structure is invariant under discrete translational steps, it is convenient to introduce periodic boundary conditions [70] both for (one-dimensional) cyclic and for infinitely extended aggregates (for more details see Chapter 3.2). The excitons formed are delocalized over the whole aggregate and thus cannot be distinguished with the help of the labels $n$ of the involved sites. Instead, they form bands in which each state is characterized by a quasi-momentum $k$. In many limiting cases, a fully analytical discussion of the excitonic band formation can be performed (see right part in compilation in Figure 2.1).

To extend the application range to finite aggregates [71, 72] which lack translational symmetry, correct boundary conditions must be adapted. Already the introduction of idealized boundaries [71] (for more details see Chapter 4.4.1) alters the structure of the excited states considerably. However, the excitons are still extended over the whole aggregate and can be exclusively described by a discrete wave vector $k$. In principle, the number $N$ of possible sites in the aggregate is not restricted, but nevertheless finite (cf. overview Figure 2.1).

With the inclusion of defects and disorder [72, 73], the delocalization of the excitonic wave functions generally breaks down. The treatment of such aggregates demands a large
2.2 Small radius exciton theory

\[ |0\rangle = \frac{1}{\sqrt{N+1}} \sum_{n=1}^{N} \sin \left( \frac{j \pi n}{N+1} \right) |\text{ME}_n\rangle \]

\[ j = 1, \ldots, N \]

\[ |\psi_1\rangle = \sin \left( \frac{\pi n}{N+1} \right) \quad (j = 1) \]

Figure 2.6: Visualization of basis states and interactions occurring in the Frenkel exciton model for a perfectly ordered finite chain (upper part). The individual sites are occupied by molecules described as two-level systems. Mixed by the Frenkel transfer matrix element \( M_{nn'} \) the basis states enter the collective excited states \( |\psi_j\rangle \) (middle). For one state, \( j = 1 \), the shape of the wave function in a chain containing \( N = 11 \) molecules is shown in the lowest part.

Numerical effort. Alternative analytical treatments are still possible, but require highly specific circumstances such as adjustments restricted to the outermost site of a semi-infinite linear aggregate [74].

To discuss lowest energy excitons in the materials mentioned in Chapter 1, the amount of necessary basis states and interactions which have to be taken into account to formulate an appropriate model Hamiltonian \( \hat{H} \) can be considerably narrowed. Firstly, we can specify the number of *molecular* transitions which contribute to the lowest energy collective excited states: From quantum chemical considerations we know that in PTC-derivatives...
only the lowest energy transition \([43, 45]\) is relevant. In phthalocyanines \([21, 46]\) and several porphyrin-derivatives \([31]\), the two lowest energy transitions are important. However, they are degenerate and each of them gives rise to an independent set of eigenstates in the aggregate. Hence, we can assume that the molecules under question are described well by a two level system consisting of a molecular ground state and a molecular excited state. The latter is associated with an on-site energy \(E_F(n)\) which does not vary with the site number \(E_F(n) = E_F\).

We assume further that the concentration of excited molecules is small, which allows us to implement the Heitler-London approximation: Each basis function \(|\text{ME}_n\rangle\) contains one excited molecule at site \(n\), whereas all other molecules remain in the ground state.

To account particularly for the stack formation, we assume a linear regular distribution of molecules. We expect among the matrix elements \(M_{nn'} \equiv \langle \text{ME}_n | \hat{H} | \text{ME}_{n'} \rangle \) (\(n \neq n'\)) responsible for the mixing of basis elements \(|\text{ME}_n\rangle\) and \(|\text{ME}_{n'}\rangle\), the coupling between nearest stack neighbors

\[
M_{nn'} = M_{nn'} \delta_{n \pm 1, n'} \equiv M
\]  

(2.18)
to represent the leading contribution and to be the most sensitive with respect to the mutual molecular arrangement. The final picture at which we eventually arrive is summarized in the upper part of Figure 2.6.

In case of quasi-one-dimensional materials, the assumption of weakly interacting molecules is no longer valid in general anymore, since nearest neighbor molecules in the stacks are packed much closer than the molecules in polyacenes or J-aggregates (cf. Figures 1.1.1.2 presented in Chapter 1). The overlap between the wave functions of nearest stack neighbors can become large enough to allow electronic excitations involving more than one molecule. An excited electron may reach the adjacent molecule by leaving behind a hole on its original site. Still, the packing is more loose than the arrangement of monomers covalently linked in polymers, let alone the arrangement of atoms in inorganic semiconductors. Hence, the concept of small radius excitons is still the concept of choice, but has to be extended at least by basic excitations involving two nearest stack neighbors. In such nearest neighbor charge-transfer (CT) excitations, the electron and hole are separated by one site.

The concept of a general treatment of linear molecular chains involving all basic excitations starting from molecular excitations, nearest neighbor CT excitations, and further CT excitations with larger electron-hole separation has been presented by Merrifield \([75]\). Covering the limiting cases of small (Frenkel) and large radius (Wannier-Mott) excitons as well as all intermediate cases, the model yields a closed analytical solution both for infinite linear chains consisting of weakly bound molecules and for chains of covalently bound sub-units. The impact of the possible mixing of all basis excitations on the absorption spectrum has been discussed in reference \([76]\).

The Merrifield-Hamiltonian is the ancestor of many models currently used to deal with coupled Frenkel and CT excitons \([53, 77, 78, 79, 80]\). In case of our quasi-one-dimensional materials, the number of contributing CT excitations can be reduced to nearest neighbor excitations, as done e.g. in references \([53, 54]\). This approximation is justified if the nearest-neighbor CT exciton is energetically well separated from higher CT excitations. According to the estimations published in reference \([81]\), this is the case indeed. For example, in PTCDA crystals the nearest stack neighbor CT is separated by \(\approx 0.5\) eV from the next higher localized CT.
Throughout the next chapter, we will explicitly formulate the model Hamiltonian in \textit{small radius exciton theory} by making use of the preliminary adjustments discussed above.
Formation of mixed Frenkel charge transfer excitons in finite chains

3.1 The Hamiltonian

To model a one-dimensional molecular crystal we consider a linear, rigid arrangement of sites with one molecule at each lattice site (cf. Figure 3.1). We assume further that the linear chain possesses a center of inversion. The inversion symmetry implies that all eigenstates have to be either symmetric \((A_g)\) 1 or antisymmetric \((A_u)\) with respect to inversion. The molecules are enumerated as indicated in Figure 3.1 with the site-index \(n\) running through \(1 \ldots N\) and \(N\) being the total number of molecules.

The basis set is formed of two types of localized, electronic excitations: a) Molecular excitations \(|\text{ME}_n\rangle\), which can be created (annihilated) by \(\hat{B}^\dagger_n (\hat{B}_n)\). b) Additionally, localized charge-transfer (CT) configurations involving the nearest neighbor is considered. With the help of the operator \(\hat{C}^\dagger_{n\sigma}\) \((\sigma = \pm 1)\) a localized CT exciton \(|\text{CT}_{n,\sigma}\rangle\) is formed by creating a hole at site \(n\) and an electron at site \(n \pm 1\). The counterpart of \(\hat{C}^\dagger_{n\sigma}\) is the annihilation operator \(\hat{C}_{n\sigma}\). A schematic overview is given in Figure (3.1).

With the creation (annihilation) operators introduced above, the following model Hamiltonian is considered:

\[
\hat{H} = \hat{H}^F + \hat{H}^C + \hat{H}^{FC}
\]

\[
\hat{H}^F = \sum_n E_F \hat{B}^\dagger_n \hat{B}_n + \sum_{n n'} M \delta_{n',n \pm 1} \hat{B}^\dagger_n \hat{B}_{n'}
\]

\[
\hat{H}^C = \sum_{n \sigma} E_{\text{CT}} \hat{C}^\dagger_{n\sigma} \hat{C}_{n\sigma}
\]

\[
\hat{H}^{FC} = \sum_n \left\{ \epsilon_e (\hat{B}^\dagger_n \hat{C}_{n,+1} + \hat{B}^\dagger_n \hat{C}_{n,-1}) + \epsilon_h (\hat{B}^\dagger_n \hat{C}_{n+1,-1} + \hat{B}^\dagger_n \hat{C}_{n-1,+1}) \right\} + \text{h.c.} .
\]

The first part \(\hat{H}^F\) of the Hamiltonian (3.1) describes the Frenkel excitons in Heitler-London approximation: We assume that each site is given by a two level system where the low level corresponds to the molecule in the ground state and the upper level to the excited molecule. We allow only one excitation per molecule, whereas excitations at different sites as well as multiple excitations at one site are not considered. This single excitation is taken into account with the on-site energy \(E_F\). A molecular excitation at site \(n\) can in general be transferred

\(^1\)The notation of the corresponding irreducible representation is given in brackets.
Formation of mixed Frenkel charge transfer excitons in finite chains

|0⟩
|ME⟩
|CT⟩
|CT⟩

Figure 3.1: Visualization of basis states used in the model Hamiltonian (3.1) for ideal finite chains. In the right column the related on-site energy is shown. The upper block represents the situation for equivalent nearest neighbors. The boundary conditions (lower block, first two rows) disable the CT basis states |CT⟩ and |CT⟩ at the outermost molecules (marked gray). The on-site energies of the remaining basis states at 1, N are kept equal with respect to the inner molecules. In contrast, periodic boundary conditions (last row) demand two CT states per site, realized by the conditions |CT⟩ = |CT⟩ and |CT⟩ = |CT⟩.

The second part $\hat{H}_C$ contains the on-site energy $E_{CT}$ of a localized CT exciton. In contrast to the Frenkel part, an analogous nearest neighbor transfer of a CT exciton is omitted. The amount of $E_{CT}$ is independent of the direction $\sigma$ of the CT and is kept constant for each molecule, in particular at the outermost molecules (see Figure 3.1).

These two parts $\hat{H}_F$, $\hat{H}_C$ of the Hamiltonian are completely independent. With the introduction of the third part $\hat{H}_{FC}$, however, the mixing of Frenkel and CT excitons can be realized. Here, the nonlocal transformation of a CT state into a Frenkel state at the

to a different site $n'$ with the Frenkel transfer integral $M_{nn'}$. Since the interactions strongly decrease with the separation of the involved sites [54], we consider only the nearest neighbor hopping integral $M = M_{n\pm1,n}$. It is responsible for the mixing of molecular excitations located at nearest neighbors. Both the on-site energy and the hopping integral are chosen independent of the lattice site $n$, i.e. these parameters are constants (see Figures 3.1, 3.2).

The second part $\hat{H}_C$ contains the on-site energy $E_{CT}$ of a localized CT exciton. In contrast to the Frenkel part, an analogous nearest neighbor transfer of a CT exciton is omitted. The amount of $E_{CT}$ is independent of the direction $\sigma$ of the CT and is kept constant for each molecule, in particular at the outermost molecules (see Figure 3.1).
3.1 The Hamiltonian

\[ \hat{H} = \hat{H}_{\text{NN}} + \hat{H}_{\text{bc}} \]  \hspace{1cm} (3.2)

where $\hat{H}_{\text{NN}}$ involve all bulk molecules, i.e., molecules which have two nearest neighbors, and $\hat{H}_{\text{bc}}$ which contains the boundary conditions. Hence, in $\hat{H}_{\text{NN}}$ the summation index $n$ runs
from 2 through \(N - 1\):  
\[
\hat{H}_\text{NN} = \sum_{n=2}^{N-1} \left\{ E_F \hat{B}_n^\dagger \hat{B}_n + E_{\text{CT}} (\hat{C}_{n+1}^\dagger \hat{C}_{n+1} + \hat{C}_{n-1}^\dagger \hat{C}_{n-1}) \right\} + \sum_{n'} M \hat{B}_{n',n+1}^\dagger \hat{B}_{n',n'}^\dagger + \epsilon_e (\hat{B}_n^\dagger \hat{C}_{n+1} + \hat{B}_{n+1}^\dagger \hat{C}_{n-1}) + \epsilon_h (\hat{B}_n^\dagger \hat{C}_{n+1,-1} + \hat{B}_{n+1}^\dagger \hat{C}_{n-1,+1}) \right\} + \text{h.c.} 
\]  
(3.3)

As boundary conditions we choose free ends  
\[
\hat{H}_\text{bc}^{\text{fe}} = E_F (\hat{B}_1^\dagger \hat{B}_1 + \hat{B}_N^\dagger \hat{B}_N) + E_{\text{CT}} (\hat{C}_{1,1}^\dagger \hat{C}_{1,1} + \hat{C}_{N,-1}^\dagger \hat{C}_{N,-1}) + \epsilon_e (\hat{B}_1^\dagger \hat{C}_{1,1} + \hat{B}_N^\dagger \hat{C}_{N,-1}) + \epsilon_h (\hat{B}_1^\dagger \hat{C}_{0,-1} + \hat{B}_N^\dagger \hat{C}_{N+1,-1}) . 
\]  
(3.4)

In idealized chains, which shall be considered here, the on-site energies \(E_F, E_{\text{CT}}\) for each molecule and the coupling matrix elements \(M, \epsilon_e, \epsilon_h\) between the molecules are the same, even at the outermost molecules. Only the CT excitations \(|\text{CT}_{1,-1}\rangle, |\text{CT}_{N,+1}\rangle\) from the outermost molecules to the one missing neighbor are omitted (see also Figures 3.1, 3.2).

If, however, a finite chain is defined as a cyclic array, the boundary sites \(n = 1\) and \(n = N\) become nearest neighbors and the CT excitations \(|\text{CT}_{1,-1}\rangle, |\text{CT}_{N,+1}\rangle\) can be assigned as \(|\text{CT}_{1,-1}\rangle = |\text{CT}_{N+1,-1}\rangle\) and \(|\text{CT}_{N,+1}\rangle = |\text{CT}_{0,+1}\rangle\) (Figure 3.1, lowest row). Consequently, the formulation (3.4) has to be extended to periodic boundary conditions:  
\[
\hat{H}_\text{bc}^{\text{pb}} = \hat{H}_\text{bc}^{\text{fe}} + M (\hat{B}_1^\dagger \hat{B}_1 + \hat{B}_N^\dagger \hat{B}_N) + E_{\text{CT}} (\hat{C}_{1,-1}^\dagger \hat{C}_{1,-1} + \hat{C}_{N+1}^\dagger \hat{C}_{N+1}) + \epsilon_e (\hat{B}_1^\dagger \hat{C}_{1,-1} + \hat{B}_N^\dagger \hat{C}_{N+1}) + \epsilon_h (\hat{B}_1^\dagger \hat{C}_{0,-1} + \hat{B}_N^\dagger \hat{C}_{N+1,-1}) . 
\]  
(3.5)

In the limit \(N \gg 1\), such a cyclic array is used to model infinitely extended systems. Although our work is dedicated to truly finite systems, the infinite chain will accompany our considerations.

The Hamiltonian (3.1) shall act in the space of basis states constructed as follows: Let \(|\phi_n^0\rangle\) be the wave function of a molecule \(n\) in the ground state and \(|\phi_n^\ast\rangle\) the wave function of the molecule in its excited state. To describe CT-type excitations, ionized molecules have to be considered whose wave functions shall be introduced as \(|\phi_n^\ast\rangle, |\phi_n^-\rangle\). The electronic character of all these molecular wave functions requires an antisymmetrization to obey PAULI’s exclusion principle for electrons. Then, the many-electron states which serve as basis states for the whole chain, can be expressed as follows:

\[
|0\rangle = |\prod_n \phi_n^0\rangle (-) \quad \text{ground state}, 
\]

\[
|\text{ME}_n\rangle := \hat{B}_n^\dagger |0\rangle = |\phi_n^\ast \prod_{n' \neq n} \phi_{n'}^0\rangle (-) \quad \text{molecular excitation}, 
\]

\[
|\text{CT}_{n,+1}\rangle := \hat{C}_{n,+1}^\dagger |0\rangle = |\phi_n^+ \phi_{n+1}^+ \prod_{n' \neq n, n' \neq n+1} \phi_{n'}^0\rangle (-) \quad \text{CT excitation}, 
\]

\[
|\text{CT}_{n,-1}\rangle := \hat{C}_{n,-1}^\dagger |0\rangle = |\phi_n^+ \phi_{n-1}^- \prod_{n' \neq n, n' \neq n-1} \phi_{n'}^0\rangle (-) \quad \text{CT excitation}, 
\]
3.2 The diagonalization method of the infinite chain

where the symbol (−) at the brackets | ... ⟩(−) indicates that the product wave function has additionally been antisymmetrized with respect to the coordinates of all involved electrons.

The diagonalization of the Hamiltonian (3.1) yields the eigenstates with Frenkel excitations superimposed with CT excitations. To determine the eigensystem of the Hamiltonian 3.1, we introduce the linear transformation to new operators $\hat{\zeta}$ and $\hat{\zeta}^\dagger$,

$$
\hat{\zeta} = \sum_{n=1}^{N} u_n \hat{B}_n + \sum_{n=1}^{N-1} v_{n+1} \hat{C}_{n+1} + \sum_{n=2}^{N} v_{n-1} \hat{C}_{n-1},
$$

with which the Hamiltonian takes a diagonal form:

$$
\hat{H} = \sum_{j} E_j \hat{\zeta}_j^\dagger \hat{\zeta}_j.
$$

Then, each eigenstate of the chain can be created from the ground state $|0\rangle$ by applying $\hat{\zeta}^\dagger$:

$$
|\psi_j\rangle = \hat{\zeta}_j^\dagger |0\rangle ,
$$

$$
= \sum_{n=1}^{N} u_n^2 |B_n^\dagger 0\rangle + \sum_{n=1}^{N-1} v_{n+1}^2 |C_{n+1}^\dagger 0\rangle + \sum_{n=2}^{N} v_{n-1}^2 |C_{n-1}^\dagger 0\rangle .
$$

$$
|\psi\rangle = \sum_{n=1}^{N} u_n |ME_n\rangle + \sum_{n=1}^{N-1} v_{n+1} |CT_{n+1}\rangle + \sum_{n=2}^{N} v_{n-1} |CT_{n-1}\rangle
$$

The contribution of molecular configurations $|ME_n\rangle$ and the CT contributions $|CT_{n+1}\rangle$ is given by the coefficients $u_n$ and $v_{n+1}, v_{n-1}$, respectively. In relations (3.7, 3.9) the terms with $v_{1,-1}$ and $v_{N,+1}$ are absent because the corresponding CT states are missing in a finite chain.

Each wave function $|\psi\rangle$ is normalized if

$$
\sum_{n=1}^{N} |u_n|^2 + \sum_{n=1}^{N-1} |v_{n+1}|^2 + \sum_{n=2}^{N} |v_{n-1}|^2 = 1 .
$$

The diagonalization of the Hamiltonian (3.1) given in the basis set (3.6) can be immediately carried out numerically, yielding a set of $3N-2$ eigenstates in the form (3.9). Nevertheless, it is possible to specify the solutions with the help of its intrinsic properties. In order to reveal a further structure among the eigenstates, we apply an analytical treatment which we adapted from the description of infinite chains. I.e., we modify the diagonalization procedure applied to the Hamiltonian (3.1) with periodic boundary conditions. Since our finite system differs from the infinitely extended system only in the choice of the boundary conditions, the theory of the infinite chain [53] can be extended to finite chains without introducing a new parameter.

3.2 The diagonalization method of the infinite chain

The behavior of infinite chains showing a strong coupling between Frenkel and CT excitons is already fully understood. The straightforward diagonalization procedure of the corresponding Hamiltonian is explained in detail in [54]. The Hamiltonian presented there is extended
with additional vibronic excitations. The pure electronic problem can be easily retrieved if the number of permitted phonons is set to zero. Since we can immediately establish a correspondence between our context and reference [54], we will restrict ourselves to give an overview of all ideas necessary for our further considerations.

The case of infinite chains can be conveniently described with finite cyclic molecular arrays linked together with periodic boundary conditions. This construction ensures translational symmetry. Hence, the Hamiltonian (3.1) is appropriately represented in the momentum space. The creation operators $\hat{B}_n$ and $\hat{C}_{n\sigma}$ are transformed into

$$
\hat{B}_k := \frac{1}{\sqrt{N}} \sum_n e^{-ikn} \hat{B}_n ,
$$

$$
\hat{C}_{k\sigma} := \frac{1}{\sqrt{N}} \sum_n e^{-ikn} \hat{C}_{n\sigma} .
$$

Since the system obeys translational symmetry, the quantum number $k$, running from 0 through $\pi$, has the character of a momentum. The quantum number is not a momentum in the strict sense, since the lattice is not invariant under arbitrary translational steps. However, the system is invariant under translations of fixed length compatible with the lattice spacing. The quantum number $k$, which nevertheless reflects the lattice periodicity, is assigned as quasi-momentum. The quasi-momentum is a preserved quantity, and therefore has to be conserved upon excitations.

The Hamiltonian in momentum space representation follows after inserting the operators (3.13, 3.14) into (3.1):

$$
\hat{H} = \sum_k \hat{H}_k = \sum_k ( \hat{H}_k^F + \hat{H}_k^C + \hat{H}_k^{FC} )
$$

$$
\hat{H}_k^F = ( E_F + 2M \cos k ) \hat{B}_k^\dagger \hat{B}_k
$$

$$
\hat{H}_k^C = \sum_\sigma E_{CT} \hat{C}_{k\sigma}^\dagger \hat{C}_{k\sigma}
$$

$$
\hat{H}_k^{FC} = \hat{B}_k^\dagger \left\{ (\epsilon_e + \epsilon_h e^{-ik}) \hat{C}_{k,+1} + (\epsilon_e + \epsilon_h e^{ik}) \hat{C}_{k,-1} \right\} + h.c.
$$

We used the fact that ansatz (3.13, 3.14) and the translational invariance (3.5) only permits combined operators $\hat{X}_k^\dagger \hat{Y}_{k'}$ with equal $k$ [54]:

$$
\hat{X}_k^\dagger \hat{Y}_{k'} = \delta_{kk'} .
$$

Besides invariance with respect to translation, the system possesses inversion symmetry. In a further step, the charge-transfer contributions in Hamiltonian (3.15) can be separated into symmetric and antisymmetric parts. We combine the CT related operators into symmetry adapted operators

$$
\hat{C}_{kg} := \frac{1}{\sqrt{2 \epsilon_k}} \cdot \left\{ (\epsilon_e + \epsilon_h e^{ik}) \hat{C}_{k,+1} + (\epsilon_e + \epsilon_h e^{-ik}) \hat{C}_{k,-1} \right\}
$$

$$
\hat{C}_{ku} := \frac{1}{\sqrt{2 \epsilon_k}} \cdot \left\{ (\epsilon_e + \epsilon_h e^{ik}) \hat{C}_{k,+1} - (\epsilon_e + \epsilon_h e^{-ik}) \hat{C}_{k,-1} \right\},
$$

with $\epsilon_k$ defined as

$$
\epsilon_k := \sqrt{(\epsilon_e + \epsilon_h)^2 \cos^2 \frac{k}{2} + (\epsilon_e - \epsilon_h)^2 \sin^2 \frac{k}{2}}.
$$
Expressed with the new operators, the parts $\hat{H}_{\text{CT}} + \hat{H}_{\text{FC}}$ of the Hamiltonian involving CT states now read:

\[ \hat{H}_{\text{CT}} = E_{\text{CT}} \{ \hat{C}^\dagger_{kg} \hat{C}_{kg} + \hat{C}^\dagger_{ku} \hat{C}_{ku} \} \]  
\[ \hat{H}_{\text{FC}} = \sqrt{2}\epsilon_k \cdot \hat{B}^\dagger_k \hat{C}_{kg} + \text{h.c.} \]  

where the odd operator $\hat{C}^\dagger_{ku}$ does not mix with the Frenkel operators $\hat{B}^\dagger_k$ anymore.

At this stage of transformation, the subsystems $\hat{H}_{\text{F}}, \hat{H}_{\text{C}}$ are diagonal in the occupation operators $X^\dagger_k X_k$. The eigenstates within the independent subsystems are therefore fully available (see also Figure 3.3):

The Hamiltonian $\hat{H}_{\text{F}}$ (3.15) describes a system of pure Frenkel excitons $|\text{FE}_k\rangle$. Using the creation operator $\hat{B}^\dagger_k$ we can express the Frenkel excitons within an infinite chain as

\[ |\text{FE}_k\rangle := \hat{B}^\dagger_k |0\rangle \]  

which have the energy

\[ E_k = E_F + 2M \cos k . \]  

Without the Frenkel transfer interaction ($M = 0$), all Frenkel states, i.e., states exclusively consisting of molecular excitations, are found at the energy $E_F$ (Figure 3.3(a)). When turning on the Frenkel transfer ($M \neq 0$), the manifold of states at $E_F$ splits and gives rise to a cosine shaped band $E(k)$ of Frenkel excitons which is centered at $E_F$ and has a width of $4M$ (Figure 3.3(b)).

The Hamiltonian $\hat{H}_{\text{C}}$ describing the CT subsystem acts on a space spanned by the symmetric (odd, $A_g$) and antisymmetric (even, $A_u$) CT excitons:

\[ \hat{H}_{\text{C}} = E_{\text{CT}} \hat{C}^\dagger_{kg} \hat{C}_{kg} + E_{\text{CT}} \hat{C}^\dagger_{ku} \hat{C}_{ku} \]  

Each of the $A_g$ and $A_u$ CT excitons

\[ |\text{CT}_{kg}\rangle = \hat{C}^\dagger_{kg} |0\rangle \]  
\[ |\text{CT}_{ku}\rangle = \hat{C}^\dagger_{ku} |0\rangle \]

are the eigenstates of $\hat{H}_{\text{C}}$. Since $\hat{H}_{\text{C}}$ exclusively consist of occupation operators $X^\dagger_k X_k$.

The full Hamiltonian $\hat{H}_k$ in momentum space representation shall now act within the basis states $\{|\text{ME}_k\rangle, |\text{CT}_{kg}\rangle, |\text{CT}_{ku}\rangle\}$. In this basis set, $\hat{H}_k$ corresponds to the matrix representation:

\[ H(k) = \begin{pmatrix} E_F + 2M \cos k & \sqrt{2}\epsilon_k & 0 \\ \sqrt{2}\epsilon_k & E_{\text{CT}} & 0 \\ 0 & 0 & E_{\text{CT}} \end{pmatrix} \]  

The structure of (3.27) emphasizes that for each $k$, also an odd CT state with the energy $E_{\text{CT}}$ is formed. In the Brillouin zone, these $A_u$ states form a band without dispersion (Figure
Figure 3.3: Formation of excitonic bands. In (a), no coupling is present and all states are found at either $E_F = 0$ or $E_{CT} = 0.2$ eV. With Frenkel transfer $M = 0.2$ eV enabled (b), all molecular excitations, initially found at $E_F$, form the Frenkel band (dashed line). In (c), the additional Frenkel charge transfer coupling ($\epsilon_e = \epsilon_h = 0.14$ eV) mixes the $A_g$ CT band with the Frenkel band into two bands $E_1(k)$ and $E_2(k)$ (cf. Eq. 4.16).
After inserting representation (3.28) of the desired eigenstates into equation (3.29), the energies are required to fulfill:

\[
\det(H(k) - E(k) \cdot I) = 0
\]

\[
= \left( (E_F - E) + 2M \cos k \right) (E_{CT} - E) - 2(\epsilon_e^2 + \epsilon_h^2 + 2\epsilon_e\epsilon_h \cos k)
\]

where we introduced the unity matrix with the symbol \(I\). The equation above is solved by

\[
E_{1,2}(k) = \frac{E_{CT} + E_F + 2M \cos k}{2} \pm \sqrt{\left( \frac{E_F - E_{CT} + 2M \cos k}{2} \right)^2 + 2\epsilon_k^2}.
\]

These two solutions correspond to two mixed bands \(E_1(k)\) and \(E_2(k)\) (see Figure 3.3(c)). The original Frenkel and \(A_g\)-CT states at a fixed \(k\) repel each other dependent on the amount of \(\epsilon_k\).

In Section 4.1, we will investigate the dependence of the band shape \(E(k)\) on the describing parameters. While doing so, the composition of the corresponding eigenstates in terms of Frenkel and CT excitons will be studied in detail. At the present stage, however, we first turn to the treatment of finite chains.

### 3.3 The diagonalization method for finite chains

#### (a)

\[
\begin{array}{cccccccc}
1 & 2 & \cdots & & \cdots & N-1 & N \\
\circ & \circ & \cdots & \circ & \circ & \circ & \circ \\
-m & -(m-1) & \cdots & -1 & 0 & 1 & m-1 & m \\
\end{array}
\]

\(N\) odd, \(N = 2m + 1\)

#### (b)

\[
\begin{array}{cccccccc}
1 & 2 & \cdots & & \cdots & N-1 & N \\
\circ & \circ & \cdots & \circ & \circ & \circ & \circ \\
-(m-\frac{1}{2}) & -(m-\frac{3}{2}) & \cdots & -\frac{1}{2} & \frac{1}{2} & m-\frac{3}{2} & m-\frac{1}{2} \\
\end{array}
\]

\(N\) even, \(N = 2m\)

#### Figure 3.4:
Indices of the molecular sites for chains containing an odd number (a) and even number (b) of molecules.

In a finite system, the translational symmetry is broken. Therefore, nearest neighbor sites are not necessarily translationally equivalent anymore. However, the chain obeys inversion symmetry and molecules separated by the same distance from the boundaries can be considered as symmetry-equivalent. In the following, this fact shall be supported by a renotation of the molecular sites:

If the chain contains an odd number of molecules \(N = 2m + 1\), we will label the sites \(n = 0, \pm 1, \pm 2, \ldots, \pm m\). For an even number \(N = 2m\) of molecules, we will use \(n = \pm \frac{1}{2}, \pm \frac{3}{2}, \ldots, \pm (m - \frac{1}{2})\) (see Figure 3.4). Symmetry-equivalent molecules are automatically labeled with the same \(|n|\), i.e. with \(-n\) and \(n\). Similarly to the diagonalization concept of infinite chains, we would like to transform the basis functions such that the internal structure of the basis states is described by a quantum number \(\kappa\) similar to the quasi-momentum \(k\).

Due to the free chain ends, each eigenstate will carry information to what extend a contributing basis state is separated from the chain end. Hence, it is impossible to characterize the eigenstates by exclusively two quantum numbers \(E\) and \(\kappa\). A full description will always
involve the site numbers \( n \) in combination with the chain length \( N \). The next sections describe in detail the formalism to obtain the set of eigenstates with quantum numbers \( E \) and \( \kappa \).

### 3.3.1 Formalism for chains containing an odd number of molecules

We demonstrate the diagonalization method for odd \( N \) chains. We will see in Section 3.3.2 that the analogous treatment for the even-\( N \) case yields the same physical situation.

The inversion symmetry demands either symmetric or antisymmetric eigenstates. Consequently, the coefficients of symmetry-equivalent molecules are related to each other as follows:

\[
 u_n = \pm u_{-n}, \quad v_{n+1} = \pm v_{-n-1}
\]

To solve the problem given by Hamiltonian (3.1), we insert representation (3.9) into the Schrödinger equation

\[
 \langle \psi_j | \hat{H} | \psi_j \rangle = E_j.
\]

Then, solving the Schrödinger equation is equivalent with solving a system of equations for the coefficients \( u_n, v_{n+1} \) and \( v_{n-1} \):

For each bulk molecule \(|n| < m\), the coefficients have to obey the system of equations:

\[
\begin{align*}
(E_F - E)u_n + M(u_{n+1} + u_{n-1}) + & \epsilon_e (v_{n+1} + v_{n-1}) + \epsilon_h (v_{n-1} + v_{n+1}) = 0 \\
(E_{CT} - E)v_{n+1} + & \epsilon_e u_n + \epsilon_h u_{n+1} = 0 \\
(E_{CT} - E)v_{n-1} + & \epsilon_e u_n + \epsilon_h u_{n-1} = 0.
\end{align*}
\]

The equations for \( n = \pm m \) describe the boundary conditions:

\[
\begin{align*}
(E_F - E)u_{-m} + M u_{-m+1} + \epsilon_e v_{-m+1} + \epsilon_h v_{-m-1} = 0 \\
(E_{CT} - E)v_{-m+1} + \epsilon_e u_m + \epsilon_h u_{m+1} = 0 \\
(E_{CT} - E)v_{-m-1} + \epsilon_e u_m + \epsilon_h u_{m-1} = 0.
\end{align*}
\]

In the case \( u_n = 0 \) for all sites \((|n| = 0..m)\), both systems of equations (3.34, 3.35) reduce to a pure CT problem

\[
\begin{align*}
\epsilon_e (v_{n+1} + v_{n-1}) + \epsilon_h (v_{n-1} + v_{n+1}) = 0 & \quad (|n| < m) \\
\epsilon_e v_{\pm m+1} + \epsilon_h v_{\pm (m-1)+1} = 0 & \quad (|n| = m) \\
(E_{CT} - E)v_{n+1} = 0 & \quad (n < m) \\
(E_{CT} - E)v_{n-1} = 0 & \quad (-m < n)
\end{align*}
\]

which involves exclusively the \( 2(N-1) \) CT-type basis functions. Thereby, equations (3.36.3, 4) fix the energy of the \( N - 2 \) resulting states at \( E_{CT} \). The remaining \( 2N \) solutions contain both Frenkel and CT-type basis functions. With

\[
v_{n\pm 1} = \frac{1}{E - E_{CT}} (\epsilon_e u_n + \epsilon_h u_{n\pm 1}) \quad \begin{cases} (n < m) \\ (-m < n) \end{cases}
\]
3.3 The diagonalization method for finite chains

derived from the last two equations of the system (3.34) and (3.35), respectively, the coefficients \( v \) can be eliminated from equations (3.34, 3.35):

\[
\begin{align*}
(E_F - E)u_n + & \left[ M - \frac{2\epsilon_e\epsilon_h}{E_{CT} - E} \right] (u_{n+1} + u_{n-1}) - 2 \frac{\epsilon_e^2 + \epsilon_h^2}{E_{CT} - E} u_n = 0 \quad (|n| < m) \\
(E_F - E)u_{\pm m} + & M u_{\pm m-1} - \frac{\epsilon_e^2 + \epsilon_h^2}{E_{CT} - E} u_{\pm m} + \frac{2\epsilon_e\epsilon_h}{E_{CT} - E} u_{\pm (m-1)} = 0 \quad (|n| = m).
\end{align*}
\] (3.38)

To extract the eigenstates from the system of equations (3.38), we choose the general ansatz

\[ u_n = A e^{\kappa n}. \] (3.39)

The parameter \( \kappa \) will play the role of the quantum number \( k \) introduced to describe infinite chains. In general, \( \kappa \) is a complex number, \( \kappa = \text{Re} \kappa + i k \), with \( \text{Re} \kappa \) and \( k \) being real values. In case of periodic boundary conditions, \( \kappa \) becomes purely imaginary and \( k \) is the quasi-momentum. Within infinitely extended chains, \( k \) is an continuous parameter covering the whole Brillouin zone \([0, \pi]\). In finite systems, however, \( \kappa \) is not a continuous parameter anymore. We will show below that the imaginary parts \( k \) takes discrete values if the boundary conditions (3.38,2) are applied.

Substituting ansatz (3.39) into the first equation of (3.38) we obtain:

\[
(E_F - E) + 2 \left[ M - \frac{2\epsilon_e\epsilon_h}{E_{CT} - E} \right] \cosh \kappa - 2 \frac{\epsilon_e^2 + \epsilon_h^2}{E_{CT} - E} = 0 .
\] (3.40)

This equation gives the dependence of energy \( E \) on \( \kappa \). Since equation (3.40) does not depend on the sign of \( \kappa \), the general solution for \( u_n \) is

\[ u_n = A e^{\kappa n} + B e^{-\kappa n} , \] (3.41)

where the coefficients \( A \) and \( B \) have to be determined from the boundary conditions (3.38,2), and the normalization condition (3.12). From the symmetry requirement (3.32), we can conclude that \( B = \pm A \) and that

\[
\begin{align*}
u_n &= A \cosh (n\kappa) \quad \text{for symmetric solutions and} \\
u_n &= A \sinh (n\kappa) \quad \text{for antisymmetric solutions.}
\end{align*}
\] (3.42, 3.43)

By substituting the symmetric (3.42) and antisymmetric solutions (3.43) for \( u_n \) in equations (3.38), we obtain two equations which yield the energy \( E \) and \( \kappa \) of the excited states.

For future discussions it is convenient to introduce the parameters of the Hamiltonian (3.1) as dimensionless quantities. In case of a nonvanishing Frenkel transfer integral \((M \neq 0)\), all parameters related to the on-site energies or the charge-transfer integrals, respectively, are given in units of \( M \):

\[
\begin{align*}
\Delta_F &= \frac{E_F - E}{M} , & \Delta_{CT} &= \frac{E_{CT} - E}{M} , & \tilde{\Delta} &= \Delta_F - \Delta_{CT} , \\
\alpha &= \frac{\epsilon_e^2 + \epsilon_h^2}{M^2} , & \beta &= \frac{2\epsilon_e\epsilon_h}{M^2} .
\end{align*}
\] (3.44, 3.45)
Instead of using the parameters $E_F$ and $E_{CT}$ independently, their combination to the quantity $\Delta$ describes the separation of the on-site energies of the molecular and the charge-transfer excitation with respect to the Frenkel transfer integral. The form of the electronic spectrum is determined by the difference $E_F - E_{CT}$, whereas any chosen $E_F$ will simply shift the overall spectrum in energy. The new parameter $\alpha$ weights the combined charge transfer coupling matrix elements with respect to the Frenkel transfer integral. With $\beta$, however, the balance of $\epsilon_e$ and $\epsilon_h$ is reflected. If a material strongly suppresses the electron or the hole transport, respectively, $\beta$ goes to zero. If, on the other hand, the electron and the hole transport integrals are balanced equally, $|\beta|$ becomes equal $\alpha$. Evidently, the absolute value of $\beta$ never exceeds $\alpha$:

$$\alpha \geq |\beta|.$$  

(3.46)

Inspired by the definition of $\epsilon_k$ (3.19), we introduce a further quantity

$$\epsilon_k^2 = (\epsilon_e + \epsilon_h e^\kappa) (\epsilon_e + \epsilon_h e^{-\kappa}).$$  

(3.47)

In the infinite chain, $\epsilon_k$ is responsible for the interaction between a pure Frenkel and a CT exciton for a given $k$ (cf. Eq. 3.27).

The first equation, which corresponds to the "bulk"-equation (3.38.1), can be directly obtained from (3.40):

$$\Delta_F + 2 \cosh \kappa - \frac{2(\alpha + \beta \cosh \kappa)}{\Delta_{CT}} = 0.$$  

(3.48)

The second equation, into which the boundary equations (3.38.2) will be transformed, depends on the symmetry of the states which we are interested in, and on the number of molecules $N$ within the chain. For symmetric solutions (3.42), the equation (3.38.2) becomes:

$$\Delta_F \cosh m\kappa + \cosh (m - 1)\kappa - \frac{\alpha \cosh m\kappa + \beta \cosh (m - 1)\kappa}{\Delta_{CT}} = 0.$$  

(3.49)

Analogously the boundary condition for the antisymmetric solutions (3.43) can be expressed as follows:

$$\Delta_F \sinh m\kappa + \sinh (m - 1)\kappa - \frac{\alpha \sinh m\kappa + \beta \sinh (m - 1)\kappa}{\Delta_{CT}} = 0.$$  

(3.50)

After substituting $\Delta_F$ of Eq. (3.48) into (3.49) for symmetric and into (3.50) for antisymmetric solutions, the energy of the new excited states and the corresponding value of $\kappa$ can be found from the following equations:

a) for symmetrical solutions:

$$\Delta_{CT} = \beta + \alpha \frac{\cosh m\kappa}{\cosh (m + 1)\kappa},$$  

(3.51)

$$\left(\Delta + \beta\right) + 2 \cosh \kappa + \frac{\alpha \cosh m\kappa}{\cosh (m + 1)\kappa} =$$  

(3.52)

$$2 \cosh (m + 1)\kappa \frac{\alpha + \beta \cosh \kappa}{\alpha \cosh m\kappa + \beta \cosh (m + 1)\kappa}.$$
b) for antisymmetrical solutions:

\[ \Delta_{CT} = \beta + \alpha \frac{\sinh m\kappa}{\sinh (m + 1)\kappa}, \quad (3.53) \]

\[ (\tilde{\Delta} + \beta) + 2 \cosh \kappa \quad + \quad \frac{\alpha \sinh m\kappa}{\sinh (m + 1)\kappa} = \quad (3.54) \]

\[ 2 \sinh (m + 1)\kappa \quad \cdot \quad \frac{\alpha + \beta \cosh \kappa}{\alpha \sinh m\kappa + \beta \sinh (m + 1)\kappa}. \]

Both equations (3.51, 3.52) of the symmetric case and equations (3.53, 3.54) of the antisymmetric case restrict the parameter \( \kappa \) to a discrete set of allowed values. Several conditions can be derived to determine the permitted set of \( \kappa \).

So far, \( \kappa \) was simply introduced as a complex number. At first we will derive criteria for \( \kappa \) which ensure physical solutions \( E(\kappa) \). Therefore we have to ask under which conditions the equations (3.51, 3.53) yield real energy eigenvalues. During the derivations we will often make use of the following trigonometric identities:

\[ \cosh(x \pm y) = \cosh x \cosh y \pm \sinh x \sinh y \quad (3.55) \]

\[ \sinh(x \pm y) = \sinh x \cosh y \pm \cosh x \sinh y. \quad (3.56) \]

Since the parameters \( \alpha, \beta \) in Eq. (3.51) are real, the condition given below must hold to obtain the \( \kappa \) determining symmetric solutions:

\[ \frac{\cosh m\kappa}{\cosh(m + 1)\kappa} \in \mathbb{R} \quad \text{which is equivalent to} \]

\[ \text{Im} \left( \frac{\cosh m\kappa}{\cosh(m + 1)\kappa} \right) = 0. \quad (3.57) \]

With the decomposition

\[ \kappa = \kappa_R + ik \quad (3.58) \]

the hyperbolic expressions in Eq. (3.57) can be transformed into

\[ \cosh m\kappa \quad \overset{(3.55)}{=} \quad \cosh(m\kappa_R) \cosh(ik) + \sinh(m\kappa_R) \sinh(ik) \]

\[ = \quad \cosh(m\kappa_R) \cos(k) + i \sinh(m\kappa_R) \sin(k). \quad (3.59) \]

By inserting the identity (3.59) into condition (3.57) we finally get:

\[ 0 \quad = \quad \text{Im} \left( \frac{\cosh m\kappa}{\cosh(m + 1)\kappa} \right) = \text{Im} \left( \frac{\cosh m\kappa \cdot [\cosh(m + 1)\kappa]^*}{\cosh(m + 1)\kappa \cdot [\cosh(m + 1)\kappa]^*} \right) \]

\[ \Leftrightarrow \]

\[ 0 \quad = \quad \text{Im} \left( \cosh m\kappa \cdot [\cosh(m + 1)\kappa]^* \right) \]

\[ \overset{(3.59)}{=} \quad \text{Im} \left( (\cosh(m\kappa_R) \cos(k) + i \sinh(m\kappa_R) \sin(k)) \times (\cosh((m + 1)\kappa_R) \cos((m + 1)k) - i \sinh((m + 1)\kappa_R) \sin((m + 1)k)) \right) \]

\[ \overset{\text{evaluate Im}}{=} \quad 0 \quad = \quad \sin((m + 1)k) \cos(k) \cdot \sinh((m + 1)\kappa_R) \cosh(m\kappa_R) \]

\[ - \cos((m + 1)k) \sin(k) \cdot \cosh((m + 1)\kappa_R) \sinh(m\kappa_R). \quad (3.60) \]
This form (3.60) enables us to investigate the contribution of the real and imaginary part of \( \kappa \) separately. We aim to find the \( \kappa \) such that both summation terms in equation (3.60) to compensate each other.

a) \( k = l\pi \) (\( l = 0, 1 \)):
For any \( \kappa_R \) the compensation of both terms in equation (3.60) can be equivalently formulated with two conditions for \( k \):

\[
0 = \sin((m + 1)k) \cos(mk) \\
0 = \cos((m + 1)k) \sin(mk) .
\] (3.61)

With \( \sin l\pi = 0 \) for each integer \( l \), these two conditions hold simultaneously. The formal solution \( \kappa = 0 + l\pi \) (\( \kappa_R = 0 \)) of (3.60) must be excluded, because any state with \( u_n \sim \cosh(n \cdot 0) \) represents a state which cannot be normalized.

b) \( k \neq l\pi \) (\( l = 0, 1 \)):
With an arbitrary \( k \neq l\pi \), the real part \( \kappa_R \) has to fulfill:

\[
0 = \sinh((m + 1)\kappa_R) \cosh(m\kappa_R) \quad \text{and} \quad 0 = \cosh((m + 1)\kappa_R) \sinh(m\kappa_R) .
\] (3.62)

These conditions (3.62) require a vanishing real part of \( \kappa, \kappa_R = 0 \).

Similarly we can collect analogous conditions within the equations describing the anti-symmetrical solutions. From equation (3.53) we get the requirement

\[
\frac{\sinh m\kappa}{\sinh(m + 1)\kappa} \in \mathbb{R}, \quad \text{or equivalently}
\]

\[
\text{Im} \left( \frac{\sinh m\kappa}{\sinh(m + 1)\kappa} \right) = 0
\] (3.63)

which transforms with

\[
\sinh m\kappa \overset{(3.56)}{=} \cosh(m\kappa_R) \sinh(imk) + \sinh(m\kappa_R) \cosh(ikm)
\]

\[
= \sinh(m\kappa_R) \cos(mk) + i \cosh(m\kappa_R) \sin(km)
\] (3.64)

into the final expression:

\[
0 = \text{Im} \left( \frac{\sinh m\kappa}{\sinh(m + 1)\kappa} \right) = \text{Im} \left( \frac{\sinh m\kappa \cdot [\sinh(m + 1)\kappa]^*}{\sinh(m + 1)\kappa \cdot [\sinh(m + 1)\kappa]^*} \right)
\]

\( \Leftrightarrow \)

\[
0 = \text{Im} \left( \sinh m\kappa \cdot [\sinh(m + 1)\kappa]^* \right)
\]

\( \overset{(3.64)}{=} \)

\[
\text{Im} \left( (\sinh(m\kappa_R) \cos(mk) + i \cosh(m\kappa_R) \sin(km)) \times \right.
\]

\[
(\sinh((m + 1)\kappa_R) \cos((m + 1)k) - i \cosh((m + 1)\kappa_R) \sin((m + 1)k)) \right)
\]

evaluate \( \text{Im} \)

\[
0 = \sin((m + 1)k) \cos(mk) \cdot \cosh((m + 1)\kappa_R) \sinh(m\kappa_R)
\]

\[
- \cos((m + 1)k) \sin(mk) \cdot \sin((m + 1)\kappa_R) \cosh(m\kappa_R) .
\] (3.65)

From the evaluation of (3.65) for arbitrary \( k \neq l\pi \) we obtain the conditions (cf. Eq. 3.62)

\[
0 = \sinh((m + 1)\kappa_R) \cosh(m\kappa_R)
\]

\[
0 = \cosh((m + 1)\kappa_R) \sinh(m\kappa_R)
\] (3.66)
which are fulfilled simultaneously only for a vanishing $\kappa_R = 0$. For $\kappa$ with $\kappa_R \neq 0$ we get also conditions already known from the symmetric case (cf. Eq. 3.61):

\begin{align*}
0 & = \sin((m+1)k)\cos(mk) \\
0 & = \cos((m+1)k)\sin(mk)
\end{align*}

which hold both for any $k = l\pi$ ($l$ integer).

Hence, the requirement of real energy values $E(\kappa)$ given by the equations (3.51, 3.53) leads to this range of permitted $\kappa$:

\[
\kappa = \begin{cases} 
\text{Im}\kappa = k, & \text{Re}\kappa \equiv \kappa_R = 0 \\
\kappa_R, & \kappa_R \neq 0 \\
\kappa_R + i\pi, & \kappa_R \neq 0
\end{cases}
\]

(a) 
(b) 
(c) 
(d)

**Figure 3.5:** Graphical determination of the allowed $\kappa$ for a chain of $N = 5$ molecules described by the parameters $E_F = E_{CT} = 0$, $M = \epsilon_h = 0.2$ eV, and $\epsilon_e = 0$. By putting equal the l.h.s. (black curve) with the r.h.s (gray curve) of Eqs. (3.52, 3.54), the solutions are given by the junctions (indicated by vertical dotted lines). Following Eq. (3.68), the full set of $\kappa$ is divided into several contributions (a)-(d) : With $\text{Re}\kappa = 0$, $\text{Im}\kappa \equiv k$, Eq. (3.52) reduces to Eq. (3.69) in the symmetrical case (a), and Eq. (3.54) reduces to Eq. (3.70) antisymmetrical case (b), respectively. If $\text{Re}\kappa \neq 0$ does not vanish, each of the Eqs. (3.52, 3.54) yield one solution at maximum. Using the parameters listed above, only for the symmetrical case (c) a solution exist whereas the antisymmetrical case (d) cannot contribute any further $\kappa$.

A further limitation of the permitted $\kappa$ is provided by the equations (3.52) and (3.54), both are conditions which contain the dependence of $\kappa$ on $N = 2m + 1$. Such equations
Formation of mixed Frenkel charge transfer excitons in finite chains can hardly be solved analytically. Therefore we always obtain the set of allowed $\kappa$ numerically. Nevertheless, it is also possible to determine such a set of $\kappa$ by solving the equations (3.52, 3.54) graphically. Figure 3.5 displays the procedure for the case of $N = 5$ molecules with $\tilde{\Delta} = 0$, $\alpha = 1$ and $\beta = 0$. The application of condition (3.68) in equations (3.52, 3.54) yields expressions which exclusively contain real terms. Then, the solutions $\kappa$ appear as junctions of the graphs representing the l.h.s and the r.h.s of each equation, respectively. In Figure 3.5 the l.h.s is always represented by black and the r.h.s by a gray curve.

For $\kappa_R = 0$ equation (3.52) simplifies with equation (3.55) to
\begin{equation}
\tilde{\Delta} + \beta + 2 \cos k + \frac{\alpha \cos (mk)}{\cos ((m+1)k)} = \frac{\alpha + \beta \cos k}{\alpha \cos (mk) + \beta \cos ((m+1)k)},
\end{equation}
and equation (3.54) with equation (3.56) to
\begin{equation}
\tilde{\Delta} + \beta + 2 \cos k + \frac{\alpha \sin (mk)}{\sin ((m+1)k)} = \frac{\alpha + \beta \cos k}{\alpha \sin (mk) + \beta \sin ((m+1)k)}.
\end{equation}
Exemplarily, the special case considered in Figures 3.5(a), 3.5(b) points out that the numbers $k$ are not equidistantly distributed in the interval $[0, \pi]$. Inserted into the ansatz for the eigenstates, the coefficients $u_n$ becomes proportional to $\cos(\kappa n)$ for symmetric states, and proportional to $\sin(\kappa n)$ for antisymmetric states, respectively. Below, we will assign these states as bulk states which are similar to the solutions in chains with Frenkel excitons only (see Section 4.2).

For $\kappa = \kappa_R + l\pi$ ($l = 0, 1$) equation (3.52) becomes
\begin{equation}
\tilde{\Delta} + \beta \pm 2 \cosh \kappa_R + \frac{\alpha \cosh (m\kappa_R)}{\cosh ((m+1)\kappa_R)} = \frac{\alpha \pm \beta \cosh \kappa_R}{\alpha \cosh (m\kappa_R) + \beta \cosh ((m+1)\kappa_R)}
\end{equation}
and its antisymmetric counterpart (3.52) reduces to
\begin{equation}
\tilde{\Delta} + \beta \pm 2 \sinh \kappa_R + \frac{\alpha \sinh (m\kappa_R)}{\sinh ((m+1)\kappa_R)} = \frac{\alpha \pm \beta \cosh \kappa_R}{\alpha \sinh (m\kappa_R) + \beta \sinh ((m+1)\kappa_R)}.
\end{equation}
Symmetric solutions are parameterized with a set of $\kappa$ given by equation (3.69) and equation (3.71). Such a $\kappa$ enable a new type of excitonic states. We will see in Section 4.3 that for these solutions the function $u_n$ is localized near the ends of the chain.

In Figure 3.6, we collect all solutions of a system which will serve as an illustrative example throughout the next chapters. The on-site energies $E_F$ and $E_{CT}$ are in resonance. The interactions are quantified with $M = \epsilon_h = 0.2$ eV and $\epsilon_e = 0$. The upper parts contains the state energies dependent on $k = \text{Im}\kappa$ for varying system size $N$. In the infinite chain the scheme reduces to two bands containing states of mixed character. All $k$ in the Brillouin zone $k = [0, \pi]$ are allowed. In the finite chain, the number of permitted $k$ becomes restricted. With smaller $N$, the number of allowed $k$ reduces and the states are redistributed in the Brillouin zone (see $N = 41$ and $N = 5$).
3.3 The diagonalization method for finite chains

Figure 3.6: Energies and fractional oscillator strength for finite chains of different length in comparison to the corresponding infinite chain. The on-site energies $E_F$ and $E_{CT}$ are set to zero. The interaction parameters are chosen as $M = \epsilon_h = 0.2 \text{ eV}$, and $\epsilon_e = 0$. The upper part contains the energy of the solutions dependent on $k = \text{Im} \kappa$. The excitonic bands of the corresponding infinite chain are additionally indicated (black lines). In the lower part electronic spectra are given.
3.3.2 Formalism for chains containing an even number of molecules

For an even number \( N = 2m \) of molecules, the diagonalization formalism of Hamiltonian (3.1) introduced in the previous section has to be adjusted. Now we reindex the molecular sites as shown in Figure 3.4(b). This label set not only enumerates symmetry-equivalent molecules with the same \( |n| \), it also ensures that nearest neighbors are still separated by an index difference of \( 1 \). Hence, all equations and statements which do not depend on the boundary sites \( m \pm \frac{1}{2} \) can be taken directly from the odd-\( N \)-case: The system of equations for bulk molecules (3.34) can be exclusively expressed by Frenkel-type basis functions (3.38.1).

The essential symmetry condition (3.32) motivates again the ansatz for \( u_n \)

\[
\begin{align*}
u_n &= A \cosh \kappa n \quad \text{(symmetric)} \quad \quad (3.73) \\
u_n &= A \sinh \kappa n \quad \text{(antisymmetric)} \quad \quad (3.74)
\end{align*}
\]

with which the relation \( E(\kappa) \) (3.40, 3.48) can be generated immediately. To find the set of allowed \( \kappa \) and the corresponding energies, the boundary conditions must be adjusted to the label set presently used. The form of the responsible equations, however, will not change. Whereas an outermost molecule in the odd-\( N \)-chain has an index \( \pm m \), it has the label \( \pm (m - \frac{1}{2}) \) in the even-\( N \)-chain. By substituting consequently \( m \to m - \frac{1}{2} \), we easily obtain all equations which describe even-\( N \)-chains: The energies are inherited from expressions (3.51) and (3.53):

\[
\begin{align*}
\Delta_{\text{CT}} &= \beta + \alpha \frac{\cosh \left( m - \frac{1}{2} \right) \kappa}{\cosh \left( m + \frac{1}{2} \right) \kappa} \quad \text{(symmetric)}, \quad (3.75) \\
\Delta_{\text{CT}} &= \beta + \alpha \frac{\sinh \left( m - \frac{1}{2} \right) \kappa}{\sinh \left( m + \frac{1}{2} \right) \kappa} \quad \text{(antisymmetric).} \quad (3.76)
\end{align*}
\]

As shown in the previous Section 3.3.1, the demand of real \( E(\kappa) \) values is a major tool to get essential restriction conditions on the form of \( \kappa \). Therefore the impact of the relabeled boundary sites has to be checked. With \( m \to \tilde{m} := m - \frac{1}{2} \), the conditions

\[
\begin{align*}
\frac{\cosh \left( m - \frac{1}{2} \right) \kappa}{\cosh \left( m + \frac{1}{2} \right) \kappa} &= \frac{\cosh \tilde{m}\kappa}{\cosh(\tilde{m} + 1)\kappa} \in \mathbb{R} \quad \text{and} \\
\frac{\sinh \left( m - \frac{1}{2} \right) \kappa}{\sinh \left( m + \frac{1}{2} \right) \kappa} &= \frac{\sinh \tilde{m}\kappa}{\sinh(\tilde{m} + 1)\kappa} \in \mathbb{R}
\end{align*}
\]

are equivalent with the formulations (3.57, 3.63). Both yield the final conditions (3.62) and (3.61) which permit the same range (3.68) of \( \kappa \), as already found for the odd-\( N \)-case:

\[
\kappa = \begin{cases} 
\text{Im} \kappa = k, & \text{Re} \kappa \equiv \kappa_R = 0 \\
\kappa_R, & \kappa_R \neq 0 \\
\kappa_R + i\pi, & \kappa_R \neq 0 .
\end{cases} \quad (3.79)
\]

The relations which finally determine \( \kappa \) from the boundary conditions are

\[
\begin{align*}
(\tilde{\Delta} + \beta) + 2 \cosh \kappa + \alpha \frac{\cosh \left( m - \frac{1}{2} \right) \kappa}{\cosh \left( m + \frac{1}{2} \right) \kappa} &= \frac{\alpha + \beta \cosh \kappa}{\alpha \cosh \left( m - \frac{1}{2} \right) \kappa + \beta \cosh \left( m + \frac{1}{2} \right) \kappa} \quad (3.80)
\end{align*}
\]
3.4 The oscillator strength

The contribution of each eigenstate $|j\rangle$ to the optical absorption spectrum of a molecular chain is provided by the oscillator strength $F^j$. It is assumed that the length of the chain is small in comparison with the optical wavelength corresponding to the energy of electronic excitation. In this case, the effects of retardations (polaritonic effects) can be neglected and $F^j$ is primarily determined by the length of the transition dipole moment $p^j$ squared [82]:

$$F^j = \frac{2m_e^2}{\epsilon^2 \hbar^2} E^j |p^j|^2 \quad .$$

(3.82)

The change of the optical electric field along the chain can be neglected in the evaluation of the exciton transition dipole moment. In this approximation, the total transition dipole moment from the ground $|0\rangle$ to the excited crystal state $|j\rangle$ is:

$$p^j = \langle j| \hat{p} |0\rangle$$

(3.83)

$$= \left( \sum_{n=1}^{N} u_n^j \langle \text{ME}_n | + \sum_{n=1}^{N-1} v_{n+1}^j \langle \text{CT}_{n+1} | + \sum_{n=2}^{N} v_{n-1}^j \langle \text{CT}_{n-1} | \right) \hat{p} |0\rangle$$

$$= p^F \sum_{n=1}^{N} u_n^j + p^{+\text{CT}} \sum_{n=1}^{N-1} v_{n+1}^j + p^{-\text{CT}} \sum_{n=2}^{N} v_{n-1}^j ,$$

where $\hat{p}$ is the dipole operator. With $p^F$ we denote the molecular transition dipole moment

$$p^F = \langle \text{ME}_n | \hat{p} |0\rangle$$

(3.84)

which is the same for each site $n$. The transition dipole moments attributed to the $\pm$ CT states are $p^{+\text{CT}}$ and $p^{-\text{CT}}$, respectively:

$$p^{\pm\text{CT}} = \langle \text{CT}_{n\pm1} | \hat{p} |0\rangle .$$

(3.85)

With its vector character, the transition dipole moment $p$ carries two information [83]: Its absolute value enters the oscillator strength (see equation 3.82) and therefore mainly determines the intensity with which a state contributes to the absorption spectrum. Its direction describes how effectively the electrical field component $E$ of the incident wave can excite the transition. Only the component $p_{\text{eff}} = p \cdot \frac{E}{|E|}$ parallel to the electrical field enters the oscillator strength. For $p \perp E$ and therefore $p \parallel k_{\text{light}}$ no excitation takes place.

In general, the CT transition dipole moments are oriented along directions different from $p^F$. Due to the varying admixture of CT-type excitations, the total transition dipole

\[
(\tilde{\Delta} + \beta) + 2 \cosh \kappa = \frac{\alpha \sinh \left( m - \frac{1}{2} \right) \kappa}{\sinh \left( m + \frac{1}{2} \right) \kappa} + \alpha \beta \cosh \kappa + \alpha \beta \sinh \left( m - \frac{1}{2} \right) \kappa + \beta \sinh \left( m + \frac{1}{2} \right) \kappa .
\]

(3.81)

for symmetric and antisymmetric solutions, respectively (cf. Eq. 3.52, 3.54).

Therefore we can restrict our further demonstrations to chains with an odd number of molecules, because the even-$N$ case can be generated by the substitution $m \rightarrow \tilde{m} := m - \frac{1}{2}$ anytime.
moments $\mathbf{p}^j$ do not share the same direction. The resulting electronic spectrum observed depends on the polarization of the probing electrical field. However, the intrinsic CT transition dipole moment $\mathbf{p}_{\pm}^{\text{CT}}$ is (at least) an order of magnitude smaller than $\mathbf{p}^F$ \cite{53}. As a consequence, the absolute value of $\mathbf{p}^j$ is mainly given by the Frenkel part $\left(\sum_{n=1}^{N} u^j_n\right) \mathbf{p}^F$, even if the Frenkel coefficients $u^j_n$ are rather small. Thus, the CT contribution is omitted in the following. This approximation ensures equally directed transition dipole moments $\mathbf{p}^j$ for all $j$ and therefore electronic spectra independent from the polarization of the probing light.

The *fractional oscillator strength*

$$f^j = \frac{(\mathbf{p}^j)^2}{(\mathbf{p}^F)^2} = \left(\sum_{n=1}^{N} u^j_n\right)^2$$  \hspace{1cm} (3.86)

provides a measure of the oscillator strength of a state $|j\rangle$ in relation to the molecular excitation with the transition dipole moment $\mathbf{p}^F$. The less a state oscillates, i.e., the less the sign of the $u_n$ change, the larger the sum in (3.86) becomes. The nodal structure of the eigenstates is described by the quantum number $k$. At $k = 0$ all molecular transition dipole moments $\mathbf{p}^F$ are *oriented* equally. With larger $k$, the contributions to $f^j$, $u_n$, $\mathbf{p}^F$, start to compensate each other. At $k = \pi$, finally the opposite situation is realized with the molecular transition dipole moments of neighboring sites oriented against each other.

Adjusted for inversion symmetry, $f^j$ reads for odd-$N$ chains:

$$f^j = \left(\sum_{n=-m}^{m} u^j_n\right)^2.$$  \hspace{1cm} (3.87)

The inversion symmetry immediately forbids a transition from the ground state into an antisymmetric state ($u_n = -u_{-n}$). The corresponding transition dipole moment $\mathbf{p}^j$ in relation (3.87) becomes exactly zero. In case of periodic boundary conditions, the dipole-selection demand zero $\mathbf{p}^j$ for all states $|j\rangle$ with $k \neq 0$.

The lower part of Figure 3.6 displays the energy versus the fractional oscillator strength $f$ for the representative system with $E_F$ and $E_{\text{CT}}$ in resonance. For the infinite case only the band edges at $k = 0$ have oscillator strength. Since at $k = 0$ the admixture of CT excitations in the upper band is smaller than in the lower band, $f^j$ is larger for the state at higher energy. In finite systems the oscillator strength is distributed over all available symmetric states. For a rather large number of molecules ($N = 41$), the distribution of $f^j$ does not strongly differ from the infinite case, still the states with $k \approx 0$ (but $k \neq 0$) govern the spectrum. In small chains, however, more states get substantial oscillator strength.
4

Structure of the excited states

With the knowledge of the preceding chapter, we can associate the eigenstates of arbitrary finite and infinite chains with two quantum numbers: The energy $E$ and the wave vector $\kappa$. Both quantum numbers depend on the parameters $E_F$, $E_{CT}$, $M$, $\epsilon_e$, and $\epsilon_h$ in a subtle way. The form of the wave vectors permitted (cf. Eq. (3.68)) already suggests that the whole set of eigenstates decomposes into sub-spaces with very different properties. Throughout the following chapter, we will analyze the internal structure of the states separately for each sub-space and discuss the consequences for the absorption spectra.

4.1 The infinite chain

In Section 3.2 we solved the Hamiltonian (3.1) for the infinite chain. Owing to the periodic boundary conditions, three continuous excitonic bands $E(k)$ were formed. The two mixed bands $E_{1,2}(k)$ are given as

$$E_{1,2}(k) = \frac{E_{CT} + E_F + 2M \cos k}{2} \pm \sqrt{\left(\frac{E_F - E_{CT} + 2M \cos k}{2}\right)^2 + 2\epsilon_k^2}.$$ (4.1)

Transformed into dimensionless quantities (cf. Eqs. (3.44, 3.45)), the dispersion relation (4.1) becomes:

$$\Delta_{CT1,2} = -\frac{1}{2} \left\{ \hat{\Delta} + 2 \cos k \pm \sqrt{\left(\hat{\Delta} + 2 \cos k\right)^2 + 8(\alpha + \beta \cos k)} \right\}.$$ (4.2)

The wave function corresponding to the state described with $E_i(k)$ ($i = 1, 2$) has the form (cf. Eq. (3.28))\(^1\):

$$|\psi_i(k)\rangle := \zeta_k^i |0\rangle = u_i(k) |\hat{B}_k^i 0\rangle + v_{gi}(k) |\hat{C}_k^i 0\rangle = u_i(k) |FE_k\rangle + v_{gi}(k) |CT_k\rangle.$$ (4.3)

$$= u_i(k) |FE_k\rangle + v_{gi}(k) |CT_k\rangle.$$ (4.4)

The coefficients $u_i(k)$ and $v_{gi}(k)$ are determined by the equation

$$(H(k) - E_i(k) \cdot \hat{I}) \begin{pmatrix} u_i(k) \\ v_{gi}(k) \end{pmatrix} = 0.$$ (4.5)

\(^1\)To introduce a band label we changed the notation $u_k$ given in Eq. (3.28) to $u(k)$ and $v_k$ to $v(k)$, respectively.
With the known solutions $E_i(k)$ the coefficients obey

$$
\begin{align*}
(E_F + 2M \cos k - E_i(k)) u_i(k) + \sqrt{2\epsilon_k} v_g(k) &= 0 \\
\sqrt{2\epsilon_k} u_i(k) + (E_{CT} - E_i(k)) v_g(k) &= 0.
\end{align*}
$$

(4.6)

Additionally the coefficients have to ensure normalized wave functions:

$$
u_i^2(k) + v_g^2(k) = 1.
$$

(4.7)

An important feature of each state is the ratio of Frenkel and CT admixture. We introduce the mixing ratio $\eta$ as

$$
\eta_i(k) := \frac{v_g(k)}{u_i(k)}.
$$

(4.8)

With the help of $\eta$, we can decide the parentage of the state: For $|\eta_i(k)| < 1$, the state is dominated by the Frenkel part $u_i(k)$ and therefore of Frenkel parentage. If $|\eta_i(k)| > 1$, the state is governed by $v_g(k)$ and has CT parentage. If we introduce the relationships between $u_i(k)$ and $v_g(k)$ given by conditions (4.6), $\eta_i(k)$ takes the form:

$$
\eta_i^2(k) = \left(\frac{v_g(k)}{u_i(k)}\right)^2 = \frac{E_i(k) - (E_F + 2M \cos k)}{E_i(k) - E_{CT}} = \frac{\Delta_{CT} + (\tilde{\Delta} + 2 \cos k)}{\Delta_{CT}}.
$$

(4.9)

(4.10)

The mixing ratio squared, $\eta^2$, of states with equal Frenkel - CT admixture becomes unity. From equation (4.9), we can extract the value of $k$ at which a Frenkel parentage turns into a CT parentage:

$$
\eta_i^2(\tilde{k}) = \frac{E_i(\tilde{k}) - (E_F + 2M \cos \tilde{k})}{E_i(\tilde{k}) - E_{CT}} = 1
$$

(4.11)

$$
\Leftrightarrow \cos \tilde{k} = \frac{E_F - E_{CT}}{2M} = -\frac{\tilde{\Delta}}{2}.
$$

(4.12)

The $k$-value of turning parentage, $\tilde{k}$, is given by the separation $\tilde{\Delta}$ of the Frenkel and CT on-site energies, but is entirely independent of the Frenkel-CT interaction parameters.

Using form (4.1), the curvature of the bands $E(k)$ (or $\Delta_{CT}(k)$ with (4.2), respectively) can be studied easily as a function of the parameters introduced with Hamiltonian (3.1). Figures (4.1, 4.2) display several representative situations. We already give the plots together with the corresponding picture in dimensionless parameters.

As the choice of dimensionless parameters suggests, it is important to know how the separation of the Frenkel on-site energy $E_F$ and the CT on-site energy $E_{CT}$ influences the band shapes. In Figure 4.1, we compare the excitonic bands of the most common case $E_F < E_{CT}$ ($\tilde{\Delta} < 0$) with resonance $E_F = E_{CT}$ ($\tilde{\Delta} = 0$), and with $E_F > E_{CT}$ ($\tilde{\Delta} > 0$) while the interaction parameters $M$, $\epsilon_e$, and $\epsilon_h$ are fixed. The parentage of a band state is determined by its relative energetical position with respect to the pure Frenkel and to the CT band: In Figure 4.1(a), for example, the upper band $E_1$ starts at $k = 0$ as Frenkel governed state. With increasing $k$, the CT admixture rises. Eventually, the $k$-value is crossed so that beyond $\tilde{k}$ the state at $E_1(k)$ is dominated by the CT part. In $k = \pi$, $E_1(\pi)$ approaches $E_{CT}$ and $\eta_1(\pi)$ reaches its maximum. Tracking $E_2(k)$ from $k = 0$ to $k = \pi$, the ratio of
4.1 The infinite chain

Frenkel-CT admixture changes in the opposite way. With lowering $E_{CT} - E_F$, the point of turning parentage is shifted towards higher $k$.

Another important factor is the coupling due to $\epsilon_e$ and $\epsilon_h$, particularly its balance expressed with $\beta$. The effect of the charge transfer integrals is $k$-dependent (cf. Eq. (3.19)). As it follows from equation (3.19), at $k = 0$ only the sum of $\epsilon_e$ and $\epsilon_h$ enters the coupling expression in $\epsilon_0$. Exactly opposite, $\epsilon_\pi$ is fully determined by the difference of $\epsilon_e$ and $\epsilon_h$ at $k = \pi$:

$$\epsilon_0 = \epsilon_e + \epsilon_h, \quad \epsilon_\pi = \epsilon_e - \epsilon_h.$$

The better the charge transfer integrals are balanced ($|\beta| \to \alpha$), the more pronounced the difference between $\epsilon_0$ and $\epsilon_\pi$ becomes (Figure 4.2). We consider first that the charge transfer integrals are perfectly balanced (Figure 4.2(a)). With $\epsilon_e = \epsilon_h$ ($\beta = \alpha$), the Frenkel and CT excitons do not mix ($\epsilon_\pi = 0$) at the boundary of the Brillouin zone. Thus, the state at the band edge $E_1(\pi)$ is a pure Frenkel exciton and the state corresponding to $E_2(\pi)$ a CT exciton. In case that one of the charge transfer integrals vanishes ($\epsilon_e = 0$ in Figure 4.2(b)), $\epsilon_k$ becomes independent of $k$ (in Figure 4.2(b): $\epsilon_k = \epsilon_h$). In the last case (see Figure 4.2(c)), we finally return to the perfectly balanced case, but now with the charge transfer integrals carrying the opposite sign, $\epsilon_h = -\epsilon_e$ ($\beta = -\alpha$). Opposite to the situation in Figure 4.2(a), $\epsilon_0$ vanishes completely and leaves the band edges at $k = 0$ as pure Frenkel ($E_1(0)$) and CT exciton ($E_2(0)$), respectively.

Note that in both examples the choice of parameters used enables perfectly flat bands. So far, the discussion of the band formation (see Figure 3.3) taught us that absent interactions are responsible for flat bands. Now, the interaction parameters in Figure 4.1(c) and in Figure 4.2(c) represent a rather strong coupling. Evidently, there are combinations of parameters providing a coupling situation such that any $k$-dependence is suppressed, although the parameters have large values. We investigate this situation in more detail in Section 4.4.3.

To complete the set of solutions found for an infinite chain, we have to mention the appearance of a third band. This bands consists of pure $A_u$ CT excitons which are not allowed to couple either to Frenkel or to $A_g$ CT excitons. As already derived in Section 3.2, these $|CTu\rangle$ states are degenerate at $E_{CT}$, but can be assigned with the quantum number $k$ (cf. Eq. (3.26)).

Combined with Section 3.2, the remarks given above illustrate the formation of excitonic bands in infinite systems for an arbitrary set of model parameters. We will see in the next section that this knowledge easily grants access to solutions of finite chains.
Figure 4.1: Shape of excitonic bands determined by the offset of $E_F$ and $E_{CT}$ (a). The coupling parameters are chosen as $M = 0.2$, $\epsilon_e = \epsilon_h = 0.14$ ($\alpha = 1$, $\beta = 1$). In (b), the corresponding situation expressed with dimensionless parameters is shown. The additional, dashed lines correspond to the pure Frenkel bands and the horizontal lines to pure CT bands, respectively.
Figure 4.2: Shape of excitonic bands determined by the balance of $\epsilon_e$ and $\epsilon_h$ (a). The on-site parameters are chosen as $E_{CT} = 0.2$ eV, $E_F = 0$ ($\tilde{\Delta} = -1$) and $M = 0.2$ (eV). In (b), the corresponding situation expressed with dimensionless parameters is shown. The additional, dashed lines correspond to the pure Frenkel bands and the horizontal lines to pure CT bands, respectively.
4.2 Bulk states

The eigenstates in finite chains are characterized by a complex wave vector $\kappa$. According to statement (3.68), these wave vectors are restricted to either purely imaginary values $i \kappa$ or to values in the form $\kappa_R + q \cdot i \pi$ ($q = 0, 1$).

For purely imaginary solutions of $\kappa$, the coefficients $u_n$ of the eigenstates become proportional to $\cos nk$. The boundary conditions (3.69, 3.70) determine the set of allowed $\kappa$. However, the energies $E(k)$ of the states are determined by

\[ ((E_F - E) + 2M \cos k)(E_{CT} - E) - 2(\epsilon_e^2 + \epsilon_h^2 + 2\epsilon_e\epsilon_h \cos k) = 0 \]  
(4.15)

which yields $E(k)$ exactly in the form already known from the infinite system (cf. Eq. (3.30)):

\[ E_{1,2}(k) = \frac{E_{CT} + E_F + 2M \cos k}{2} \pm \sqrt{\left(\frac{E_F - E_{CT} + 2M \cos k}{2}\right)^2 + 2\epsilon_k^2} \cdot \]  
(4.16)

With the discrete set of permitted $k$, a finite number of such states appears; all of them are aligned on the bands of the corresponding infinite chain. This exact matching motivates to call them bulk states.

Owing to the boundary conditions, the bulk states are not equally spaced in the Brillouin zone. Their number varies with the total number of molecules $N$. At maximum, $2N$ bulk states can appear, provided that equations (3.52, 3.54) yield exclusively imaginary wave vectors $\kappa$.

The similarity of bulk states with the band states is very well reflected by the distribution of the bulk states over the chain. Since the coefficients $v_{n,\pm 1}$ which represent the CT part of each state are coupled to the Frenkel part $u_n$ by equation (3.37), the states can be sufficiently visualized with the behavior of the $u_n$. To demonstrate the relationship of the Frenkel and charge transfer coefficients efficiently, we introduce symmetry-adapted charge transfer coefficients (cf. Eq. (3.32)):

\[ v_{n+} := \frac{1}{\sqrt{2}} (v_{n-1} + v_{n+1}) \quad (n = -m, \ldots, m - 1) \]  
(4.17)

\[ v_{n-} := \frac{1}{\sqrt{2}} (v_{n-1} - v_{n+1}) \quad (n = -m+1, \ldots, m) \]  
(4.18)

For symmetric states, the $v_{n-}$ are exactly zero. Vice versa, the $v_{n+}$ are found zero in antisymmetric states. According to the boundary conditions for free ends, the CT states with $v_{n+}$ and $v_{n-}$ at the outermost molecules are omitted. In Figure 4.3 we illustrate typical bulk states of the example system introduced in Figure 3.6. We have chosen the states with smallest available wave vectors $k$ of the upper band. Both the symmetric and the antisymmetric state are fully delocalized over the whole chain. The charge transfer contributions follow the behavior of the $u_n$ (as expected from Eq. (3.37)). Reflecting the leading Frenkel character, the absolute value of $u_n$ is larger than the charge transfer coefficient $v_{n\pm}$.

The band structure in the first Brillouin zone of the corresponding infinite chain turns out to be a useful tool to study the $N$-dependence of bulk states. First, the bulk states can be assigned to the underlying excitonic band states. The composition in terms of Frenkel
4.2 Bulk states

(a) symmetric state

(b) antisymmetric state

Figure 4.3: Bulk states in site representation found in a chain of $N = 41$ molecules with $E_F = E_{CT} = 0$, $M = \epsilon_h = 0.2$ eV, and $\epsilon_e = 0$ (see Figure 3.6). Both states are located in the upper band and represent the symmetric state (a) and the antisymmetric state (b) with smallest $k$ each. The distribution of $u_n$ is displayed in the black curve (open circles). The charge transfer contribution (solid circles) is shown with the help of the symmetry-adapted coefficients $v_{n\pm}$ (cf. Eqs. (4.17), (4.18)). The symmetry adaption demands $v_{n-} = 0$ for symmetric states, and $v_{n+} = 0$ for antisymmetric states.

and charge transfer excitons of a bulk state is expressed by

$$\eta^2_i(k) := \frac{v^2_{\pm i}(k)}{u^2_i(k)} = \sum_{n=-m}^{m} \frac{|v_{n\pm}(k_i)|^2}{\sum_{n=-m}^{m} |u_{n}(k_i)|^2} \begin{cases} + : \text{ symmetric} \\ - : \text{ antisymmetric} \end{cases} \quad (4.19)$$

In Figure 4.4, we display for the sample chain (cf. Figure 3.6) the mixing ratio for $N = 5$ and $N = 41$ and compare the values to the mixing ratio calculated for the infinite chain (cf. Eq. (4.9)). For rather long chains, $\eta$ is comparable with the mixing ratio of the underlying band state. However, for small aggregates we observe a significant deviation from the infinite chain. The reason for this can be seen in Figure 3.6. In the dispersion graph, e.g., for $N = 5$ (right upper image), we observe states in the band gap which clearly do not belong to the bulk states. We will discuss them in the next section. Nevertheless, it should be mentioned already now that a certain amount of Frenkel contribution is raised from such states; a process which intensifies with decreasing chain length (see also Section 5.3).

The larger the chain, the closer the smallest allowed wave vector $k$ gets to zero, which is the limit given by the infinite chain. The energy of the states closest to the center of the first Brillouin zone is shifted, because their wave vectors shift towards higher $k$ (cf. Figure 3.6). The direction and the amount of this shift is determined by the dispersion of the bands.

For very long chains the energy range spanned by the bands is tightly filled with states. Hence, the energy of bulk states closest to $k = 0$ is identical with the band edges of the infinite chain. Similarly, states with a $k$ closest to $\pi$ lie almost exactly at the position of the band edges at the boundary of the Brillouin zone. In further discussions which are devoted
Figure 4.4: Mixing ratio squared, $\eta^2$, of bulk states for several chains with $E_F = E_{\text{CT}} = 0$, $M = \epsilon_h = 0.2$ eV, and $\epsilon_e = 0$ (see Figure 3.6). Graph (b) shows $\eta^2$ for the upper band; image (c) $\eta^2$ for the lower one. The solid lines represent $\eta^2$ of the infinite chain (from Eq. (4.9)). With open symbols, $\eta^2$ for chains of $N = 5$ and $N = 41$ molecules, respectively, are indicated. In graph (a), we also give the band structure of the infinite chain. For rather small chains, $\eta^2$ differ considerably from the expectation for infinite chains, especially pronounced for bulk states near the band gap.

to sufficiently long chains, the usage of the band edges instead of the bulk states with $k$ closest to 0 or $\pi$ is legitimate (see Figure 3.6).

From the expression for the fractional oscillator strength $f^i$ (Eq. (3.86)), it can be expected that the states with $k$ close to zero will carry the largest oscillator strengths (similarly to analogous states in molecular chains with Frenkel excitons [71]). With increasing chain length $N$, the oscillator strength of the bulk states belonging to one excitonic band is successively redistributed to the state with lowest $k$. The pure CT states which cannot be described by the diagonalization formalism have to be added to the manifold of bulk states as well.
4.3 Surface states

In this section we will analyze the nature of states found with \( \text{Re} \kappa \neq 0 \) more deeply. This type of solutions does not correspond to a solution already known from the infinite chain. As already mentioned in Section 3.3.1, the effect of a partly real quantum number \( \kappa \) can be revealed best in very long chains.

Without loss of generality, we assume that equation (3.52) has solutions \( \kappa \) with \( \text{Re} \kappa > 0 \). Hence, \( |e^{-\kappa}| \) must be smaller than 1. For long chains \( (N \gg 1) \) the term \( |e^{-N\kappa}| \ll 1 \) can be neglected and therefore all further considerations become independent of the difference between odd-\( N \)-chains and even-\( N \)-chains. Exemplarily, we demonstrate the implications for odd-\( N \)-chains \( (N = 2m + 1) \): The energy relation (3.51) takes in the limit \( |e^{-m\kappa}| \ll 1 \) the rather simple form

\[
\Delta_{\text{CT}} = \beta + \alpha \frac{\cosh m\kappa}{\cosh (m + 1)\kappa}
\]

which becomes with the abbreviation \( Z = e^{-\kappa} \) < 1

\[
\Delta_{\text{CT}} = \beta + \alpha Z .
\]

The equation (3.52) determining \( \kappa \) simplifies substantially as well. We will see right below, that the permitted \( \kappa \) can then be derived analytically. By means of \( Z \), the term containing \( \cosh \kappa \) in equation (3.52) can be rewritten as \( 2 \cosh \kappa = Z + \frac{1}{Z} \):

\[
0 = (\hat{\Delta} + \beta) + 2 \cosh \kappa + \frac{\alpha \cosh m\kappa}{\cosh (m + 1)\kappa} - \frac{\alpha + \beta \cosh \kappa}{\alpha \cosh m\kappa + \beta \cosh (m + 1)\kappa}
\]

\[
|e^{-m\kappa}| \ll 1
\]

\[
(\hat{\Delta} + \beta) + \left( Z + \frac{1}{Z} \right) + \alpha Z - 2 \left( \alpha + \frac{1}{\alpha} \right) \beta \left( Z + \frac{1}{Z} \right)
\]

collect terms with \( Z^x \)

\[
\alpha(1 + \alpha)Z^3 + \alpha(\hat{\Delta} + 2\beta)Z^2 + \left( \beta(\hat{\Delta} + \beta) - \alpha \right) Z
\]

\[
\Rightarrow 0 = Z^2 + Z \frac{\hat{\Delta} + 2\beta}{1 + \alpha} - \frac{1}{\alpha}(\alpha - (\hat{\Delta} + \beta)\beta).
\]

The solutions of equation (4.22) for \( Z \) are:

\[
Z_{1,2} = -\frac{\hat{\Delta} + 2\beta}{2(1 + \alpha)} \pm \frac{1}{2(1 + \alpha)} \sqrt{(\hat{\Delta} + 2\beta)^2 + 4\left( \alpha - (\hat{\Delta} + \beta)\beta \right)(1 + \alpha)}
\]

Exactly the same relationships \( Z(\hat{\Delta}, \alpha, \beta) \) and \( \Delta_{\text{CT}}(Z) \) emerge if the energy (3.53) of an antisymmetric state with \( \kappa_R \neq 0 \) is simplified by neglecting \( |e^{-m\kappa}| \ll 1 \) (analogously to

\[\footnote{It is easy to check that in case of \( \text{Re} \kappa < 0 \) the same results can be obtained.} \]
Eq. (4.20)). Therefore we can expect at maximum four states. Owing to the definition of $Z$, all physical solutions $Z$ have to obey $0 < |Z_{1,2}| < 1$ and $Z \in \mathbb{R}$. If a formal solution $Z_1$ or $Z_2$ of (4.23) fulfills the aforementioned conditions, the corresponding $\kappa$ is shared by two degenerate states (cf. Eq. (4.21)), i.e., one symmetric and antisymmetric state.

We illustrate equations (4.21, 4.23) with the help of the already well familiar example constellation. With the assumption that the energies $E_F$ and $E_{CT}$ coincide, $\Delta$ is equal to zero. Further, we set $\beta = 0$. This set of parameters yields two real solutions $Z_1$, $Z_2 = \pm \sqrt{\frac{1}{1+\alpha}}$ and hence

$$Z_{1,2} = \pm \frac{1}{\sqrt{1+\alpha}}$$

and

$${\kappa}_1 = \frac{1}{2}\ln(1+\alpha)$$

$${\kappa}_2 = \frac{1}{2}\ln(1+\alpha) + i\pi .$$

Both solutions fulfill the condition $0 < |Z_{1,2}| < 1$. As a consequence, near the ends of the chain where $n = \pm m, \pm(m-1), \pm(m-2)\ldots$ for odd-$N$-chains or $n = \pm(m-1/2), \pm(m-3/2), \pm(m-5/2)\ldots$ for even-$N$-chains, respectively, the function $u_n$ decreases exponentially with decreasing $|n|$. For the first solution $Z_1$, this decay is monotonous:

$$u_n \sim \cosh(n\kappa_1) \approx \frac{1}{2} e^{\kappa_1 |n|} ;$$

the second solution $Z_2$ has an oscillating decay:

$$u_n \sim \cosh(n\kappa_2) \approx - \frac{1}{2} e^{\kappa_1 |n|} .$$

This behavior of the coefficients $u_n$ is shown in Figure 4.5(a). It follows from equation (4.21) that the energy $\Delta_{CT}$ of the corresponding states is given by

$$\Delta_{CT,1} = \frac{\alpha}{\sqrt{1+\alpha}}$$

$$\Delta_{CT,2} = - \frac{\alpha}{\sqrt{1+\alpha}} .$$

These states occur within the gap of the upper and lower bulk band, closely to the band edges. We indicate both of them in Figure 3.6, where the case $N = 41$ represents our long chain with $\alpha = 1$. The oscillating state (diamond) is found closely beneath the lower edge (at $k = \pi$) of the upper band, whereas the non-oscillating state (triangle) shows up above the upper edge (at $k = 0$) of the lower band.

The exponential decay of the $u_n$ into the inner of the chain, which we observed for a special constellation in the example above, is a general property of all states with $\kappa_R \neq 0$. The exponential damping factor can be extracted in all cases: Without loss of generality, we assign a solution of (4.23) with $Z_1$ if positive and with $Z_2$ if negative. Thus, the $\kappa$ can be generated in the form

$$\kappa_1 := \ln Z_1 , \quad Z_1 > 0$$

$$\kappa_2 := \ln |Z_2| + i\pi , \quad Z_2 < 0$$

and the coefficients $u_n$ become:

$$u_n \sim \cosh n\kappa_1 \approx \frac{1}{2} e^{\kappa_1 |n|} \quad \left\{ \begin{array}{l} \frac{1}{2} e^{\kappa_1 |n|} \ln Z_1 \\ \frac{1}{2} e^{\kappa_1 |n|} |n| \end{array} \right. , \quad |n| = m, m-1, \ldots$$

$$u_n \sim \cosh n\kappa_2 \approx \frac{1}{2} e^{\kappa_2 |n|} \quad \left\{ \begin{array}{l} \frac{1}{2} e^{\kappa_2 |n|} \ln |Z_2| \\ \frac{1}{2} e^{\kappa_2 |n|} |Z_2| \end{array} \right. , \quad |n| = m, m-1, \ldots$$
4.3 Surface states

(a) molecular excitations $|ME_n\rangle$

(b) symmetric CT excitations

(c) antisymmetric CT excitations

Figure 4.5: Site representation of surface states found in a chain of $N = 41$ molecules with $E_F = E_{CT} = 0$, $M = \epsilon_h = 0.2$ eV, and $\epsilon_e = 0$ (see Figure 3.6). The distribution of $u_n$ is displayed in (a) for both the oscillating state and the non-oscillating state. The charge transfer contribution is shown with the help of the symmetry-adapted coefficients $v_{n+}$ (b) and $v_{n-}$ (c) (cf. Eqs. (4.17), (4.18)). The symmetry adaption demands $v_{n+} = 0$ for antisymmetric and $v_{n-} = 0$ for symmetric states, therefore in each case the state with the non-vanishing $v_{n\pm}$ is given. According to the boundary conditions one site is not involved. For better visualization, some curves have been shifted with respect to each other.

In both kinds of states the real part of $\kappa$ is responsible for a monotonous exponential decay $e^{i|n|\text{Re}(\kappa_{1,2})}$ from the outermost molecules into the inner chain and localizes the states at the outermost molecules. An additional phase $\pi$ in $\kappa_2$ causes an oscillating decay ($\sim (-1)^{|n|}$). The localization at the ends of the chain finally gives reason for calling these states surface states. We will discuss below in more detail that they are fully analogous to Tamm-states for electrons [84].

The use of the word localization in this context may give rise to confusion: Here, we will refer to a state as a localized state if the overwhelming part of the sites $n'$ do not contribute to the state, i.e., if the coefficients corresponding to $n'$ are negligible ($u_{n'} \approx 0$). It does not necessarily mean that the state is essentially located around one site. Since the surface
states obey inversion symmetry, i.e., they are either symmetric or antisymmetric, they have to involve both sides of chain in the same manner. Nevertheless, the main contribution of the $u_n$ is concentrated at the ends of the chain ($|n| = m, m - 1,...$). An exact definition of the property localization will be introduced later in Section 5.1.

Each surface state consists of two tails localized at the chain end which have no overlap in the inner chain. In Figure 4.5, this typical distribution of surface state coefficients $u_n, v_n\pm$ over the sites $n$ is shown. Both the symmetric and the antisymmetric state become degenerate in long chains, since both involve the same number of molecules. Since the CT coefficients $v_n\pm$ are directly connected to the Frenkel coefficients $u_n$, the localization can be equivalently observed among the $v_n\pm$ (cf. Eq. (3.37)) or the symmetry-adapted coefficients $v_n\pm$ (Figure 4.5), respectively.

With equation (4.21), the energies following from $Z_1,2$ are

$$\Delta_{CT,1} = \beta + \alpha Z_1 \quad \text{(non-oscillating state)}, \quad \Delta_{CT,2} = \beta - \alpha |Z_2| \quad \text{(oscillating state)}.$$  \hspace{1cm} (4.34) \hspace{1cm} (4.35)

Surface states occur at energies which are not already occupied by the excitonic bands of the infinite chain: Valid $Z$ with $-1 < Z < 1$ lead to surface states with energies between (cf. Eq. (4.21))

$$\beta - \alpha < \Delta_{CT,i} < \beta + \alpha \quad (i = 1, 2).$$  \hspace{1cm} (4.36)

Bulk states cover energies (cf. Eqs. (3.51, 3.53))

$$\Delta_{CT,b}^{\text{sym}} = \beta + \alpha \frac{\cos mk}{\cos(m+1)k} \quad \text{and}$$

$$\Delta_{CT,b}^{\text{asym}} = \beta + \alpha \frac{\sin mk}{\sin(m+1)k}.$$  \hspace{1cm} (4.37) \hspace{1cm} (4.38)

In the limit $m \to \infty (N \gg 1)$, the smallest permitted bulk state wave vector, $k_{\text{min}}$, approaches 0, whereas the largest permitted wave vector $k_{\text{max}}$ approaches $\pi$. The energies of the states which border the gap between the excitonic bands can be expressed as

$$\Delta_{CT,b1}(k_{\text{min}}) \approx \beta + \alpha \cdot x \quad \text{with} \quad x > 1$$

$$\Delta_{CT,b2}(k_{\text{max}}) \approx \beta - \alpha \cdot x \quad \text{with} \quad x > 1.$$  \hspace{1cm} (4.39) \hspace{1cm} (4.40)

Therefore, independently of the type of decay, each surface state is located energetically between the bands of the infinite chain:

$$\Delta_{CT,b2} \leq \beta - \alpha \cdot x \leq \beta - \alpha < \Delta_{CT,i} \quad \text{and}$$

$$\Delta_{CT,b1} \geq \beta + \alpha \cdot x \geq \beta + \alpha > \Delta_{CT,i} \quad \text{for both} \ i = 1, 2.$$  \hspace{1cm} (4.41)

The alignment within the band gap implies the overwhelming CT character of the surface states (see Figure 4.5). Surface states arrange closer to the charge transfer on-site energy $E_{CT}$ than any other available mixed bulk state.

From the investigations above, we learned that surface states in general share two properties: They are localized at the outermost molecules and they occur energetically near the band edges. These properties are the fingerprint of the Tamm states. Originally such a type of surface states was found by Tamm [84] who investigated electrons in finite atomic chains.
4.3 Surface states

The on-site energy at the boundary site and coupling integral to the boundary site were altered with respect to the bulk sites. In the meanwhile, the term *Tamm states* is generally used for states exhibiting the aforementioned characteristics, e.g., for surface states of quasi-particles in three-dimensional crystals [85]. Typically, *Tamm states* originate from a change of on-site energies at the boundaries, a coupling to the boundary site differing from the bulk, or from the combination of both effects [74]. In our idealized treatment, however, the on-site energies of all sites as well as the coupling between them are kept equal. Here, the surface states are the direct consequence of the missing CT-type basis functions at the outermost molecules. It is important to note that such states arise even in ideal chains which have neither diagonal nor non-diagonal disorder.

However, not each possible constellation of parameters, leads to the formation of surface states. In Figure 4.6, we demonstrate exemplarily that a formal solution $Z$ not necessarily describes a surface state. If the associated energy $\Delta_{CT}$ lies within the area of an excitonic band, the formation of the surface state is inhibited. Two possible constellations are shown in Figure 4.6. At $\beta = -\alpha$, $Z_1$ becomes unity. The associated energy $\Delta_{CT,1}$ vanishes and coincides with a band edge at $k = 0$. Hence, only oscillating surface states, given by $Z_2$, exist. If we slightly change the situation by choosing $\beta = 0.9 \cdot \alpha$, $\Delta_{CT,1}$ separates from the band edge and therefore describes a valid non-oscillating surface state. Vice versa, at $\beta = \alpha$, $Z_2$ takes the value $-1$. Now, the edge of the other band coincides with $\Delta_{CT,2}$ at $k = \pi$. In this situation, only the non-oscillating surface states occur.

Therefore, we seek for conditions which immediately allow us to identify if a given system has surface states. Furthermore, we need conditions which determine what type and which total number of surface states can be expected. For $N \gg 1$, the required statements are provided by the equations (4.21, 4.23). Even though both equations became completely independent of the total number $N$ of molecules, they still contain three independent parameters ($\Delta, \alpha, \beta$). This implies that the appearance of surface states is not determined by the actual number of molecules in the (still very long) chain, but exclusively by the parameter set and is therefore an *intrinsic* property of the system.

In a previous paragraph, we already discussed the occurrence of surface states from the viewpoint of associated energies with respect to the excitonic bands (see also Figure 4.6). Now, we set out from the properties required for reasonable $Z$. Possible solutions $Z$ of (4.23) fulfill the condition $0 < |Z_{1,2}| < 1$ and $Z \in \mathbb{R}$ for only some combinations of $\alpha, \beta$ and $\Delta$. Since the inequality $\alpha \geq |\beta|$ (cf. Eq. (3.46)) always holds, the discriminant $D$ of the square root in equation (4.23) is inherently non-negative and ensures real $Z$ values:

$$D = (\Delta + 2\beta)^2 + \frac{4}{\alpha}(1 + \alpha)\left(\alpha - \left(\Delta + \beta\right)\beta\right) \geq 0 \quad \text{for} \quad |\beta| \leq \alpha \ . \quad (4.42)$$

The complexity of finding all parameter sets which permit surface states is illustrated in Figure 4.7. The formal, real solutions $Z_{1,2}$ of equation (4.23) have been plotted versus $\beta$ for $\Delta$ and $\alpha$ kept fixed. The curves $Z_{1,2}(\beta)$ are limited by the points $E_{1,2}$ where the discriminant $D$ vanishes:

$$D = 0 : \quad \beta_\pm = -\frac{1}{2}\left(\Delta \pm \sqrt{(\Delta^2 + 4\alpha)(1 + \alpha)}\right) \quad E_1, E_2 \quad (4.43)$$

All $Z$ enclosed by the frame $|Z| < 1$ and $|\beta| \leq \alpha$ describe surface states. At certain planes
Figure 4.6: Energy $\Delta_{\text{CT}}$ of surface states in a chain of $N = 41$ molecules where $\tilde{\Delta} = 0$, $\alpha = 1$. Dependent on $\beta$, the alignment of the surfaces states in comparison to the bands of the corresponding infinite chain (solid lines) are shown. The degeneracy of $E_F$ and $E_{\text{CT}}$ supports both non-oscillating (triangle) and oscillating states (diamond). For $|\beta| = \alpha$, one type of surface states vanishes, since a band fully covers the energetical range in which this surface state was allowed to occur.

$\beta(\tilde{\Delta}, \alpha)$ (positions indicated by arrows in Figure 4.7), at least one $|Z|$ becomes unity:

\begin{align*}
\beta = -\Delta - \alpha : & \quad Z_{1,2} = \frac{1}{2(1+\alpha)} \left( \tilde{\Delta} + 2\alpha \pm \sqrt{(\tilde{\Delta} - 2)^2} \right) \quad A_1, A_2 \\
\beta = \alpha : & \quad Z_{1,2} = -\frac{1}{2(1+\alpha)} \left( \tilde{\Delta} + 2\alpha \pm \sqrt{(\tilde{\Delta} - 2)^2} \right) \quad B_1, B_2 \\
\beta = -\alpha : & \quad Z_{1,2} = -\frac{1}{2(1+\alpha)} \left( \tilde{\Delta} - 2\alpha \mp \sqrt{(\tilde{\Delta} + 2)^2} \right) \quad C_1, C_2 \\
\beta = \alpha - \tilde{\Delta} : & \quad Z_{1,2} = \frac{1}{2(1+\alpha)} \left( \tilde{\Delta} + 2\alpha \pm \sqrt{(\tilde{\Delta} + 2)^2} \right) \quad D_1, D_2
\end{align*}

(4.44)

The solutions $Z_1$ and $Z_2$ of equations (4.44) are ordered such that they fulfill $Z_1 > Z_2$. At the points A,D of the aforementioned planes intersect with the Z curves. The window of valid Z is given by the points B$_{1,2}$, C$_{1,2}$. The relationships (4.44) characterize the shift of this frame over both curves $Z_1$ and $Z_2$ with changing $\alpha$ and $\tilde{\Delta}$. A major information is provided by Figure 4.7: In each case where the absolute of one of the $Z$ becomes or exceeds unity,
4.3 Surface states

\[ \beta = -\alpha \quad \beta = -\tilde{\Delta} - \alpha \quad \beta = \alpha \quad \beta = \alpha - \tilde{\Delta} \]

**Figure 4.7:** Solutions \( Z_{1,2} \) of Eq. (4.23) for fixed \( \tilde{\Delta} \) and \( \alpha \). Shown is the dependence \( Z_1 \) (black line) and \( Z_2 \) (gray line) on the balance parameter \( \beta \). Within the frame \(|Z| < 1\) and \(|\beta| \leq \alpha\) the \( Z \) found (emphasized by thick lines) correspond to surface states. At points A–D, the planes \( \beta(\tilde{\Delta}, \alpha) \) in which always one \(|Z|\) is exactly unity intersect with the \( Z \) curves. They reflect, how the frame is shifted above the \( Z \) curves with changing \( \alpha \) and \( \tilde{\Delta} \). (The picture shows a typical alignment of the frame versus \( Z \) for a \( \tilde{\Delta} \) smaller than zero.)

The corresponding state is suppressed. Only the second possible solution may give rise to a surface state. From this criterion, zones with suppressed states can be identified.

On the border of the frame, \(|\beta| = \alpha\), always one of the \( Z \) has an absolute value equal unity (B2, C1). Dependent on the amount of \( \tilde{\Delta} \), a further plane \( \beta^* = \beta(\alpha, \tilde{\Delta}) \) may exist within the frame at which either \(|Z_1| (A_1)\) or \(|Z_2| (D_2)\) equals unity. In the constellation shown in Figure 4.7, the \( Z_1 \) curve crosses \( \beta^* = -\alpha - \tilde{\Delta} \) at unity (A1). Between the frame and the plane \( \beta^* \), a zone with one \(|Z| > 1\) is formed. In Figure 4.7, this zone corresponds to the section between \( A_1 \) and \( C_1 \); between \( A_2 \) and \( C_2 \) a surface state related to \( Z_2 \) is formed.
A switching of the oscillation behavior takes place when the corresponding $Z$ vanishes:

$$Z_{1,2} = 0 \Rightarrow \beta_{1,2} = -\frac{1}{2} \left( \tilde{\Delta} \pm \sqrt{\tilde{\Delta}^2 + 4\alpha} \right) \quad \text{with } \beta_1 > \beta_2.$$  \hfill (4.45)

For negative $Z_2$, the state oscillates ($\beta > \beta_2$), for positive $Z_2$ the state decays monotonously ($\beta < \beta_2$). Alternatively, along $\beta = \alpha$ only the $Z_1$ state ($B_1$) is available.

With the help of the argumentation above, we are able to predict the number and type of surface states for each parameter constellations ($\tilde{\Delta}$, $\alpha$, $\beta$). With the collected information from the entire parameter space, we can construct phase diagrams in which all zones containing different types of surface states are distinguished. For representative $\tilde{\Delta}$, we show phase diagrams 4.8 for the full ($\alpha$, $\beta$)-subspace. All main features of the phase diagrams can be displayed if the three major alignment possibilities of $E_F$ and $E_CT$ are investigated collectively:

- $E_F < E_CT$, represented by $\tilde{\Delta} = -1$ ($M > 0$) $\rightarrow$ Figure 4.8(a)
- $E_F = E_CT$, equivalent to $\tilde{\Delta} = 0$ ($M > 0$) $\rightarrow$ Figure 4.8(b) \hfill (4.46)
- $E_F > E_CT$, represented by $\tilde{\Delta} = 1$ ($M > 0$) $\rightarrow$ Figure 4.8(c).

Areas with no surface states allowed are left white. **Within** the shaded areas surface states occur, either described by $Z_1$ or $Z_2$. Areas where only one $Z$ is associated with a valid surface state are shaded either gray for oscillating surface states or light gray for non-oscillating surface states: If $Z_1$ is found between zero and unity, the solution $Z_1$ describes non-oscillating surface states. The corresponding area in Figure 4.8(c) is enclosed by the solid lines $Z_1(\alpha, \beta) = 0$ and $Z_1(\alpha, \beta) = 1$. Beyond the $Z_1 = 0$ line, the oscillating behavior switches and the negative $Z_1$ corresponds to an oscillating surface state. Analogously, the curves $Z_2(\alpha, \beta) = 0$ and $Z_2(\alpha, \beta) = -1$ mark the area where $Z_2$ is associated with oscillating surface states.

Even both surface states can be suppressed simultaneously: For negative $\tilde{\Delta}$, i.e., $E_CT$ is larger than $E_F$, the section of the $\beta = \alpha$ plane in which $2\alpha \leq -\tilde{\Delta}$ correspond to the non-valid solutions $Z_2 = -1$ and $Z_1 > 1$ (Figure 4.8(a)). Equivalently, we can identify for positive $\Delta$ the range $2\alpha \leq \tilde{\Delta}$ along $\beta = -\alpha$ in which $Z_1 = 1$ and $Z_2 < -1$ and therefore no surface states are present (Figure 4.8(c)).

In dark gray areas both solutions $Z_{1,2}$ correspond to valid surface states. Within $Z_1 = 0$ and $Z_2 = 0$, oscillating as well as non-oscillating surface states occur. For $\alpha > 1 - \tilde{\Delta}$, additional zones between $Z_1 = 0$ and $Z_2 = -1$ containing two oscillating states or between $Z_2 = 0$ and $Z_1 = 1$ containing two non-oscillating states, respectively, appear. These zones of states with the same oscillating behavior have been framed white (see Figure 4.8(b)).

It is important to note again that along the boundary lines between white and gray areas where one $|Z|$ equals unity, the associated surface states are strictly forbidden. Remarkably, the relations defining the zone boundaries represent simultaneously very interesting classes of materials. In the case $\alpha = |\beta|$, the electron and the hole transfer integral are equally balanced. Therefore, it is immediately clear that in such materials both kinds of surface states can never occur simultaneously.

### 4.4 Parameter constellations of high relevance

In the preceding sections, all considerations of the model Hamiltonian and the discussion of its solutions have been kept as general as possible. Now, we want to pick out special
4.4 Parameter constellations of high relevance

Figure 4.8: Existence of surface states. The phase diagrams show several scenarios of the parameter $\tilde{\Delta}$ fixed. Shaded areas represent the combinations of $\alpha$ and $\beta$ which lead to surface states. In the white area no surface state are allowed. Within the area enclosed by the curves $Z_1(\alpha, \beta) = 0$ and $Z_1(\alpha, \beta) = 1$ (solid lines) the solutions $Z_1$ are associated with non-oscillating surface states (light gray). Analogously, the curves $Z_2(\alpha, \beta) = 0$ and $Z_2(\alpha, \beta) = -1$ mark the area where $Z_2$ is associated with oscillating surface states (gray). In dark gray areas the two surface states co-exist. Additionally white framed areas where both surface states have the same oscillation behavior. On the boundary lines indicated with $|Z| = 1$ one surface state is suppressed. All parts of these lines which intersect with areas where the absolute value of the second $Z$ simultaneously exceeds unity, host no surface states at all.
structures which, albeit artificial, may lead to well known limiting cases or to a separation of competing effects.

### 4.4.1 Decoupled Frenkel and charge transfer excitons

We turn again to the case of pure Frenkel and CT excitons. When the interaction between Frenkel and CT excitons \( (\epsilon_e = 0, \epsilon_h = 0) \) is turned off, our model has to provide the correct solutions for Frenkel and CT excitons in finite chains. In Section 3.2, we constructed first Frenkel and CT excitons in an infinite chain which were later mixed by the combination of \( \epsilon_e \) and \( \epsilon_h \). To complete this considerations for an arbitrary finite chain, we now go backwards:

The absence of the charge transfer integrals cancels immediately the relation (3.37) between the Frenkel and the CT contributions in the eigenstates (3.9). Thus, any eigenstate observed is either a pure Frenkel or a pure CT exciton.

With \( \alpha = \beta = 0 \), equation (3.48) breaks down to the relation:

\[
\Delta_F = -2 \cosh \kappa . \tag{4.47}
\]

With the last step, we lost the access to the charge transfer states. The above equation will only allow us to explore the manifold of Frenkel excitons:

Substituted into the boundary equation (3.49) for symmetric states\(^3\), these \( \Delta_F(\kappa) \) yield

\[
0 = -2 \cosh \kappa \cosh(m\kappa) + \cosh((m-1)\kappa)
\]

and therefore the condition:

\[
\cosh((m+1)\kappa) = 0 \iff \kappa = 0 + i \cdot \frac{\pi j}{2(m+1)} , \quad j = 1,3,\ldots \ (A_g) . \tag{4.49}
\]

With inserting the energies (4.47) into the equation (3.50), we obtain a corresponding condition for antisymmetric states:

\[
\sinh((m+1)\kappa) = 0 \iff \kappa = 0 + i \cdot \frac{\pi j}{2(m+1)} , \quad j = 0,2,\ldots \ (A_u) . \tag{4.50}
\]

The product of the two equations (4.49, 4.50) gives a general condition for \( \kappa \):

\[
2 \sinh((m+1)\kappa) \cosh((m+1)\kappa) = \sinh(2(m+1)\kappa) = 0 . \tag{4.51}
\]

Hence the solution \( \kappa \) of equation (4.51) has the form \( \kappa = i k \) (k real) with

\[
k = \frac{\pi j}{N+1} , \quad j = 1,\ldots , N , \tag{4.52}
\]

and the energy \( \Delta_F \) transforms into

\[
\Delta_F = -2 \cosh \kappa = -2 \cos k . \tag{4.53}
\]

In combination, we arrive at the most general expression for the energy of Frenkel excitons in finite chains [71, 72]:

\[
E = E_F + 2 M \cos k \quad \text{with} \quad k = \frac{\pi j}{N+1} , \quad j = 1,\ldots , N . \tag{4.54}
\]

\(^3\)The derivations for even-\( N \) chains are fully equivalent.
4.4 Parameter constellations of high relevance

Due to (3.37) the eigenstates reduce to

\[ |\psi(k)\rangle = \sum_{n=-m}^{m} u_n(k)|ME_n\rangle = \begin{cases} A \sum_{n=-m}^{m} \cos nk|ME_n\rangle & (A_g) \\ A \sum_{n=-m}^{m} \sin nk|ME_n\rangle & (A_u) \end{cases} \] (4.55)

The normalization condition fixes \( A \) as

\[ A^2 \sum_{n=-m}^{m} u_n^2(k_j) = \begin{cases} A^2 \sum_{n=-m}^{m} \cos^2(n k_j) & \text{if } j \text{ odd} \\ A^2 \sum_{n=-m}^{m} \sin^2(n k_j) & \text{if } j \text{ even} \end{cases} = \begin{cases} A^2 \cdot \frac{2(m+1)}{2} & \text{if } j \text{ odd} \\ A^2 \cdot \frac{2}{2} & \text{if } j \text{ even} \end{cases} = 1 \] (4.56)

The form of the eigenstates in the symmetry-adapted case is

\[ |\psi_j\rangle = \begin{cases} \sqrt{\frac{1}{m+1}} \sum_{n=-m}^{m} \cos \frac{j \pi n}{2(m+1)} |ME_n\rangle & j \text{ odd} (A_g) \\ \sqrt{\frac{1}{m+1}} \sum_{n=-m}^{m} \sin \frac{j \pi n}{2(m+1)} |ME_n\rangle & j \text{ even} (A_u) \end{cases} \] (4.57)

If the symmetry-adaption is dropped and and sites are enumerated conventionally from 1 to \( N \), the Frenkel states \(|\psi_j\rangle\) can be written as [71, 72]:

\[ |\psi_j\rangle = \sqrt{\frac{2}{N+1}} \sum_{n=1}^{N} \sin \frac{j \pi n}{(N+1)} |ME_n\rangle \quad j = 1, \ldots, N \] (4.58)

With the eigenstates given we can calculate the transition dipole moments

\[ p^j = \sqrt{\frac{2}{N+1}} \sum_{n=1}^{N} \sin \left( \frac{j \pi n}{N+1} \right) p^F = \begin{cases} \sqrt{\frac{2}{N+1}} \cot \left( \frac{j \pi}{2(N+1)} \right) p^F & j \text{ odd} (A_g) \\ 0 & j \text{ even} (A_u) \end{cases} \] (4.59)

which predict the exactly zero oscillator strength \( f^j \) of antisymmetric states.

To access the CT states, we have to return to the initial systems of equations (3.34-3.36). The degenerate non-mixing CT states are immediately available since they occur independently of all interaction parameters. However, with \( \epsilon_e = \epsilon_h = 0 \) none of the CT states enters any relationship with molecular excitations anymore. Hence, the equations (3.34, 3.35) join the system (3.36). Accordingly, all CT states are degenerate at the energy \( E_{CT} \).

The model introduced in Chapter 3 gives us full access to both the separated Frenkel and CT manifold. However, a Frenkel exciton and a CT exciton of a certain \( k \), provided that the pure CT exciton can be assigned with a wave vector, will never yield a mixed state with equal wave vector; the boundary restrictions for \( k \) of the Frenkel exciton (4.52) and for the mixed exciton (3.49) never match for nonvanishing charge transfer integrals. Unlike the case of infinite chains, the process of mixing is always combined with the generation of a new wave vector.
4.4.2 Vanishing Frenkel transfer integral

The discussion made so far was entirely relying on the presence of a non-vanishing Frenkel transfer integral \( M \). In the case that \( M \) vanishes indeed, the final equations retrieved from the formalism introduced in Section 3.3.1 to obtain the eigenvalues \( E(\kappa) \) (Eqs. (3.51, 3.53)) and the eigenstates \( |\psi(\kappa)\rangle \) (Eqs. (3.52, 3.54)) are not valid anymore. Instead of reformulating all equations for the limit \( M \to 0 \), we start out from the Hamiltonian (3.1) and repeat the diagonalization procedure adjusted to \( M = 0 \).

First, we separate the situation in the bulk (cf. Eqs. (3.34)) from the situation at the outermost molecules (cf. Eqs. (3.35)). The derivations are demonstrated for the case of odd-\( N \)-chains (see Figure 3.4(a)). For sites with two nearest neighbors (\( n = 0, \ldots, \pm (m-1) \)) we get for \( M = 0 \):

\[
\begin{align*}
(E_F - E) \ u_n + \epsilon_e (v_{n,1} + v_{n-1}) + \epsilon_h (v_{n-1,1} + v_{n-1,-1}) &= 0 \\
(E_{CT} - E) \ v_{n,\pm1} + \epsilon_e u_n + \epsilon_h u_{n\pm1} &= 0.
\end{align*}
\]

And for \( n = \pm m \) we obtain the boundary conditions:

\[
\begin{align*}
(E_F - E) \ u_{\pm m} + \epsilon_e v_{\pm m, \mp1} + \epsilon_h v_{\pm (m-1), \mp1} &= 0 \\
(E_{CT} - E) \ v_{\pm m, \mp1} + \epsilon_e u_{\pm m} + \epsilon_h u_{\mp1} &= 0.
\end{align*}
\]

Using the first relations of (4.60) and (4.61), the coefficients \( v \) can be eliminated:

\[
\begin{align*}
(E_F - E) - 2e^2 + \epsilon_h^2 \ E_{CT} - E \ u_n - \frac{2\epsilon_e \epsilon_h}{E_{CT} - E} (u_{n+1} + u_{n-1}) &= 0 \quad (|n| < m) \\
(E_F - E) - \frac{\epsilon_e^2 + \epsilon_h^2}{E_{CT} - E} u_{\pm m} - \frac{2\epsilon_e \epsilon_h}{E_{CT} - E} u_{\pm (m-1)} &= 0 \quad (|n| = m).
\end{align*}
\]

Inserting ansatz (3.42) for symmetric and antisymmetric states in odd-\( N \) chains in the equations above, the bulk and the boundary expressions become:

\[
\begin{align*}
(E_F - E) - 2e^2 + \epsilon_h^2 \ E_{CT} - E &= 0 \\
(E_F - E) - \frac{e^2 + \epsilon_h^2}{E_{CT} - E} \cot \kappa - \frac{2\epsilon_e \epsilon_h}{E_{CT} - E} \cosh((m-1)\kappa) &= 0 \quad (A_B) \\
(E_F - E) - \frac{e^2 + \epsilon_h^2}{E_{CT} - E} \sinh \kappa - \frac{2\epsilon_e \epsilon_h}{E_{CT} - E} \sinh((m-1)\kappa) &= 0 \quad (A_u).
\end{align*}
\]

To derive an expression which determines \( \kappa \), we eliminate \( E_F - E \) from (4.64) and (4.65) with the help of (4.63):

\[
\begin{align*}
\frac{\cosh((m-1)\kappa)}{\cosh(m\kappa)} &= \frac{2\epsilon_e \epsilon_h}{e^2 + \epsilon_h^2}, \quad \text{symmetric (} A_B \text{)} \\
\frac{\sinh((m-1)\kappa)}{\sinh(m\kappa)} &= \frac{2\epsilon_e \epsilon_h}{e^2 + \epsilon_h^2}, \quad \text{antisymmetric (} A_u \text{)}.
\end{align*}
\]

The restrictions (4.66, 4.67) entirely lack a dependence on \( E_F \) and \( E_{CT} \). Only the charge transfer integrals are responsible for the choice of \( \kappa \), and again the balance of \( \epsilon_e \) and \( \epsilon_h \) is
important. Since $\epsilon_e$ and $\epsilon_h$ are real, the permitted $\kappa$ have to secure that the l.h.s. of equations (4.66, 4.67) is real. From the evaluation of expressions (3.57, 3.63) in Section 3.3.1, we know that this condition requires $\kappa$ in the form (3.68):

$$
\kappa = \begin{cases} 
\text{Im} \kappa = k, & \text{Re} \kappa \equiv \kappa_R = 0 \\
\kappa_R, & \kappa_R \neq 0 \\
\kappa_R + i\pi, & \kappa_R \neq 0 .
\end{cases}
$$

(4.68)

The possibility of real $\kappa$ immediately leads to the expectation of surface states.

If we solve the bulk equation (4.63) for $E$, we obtain the dispersion relation $E(\kappa)$:

$$
E_{1,2}(\kappa) = \frac{E_{CT} + E_F}{2} \pm \sqrt{\left(\frac{E_F - E_{CT}}{2}\right)^2 + 2\left(\epsilon^2_e + \epsilon^2_h + 2\epsilon_e \epsilon_h \cosh \kappa\right)}
$$

(4.69)

where

$$
\epsilon^2_\kappa = \epsilon^2_e + \epsilon^2_h + 2\epsilon_e \epsilon_h \cosh \kappa .
$$

(4.70)

For bulk states with $\kappa = i k$, the energies follow:

$$
E_{1,2}(k) = \frac{E_{CT} + E_F}{2} \pm \sqrt{\left(\frac{E_F - E_{CT}}{2}\right)^2 + 2\epsilon^2_k} .
$$

(4.71)

For periodic boundary conditions and therefore continuous $k$, equation (4.71) entirely describes the two mixed excitonic bands (see Figure 4.9). Not overwhelmed by $M$, we see directly the influence of $\epsilon_e$ and $\epsilon_h$ on the dispersion of the two bands: They are symmetric to $E_F + E_{CT}$ with the curvature determined by $\epsilon_k$, but the dispersions have the opposite sign. The separation is minimized for $\epsilon_e = \epsilon_h$ at $k = 0$ or for $\epsilon_e = -\epsilon_h$ at $k = \pi$, respectively.

It is important to note that even in the absence of Frenkel transfer mixed excitonic bands of non-zero width occur. As long it is possible to move both kinds of charges to the nearest neighbor, the transfer of mixed states along the chain is possible, even though the transfer of pure molecular excitations is impossible.

To seek for surface states, we turn to very large chains ($m \gg 1$). In this limit ($e^{-m\kappa} \to 0$), the equations (4.66, 4.67) reduce to one expression

$$
e^{-\kappa} = Z = -\frac{2\epsilon_e \epsilon_h}{\epsilon^2_e + \epsilon^2_h} .
$$

(4.72)

We get the same relationship if we seek for the limit $M \to 0$ of the general expression for $Z$ (4.23):

$$
Z_{1,2} \to -\frac{\tilde{\Delta} + 2\beta}{2(1+\alpha)} \pm \frac{1}{2(1+\alpha)} \sqrt{\left(\tilde{\Delta} + \beta\right)^2 + 4\frac{(\alpha - (\tilde{\Delta} + \beta)\beta)(1+\alpha)}{\alpha}}
$$

(4.73)

This result is not surprising and can be easily motivated with the help of Figure 4.7. A vanishing $M$ implies that $\alpha, \beta \gg \tilde{\Delta}$. In this case, the relationships $Z_1(\beta)$ and $Z_2(\beta)$ are
Figure 4.9: Shape of excitonic bands in a system without Frenkel transfer under the influence of differently balanced charge transfer integrals. The parameters are chosen as $E_F = 0$, $E_{CT} = 0.1 \text{ eV}$, $M = 0$, $\epsilon_e = 0.14 \text{ eV}$. The position of the surface states in a chain of $N = 11$ molecules is indicated by the arrows. The thin lines mark the energy $(E_{CT} + E_F)/2$.

stretched to linear curves in $\beta$ (cf. Figure 4.7) and $Z_1$ and $Z_2$ become degenerate. The way the charge transfer integrals $\epsilon_e$, $\epsilon_h$ enter $Z$ in equation (4.72) automatically restricts $Z$ to

$$0 \leq |Z| \leq 1$$  \hspace{1cm} (4.74)

which ensures the correct asymptotic behavior of the surface state related to $Z$. Apart from equally balanced charge transfer integrals or a vanishing CT integral, surface states are always formed.

Both types of surface states never occur simultaneously, because equation (4.72) defines only one $Z$, describing either oscillating or non-oscillating surface states. Introduced in the general dispersion relation (4.71), $Z$ gives rise to two surface states with the same oscillation behavior (see Figure 4.9):

$$E_{1,2} = \frac{E_{CT} + E_F}{2} \pm \sqrt{\left( \frac{E_F - E_{CT}}{2} \right)^2 + \frac{(\epsilon_e^2 - \epsilon_h^2)^2}{\epsilon_e^2 + \epsilon_h^2}}.$$

Within the formalism developed for $M = 0$, we have to verify that the states arrange within the gap opened by the excitonic bands. The $k$-dependent term in the square root of dispersion relation (4.71) is always larger than the substituted term in the surface state energies (4.75):

$$\frac{(\epsilon_e^2 - \epsilon_h^2)^2}{\epsilon_e^2 + \epsilon_h^2} \leq 2(\epsilon_e^2 + \epsilon_h^2 + 2\epsilon_e\epsilon_h \cos k) \quad \forall k \in [0..\pi].$$  \hspace{1cm} (4.76)
because

\[ 2(\epsilon_e^2 + \epsilon_h^2 + 2\epsilon_e\epsilon_h \cos k)(\epsilon_e^2 + \epsilon_h^2) - (\epsilon_e - \epsilon_h)^2 \geq \begin{cases} (\epsilon_e + \epsilon_h)^4 \geq 0 & \text{for } k = 0, \\ (\epsilon_e - \epsilon_h)^4 \geq 0 & \text{for } k = \pi. \end{cases} \] (4.77)

### 4.4.3 Flat bands

Even for very strong coupling, it is possible to create a perfectly flat band mixed of Frenkel and CT excitons. Large interaction integrals, if taken separately, are responsible for bands with dispersion. However, in combination the effects of the Frenkel transfer and the charge transfer integrals may compensate each other. We shall work out the condition under which the interactions cancel each other completely.

Expressed as equation, the constellation of parameters must cancel out the \( k \)-dependence of one band in (4.2):

\[ \Delta_{CT,1,2} = -\frac{1}{2} \left\{ \tilde{\Delta} + 2 \cos k \pm \sqrt{\left(\tilde{\Delta} + 2 \cos k\right)^2 + 8(\alpha + \beta \cos k)} \right\}. \] (4.78)

To compensate the first \( 2 \cos k \) term, the discriminant of the square root must be reduced to a single sum squared containing the summation term \( 2 \cos k \):

\[ (\tilde{\Delta} + 2 \cos k)^2 + 8(\alpha + \beta \cos k) = (\tilde{\Delta} + 2\beta + 2 \cos k)^2 - 4(\beta(\tilde{\Delta} + \beta) - 2\alpha). \] (4.79)

Under the condition

\[ \beta(\tilde{\Delta} + \beta) - 2\alpha = 0 \] (4.80)

the bands take the form

\[ \Delta_{CT,1,2} = -\frac{1}{2} \left\{ \tilde{\Delta} + 2 \cos k \pm \left(\tilde{\Delta} + 2\beta + 2 \cos k\right) \right\} \] (4.81)

\[ = \begin{cases} -(\tilde{\Delta} + 2 \cos k + \beta) \\ \beta \end{cases}. \]

Hence we will find one band at \( E_{flat} = E_{CT} - M\beta \) which has no dispersion.

Since this band consist of mixed Frenkel CT states, several symmetric bulk states will have considerable oscillator strength. With varying chain length, the oscillator strength will be redistributed among the bulk states of the band. However, these contributions will additively join one single peak at \( E_{flat} \) in the absorption spectrum. Thereby we observe the total oscillator strength which was granted to the bulk states within this band as a whole.

The special circumstances (4.80) do not automatically limit the formation of surface states. The occurring types of surface states have to be determined from the general phase-diagrams (cf. Figure 4.8) with the resulting \( \alpha(\tilde{\Delta}, \beta) \).
Quantum confinement

The term *quantum confinement* has been coined when the scientific interest turned from infinitely extended to finite systems. Many confinement effects arising from the literal confinement of the system in space have been designated as *quantum confinement effect*, see, e.g., reference [86]. Behind such general considerations, effects of rather different origin might be hidden. The absence of any more precise 'definition' of quantum confinement does not immediately allow a systematical classification of possibly contributing effects and their nature.

No matter if excitons or single carriers are concerned, one standard approach is dominating in literature, in particular in publications dealing with inorganic semiconductors [86, 87, 88, 89]: "The theory" of confinement very often adopts the *particle-in-a-box* model. An object literally confined within a box of length $L$ with infinitely high potential walls is described in the one-dimensional case by the stationary wave functions

$$|j(x)| = \sqrt{\frac{2}{L}} \sin \left( \frac{j\pi x}{L} \right), \quad j = 1, 2, \ldots \quad (5.1)$$

where $m$ is the mass of the object, e.g. the mass of an electron. Such states satisfy the boundary conditions that require the wave functions to vanish at the box edges. The energy levels for the *particle-in-a-box* are given by [90]

$$E_j = \frac{j^2 \pi^2 \hbar^2}{2mL^2}. \quad (5.2)$$

Due to the characteristic $j^2/L^2$ dependence, the energy levels shift proportional to $L^{-2}$ with the box size $L$. It is clear that for small $L$ such a shift becomes large. Often, this typical size dependence is used as a finger print to identify *quantum confinement effects* in experiments [86, Chapter 9]. This point of view is not only applied for freely moving electrons or holes. It is also used to consider confinement of excitons.

For Wannier-Mott (WM) excitons, the effective mass approximation yields a corresponding behavior. In infinite crystals, these spherically-symmetric exciton states form a series of hydrogen like bound states below the band gap $E_g$:

$$E_{WM} = E_g - \frac{\mu \epsilon^4}{2\hbar^2 \epsilon^2 \cdot j^2}, \quad j = 1, 2, \ldots \quad (5.3)$$

In this Rydberg equation, $\epsilon$ is the dielectric constant and the reduced mass $\mu$ is defined with the effective masses $m_e$ and $m_h$ of the electron and hole, respectively

$$\mu = \frac{1}{\frac{1}{m_e} + \frac{1}{m_h}}. \quad (5.4)$$
In analogy to the hydrogen atom, the spatial extension of the states, i.e., the separation of electron and hole, can be introduced as exciton radius. The Bohr radius of the 'internal state' of an WM exciton with quantum number $j$ is given by [34, p. 29]:

$$L_j = \frac{j^2 e m_e}{\mu} a_B \quad \text{with} \quad a_B = \frac{\hbar^2}{m_e e^2}$$

being the Bohr radius of the hydrogen atom. Confined within a finite sphere of the radius $L$, the energy of the bulk excitons is corrected by further terms. In the case of weak confinement $L \gg L_1$, the energy of the lowest level $j = 1$ consists of the expression (5.3) from the infinite system and the particle-in-a-box term [89]:

$$E_{WM} = E_g - \frac{\mu e^4}{2 \hbar^2 c^2} + \frac{\hbar^2 \pi^2}{2M L^2}$$

where $M = m_e + m_h$ is total effective mass of electron and hole, and $E_g$ the band gap formed in the infinite system. In the limit of strong confinement $L \ll L_1$, an additional Coulomb attraction term $\sim L^{-1}$ and a different confinement term $\sim L^{-2}$ appear in equation (5.3) [87, 89]:

$$E_{WM} = E_g + \frac{\hbar^2 \pi^2}{2\mu L^2} - \frac{1.786 e^2}{\epsilon L} - 0.248 \frac{\mu e^4}{2 \hbar^2 c^2}.$$  

For pure Frenkel excitons in a finite chain, an intrinsic length comparable with the radius $L_j$ of the WM excitons does not exist. The wave functions of pure Frenkel states (cf. Eq. (4.58)) given as

$$|j\rangle = \sqrt{\frac{2}{N+1}} \sum_{n=1}^{N} \sin \left( \frac{j \pi n}{N+1} \right) |\text{ME}_n\rangle , \quad j = 1, \ldots, N$$

are required to vanish at the boundaries. The envelope of the Frenkel coefficients

$$\tilde{j}(x_n) = \sqrt{\frac{2}{L}} \sin \left( \frac{j \cdot \pi x_n}{L} \right) = \sqrt{\frac{2}{L}} \sin \left( \frac{j \cdot \pi n a}{L} \right) , \quad j = 1, \ldots, N$$

with $a$ being the lattice constant, and $L = (N + 1) \cdot a$ the chain length in real space, takes the form well known from the particle-in-a-box problem (cf. Eq. (5.1)).

The examples of Frenkel and WM excitons shown above might be generalized in the following scenario: Let us consider an arbitrary object which delocalizes completely in an infinite system or in a cyclic aggregate, equivalently. Treated as a quasi-particle, this object is described by its total (quasi-) momentum $k$ and its energy $E(k)$, despite a possible internal structure, such as the electron-hole separation in the WM exciton. Now, this freely moving particle is enclosed in a box of the size $L$. With this step, we inhibit the state from extending to its full natural (infinite) size. Hence, the quasi-momentum $k$ which describes the motion of the center of mass becomes quantized. The former dispersion relation $E(k)$ is corrected additively by an $L$-dependent term which thereby introduces the size sensitivity of the corresponding state.

To illustrate this idea, we inspect the situation for Frenkel excitons again: With both the energy $E_\infty$ of the Frenkel state in the infinite chain and the confinement correction $E'$, we
are able to estimate the energy of the Frenkel exciton confined in a finite chain. The exact dispersion relation of Frenkel excitons in infinite chains is (cf. Eq. (3.23)):

\[ E = E_F + 2 M \cos k = E_F + 2 M \cos \tilde{k} a \]  

Hence, the energy of the quasi-particle related to the state with largest oscillator strength \((k = 0)\) is

\[ E_\infty = E_F + 2 M . \]  

(5.10)

From dispersion relation (5.10), we obtain the mass \(\tilde{\mu}\) of the quasi-particle in the effective mass approximation:

\[ \frac{1}{\tilde{\mu}(k)} = \frac{1}{\hbar^2} \left( \frac{\partial^2 E}{\partial k^2} \right) = \frac{2a^2}{\hbar^2} M \cos \tilde{k} a . \]  

(5.11)

Expressed by both contributions from the infinite chain \(E_\infty\) and the confinement term \(E'_1\), the energy of the Frenkel state \(j = 1\) with largest oscillator strength in the finite system is:

\[ E_1 = E_\infty + E'_1 . \]  

(5.12)

Introduced in the particle-in-a-box energy relation (5.2), the effective mass (5.12) allows us to formulate the confinement contribution for the state \(j = 1\):

\[ E'_1 = \frac{\pi^2 \hbar^2}{2 \tilde{\mu}(0) L^2} = -\pi^2 M \frac{a^2}{L^2} = -\pi^2 M \frac{1}{(N+1)^2} . \]  

(5.13)

Thus, the total energy \(E_1\) of the Frenkel state \(j = 1\) eventually becomes:

\[ E_1 = E_\infty + E'_1 = E_F + 2 M \left( 1 - \frac{1}{2} \frac{\pi^2}{(N+1)^2} \right) . \]  

(5.14)

Compared to the exact behavior known from equation (4.54) (cf. Section 4.4.1),

\[ E_1 = E_F + 2 M \cos \left( \frac{\pi}{N+1} \right) , \]  

(5.15)

the estimated confinement corrected energy (5.15) closely matches the exact expression already for \(N > 2\).

Analogously, we can describe the weak confinement for WM excitons. The dispersion relation for WM excitons in the non-confined case is [91]:

\[ E_\infty(K) = \frac{\hbar^2 K^2}{2M} - \frac{\mu e^4}{2\hbar^2 e^2 \cdot j^2} , \ j = 1, 2, \ldots . \]  

(5.16)

The effective mass is determined by

\[ \frac{\hbar^2}{\tilde{\mu}(K)} = \left( \frac{\partial^2 E}{\partial k^2} \right) = \frac{\hbar^2}{M} \]  

(5.17)

where \(M = m_e + m_h\) is the sum of the electron and hole mass. With the introduction of \(\tilde{\mu}\) in the particle-in-a-box energy relation (5.2), we get the confinement contribution for the binding energy of state \(j = 1\):

\[ E'_1 = \frac{\pi^2 \hbar^2}{2 \tilde{\mu} L^2} = \frac{\pi^2 \hbar^2}{2 M L^2} . \]  

(5.18)
The final expression for the energy

\[ E_1 = E_\infty(0) + E'_1 = E_g - \frac{\mu e^4}{2\hbar^2 c^2} + \frac{\pi^2 \hbar^2}{2 M L^2} \] (5.20)

exactly corresponds to the result (5.6) obtained from an alternative approach [89].

In summary, the particle-in-a-box picture arises from the requirement that a wave function which is entirely delocalized in the infinite system must vanish at the boundaries of the finite system. The center-of-mass motion expressed by the wave vector \( k \) is quantized along the direction in which the system has been confined. The bulk states of our model system, which originate from the excitonic states of the infinite chain, have to obey this requirement as well. Hence we can expect such finite size effects also in our context.

However, such a picture appeals to the quasi-particle character of the exciton and does not regard its internal structure. An internal structure of the exciton gives rise to a characteristic quantum length. Possible effects which cause the formation of an intrinsic quantum length are of multifaceted nature. In case of the Wannier-Mott exciton, for example, the separation of the electron and hole provides immediately an intrinsic quantum length. Another structure is induced with the inclusion of exciton-phonon coupling which allows self-trapping. In this case, the length of the self-trapped state serves as intrinsic quantum length, independent whether the vibronic spacing is large with respect to the Frenkel transfer interaction \( M \), demonstrated in references [85, 92], or smaller than \( M \), as shown in reference [93]. With the presence of the intrinsic quantum length, the rather simple particle-in-a-box picture cannot describe the system as its extension becomes smaller than this quantum length. As we already saw in the example of WM exciton, the quasi-particle character of the exciton which was seen in weakly confined systems (cf. Eq. (5.6)), is not longer preserved in the strong confinement limit (cf. Eq. (5.7)).

In our context, the internal structure of all states is determined by the Frenkel-CT mixing ratio in the first place. As a special feature of finite systems, also the real part of the exciton wave vector \( \kappa \), i.e., the presence of a damping factor \( e^{-|n|\kappa R} \), contributes to define an internal structure. We will see below, that these two factors act not entirely independently. Strictly spoken, already the occurrence of states with a damping factor, the surface states, might be interpreted as confinement effect, for they are unknown in infinite chains.

One aim of the next sections is to identify such an intrinsic quantum length \( L \) in our system, i.e., a length uniquely defined by the parameter set \( E_F, E_{CT}, M, \epsilon_e, \epsilon_h \).

Throughout this work, we will distinguish between the two indicated origins of confinement effects. We refer to quantum confinement as soon as an intrinsic quantum length determines the composition of the state and hence its properties with respect to the system size. On the other hand, all effects inherited from the conserved quasi-particle character of the excitons which lead to the typical particle-in-a-box behavior are denoted as finite-size effects.

In this chapter, the dependence of major properties, among them the energy and oscillator strength, of both the bulk and the surface states on the chain length \( N \) are investigated. In the first section, we will provide quantities with which the spatial extension of all eigenstates dependent on the chain length \( N \) can be surveyed. As pointed out above, confinement effects which may arise both from the presence of an intrinsic length and from finite-size effects, are expected to become severe in small systems.
5.1 Participation ratio

We assign the spatial extension of a state with a quantity telling us how many sites a particular eigenstate is associated with. Originally proposed to investigate disorder effects, Dean and Bell (cf., e.g. [94]) introduced the so-called Participation Ratio. It was used to characterize the dependence of eigenvalues and eigenstates on the amount of disorder and on dimensionality of the systems, within lattice dynamical studies in particular. The original definition addressed momenta of the mean kinetic energy of a normal vibrational mode within a 1D lattice. Later, this definition was generalized to handle eigenstates given as a linear superposition of basis functions.

For a finite chain containing \( N \) sites, the participation ratio \( N_{\text{eff}} \) of an eigenstate \( |j\rangle \) is defined \([95, 96]\) as:

\[
\frac{1}{N_{\text{eff}}} = \sum_{n=1}^{N} |u_{nj}|^4
\]  

(5.21)

with \( |j\rangle \) obeying the normalization condition \( \sum_{n} |u_{nj}|^2 = 1 \). The quantity \( 1/N_{\text{eff}} \) is called Inverse Participation Ratio (IPR). States \( |j\rangle \) described with a set of coefficients \( u_{nj} \) as specified above are typically found in systems containing one basis state per site, e.g., in systems with pure Frenkel excitons. \( N_{\text{eff}} \) itself can be interpreted as the spatial extension of the particular state. \( N_{\text{eff}} \) varies between 1 and \( N \):

\[
N_{\text{eff}} = \begin{cases} 
1 & \text{: (exciton) state localized at one site} \\
N & \text{: (exciton) state evenly delocalized over } N \text{ sites} .
\end{cases}
\]

(5.22)

Statement (5.22) can be proven by introducing the explicit solutions for a finite chain into (5.21). The limit of maximum delocalization is realized most likely in cyclic arrays. In finite cyclic arrays (we restrict ourselves again to the odd-\( N \) case), the general solution can be expressed as:

\[
|j\rangle = \sum_{n=-m}^{m} u_{nj} |n\rangle
\]

(5.23)

with coefficients \( u_{nj} \) defined using a discrete set of \( k \):

\[
u_{nj} = \frac{1}{\sqrt{N}} \cos (ink_j) , \quad \text{where } k_j := \pi \frac{j}{m} \quad (j = 0, .., \pm m) .
\]

(5.24)

Among these states \( |j\rangle \), two states are considered to be perfectly delocalized. These are the solutions \( |0\rangle \) and \( |m\rangle \) with the same absolute value \( |u_{nj}| \) at each site:

\[
u_{n0} = \frac{1}{\sqrt{N}} \cos 0 \cdot n = \frac{1}{\sqrt{N}}
\]

(5.25)

\[
u_{nm} = \frac{1}{\sqrt{N}} \cos n\pi = (-1)^{|n|} \frac{1}{\sqrt{N}} .
\]

(5.26)

Inserted into (5.21), the IPR simplifies to

\[
\sum |u_{n0}|^4 = \frac{1}{N^2} \sum_{n=-m}^{m} 1 = \frac{1}{N}
\]

(5.27)

\[
\sum |u_{nm}|^4 = \frac{1}{N^2} \sum_{n=-m}^{m} (-1)^{|n|} = \frac{1}{N^2} \sum_{n=-m}^{m} 1 = \frac{1}{N} .
\]

(5.28)
For both states with maximum delocalization the quantity $N_{\text{eff}}$ becomes exactly $N$.

The opposite situation for strongest localization possible can be verified immediately: A state perfectly localized a site $n'$ has $|u_{nj}| = \delta_{nn'}$. Introduced in the equation of the IPR (5.21) we get

$$\sum |u_{nj}|^4 = \sum_{n=-m}^m \delta_{nn'} = 1$$

and therefore $N_{\text{eff}} = 1$. In finite chains with free ends, however, we always find an intermediate situation. For rather extended states, the IPR is of the order of $1/N$ (cf. Section 4.4.1, Eq. 4.58). A state localized almost completely is characterized by an IPR approaching unity.

To utilize the IPR for mixed Frenkel-CT states, we have to extend the formulation (5.21). A more general definition using so-called momenta $M_p$ was originally presented by Dean [94]. After rewriting the momenta in terms of eigenstates in site representation [97], the definition of Dean can be directly applied in our framework:

$$M_p(j) = \sum_n (u_{nj})^{2p}$$

$$\frac{1}{N_{\text{eff}}(j)} = \frac{M_2}{(M_1)^2}$$

$$(5.30) \Rightarrow \frac{1}{N_{\text{eff}}(j)} = \frac{\sum_{n=1}^N |u_{nj}|^4}{\left( \sum_{n=1}^N |u_{nj}|^2 \right)^2}.$$  

The final form (5.32) of the adapted definition is motivated by the following idea: Since we are interested in the participation of states, we can restrict the summation to the Frenkel contributions $u_{nk}$. Then, the involved coefficients do not represent the complete eigenstate anymore, i.e., $\sum_n |u_{nj}|^2 < 1$. With a renormalization to the Frenkel contribution only, the IPR can be defined as:

$$\frac{1}{N_{\text{eff}}} = \sum_{n=1}^{N} \left| \frac{u_{nj}}{u_F} \right|^4 = \frac{\sum_{n=1}^{N} |u_{nj}|^4}{\left( \sum_{n=1}^{N} |u_{nj}|^2 \right)^2}$$  

(5.33)

where the Frenkel part $\sum_{n=1}^{N} |u_{nj}|^2$ was abbreviated by $u_F$.

Of course, we have to verify that the adapted definition (5.33) provides the required localization criteria (5.22). Like in the case of pure Frenkel excitons, the perfectly delocalized state is found among the eigenstates of a cyclic array. Since the normalization of states mixed of Frenkel and CT excitons is dependent on the charge transfer integrals $\epsilon_c$ and $\epsilon_h$ (see Eq. 3.12), we leave the normalization factor $A$ unspecified:

$$u_{nj} = A \cos (ink_j) \quad \text{where} \quad k_j := \frac{\pi j}{m} \quad (j = 0, \ldots, \pm m).$$  

(5.34)
Analogously to the pure Frenkel exciton case, in the solutions with \( j = 0 \) and \( j = m \) the coefficients \( u_{nj} \) take the same absolute value independent of the site \( n \):

\[
\begin{align*}
    u_{n0} &= A \cos 0 \cdot n = A, \\
    u_{nm} &= A \cos n\pi = (-1)^{|n|} A.
\end{align*}
\]

Hence the general IPR (5.33) reads:

\[
\frac{1}{N_{\text{eff}}} = \begin{pmatrix}
    \frac{\sum |u_{n0}|^4}{\left(\sum |u_{n0}|^2\right)^2} &= \frac{A^4 \sum 1}{A^4 \left(\sum 1\right)^2} \\
    \frac{\sum |u_{nm}|^4}{\left(\sum |u_{nm}|^2\right)^2} &= \frac{A^4 \sum (-1)^{|n|}}{A^4 \left(\sum (-1)^{|n|}\right)^2}
\end{pmatrix} = \frac{1}{N}.
\] (5.37)

A state exclusively localized at one site \( n' \) must not have any CT-type admixture (otherwise automatically more than one molecule is involved) and is therefore described by \( u_{nj} = \delta_{nn'} \). Of course, the corresponding IPR becomes unity:

\[
\frac{1}{N_{\text{eff}}} = \frac{\sum |u_{nj}|^4}{\left(\sum |u_{nj}|^2\right)^2} = \frac{\sum_{n=-m}^{m} \delta_{nn'}}{\sum_{n=-m}^{m} \delta_{nn'}} = 1.
\] (5.38)

The mean position of the exciton may serve as an additional quantity to characterize the eigenstates. We can define the mean position of an exciton by means of [95]:

\[
\langle n \rangle = \sum_{n=1}^{N} n \cdot |u_{nj}|^2.
\] (5.39)

Due to the inversion symmetry assumed in our linear chains, \( \langle n \rangle \) would automatically become the chain center after summation over all sites. However, we are interested in a quantity which contains information whether the exciton is mainly located near the outermost molecules or centered in the chain. Therefore, we redefine Eq. (5.39) to get the mean radial position:

\[
\langle |n| \rangle := \frac{\sum_{n=1}^{N} |n - \langle n \rangle| \cdot |u_{nj}|^2}{\sum_{n=1}^{N} |u_{nj}|^2} = \frac{\sum_{n=-m}^{m} |n| \cdot |u_{nj}|^2}{\sum_{n=-m}^{m} |u_{nj}|^2}.
\] (5.40)

With the properties of the bulk and surface states discussed in the previous chapter, we can immediately develop an expectation for the behavior of \( N_{\text{eff}} \) and for the mean radial position \( \langle |n| \rangle \). In Figure 5.1, we illustrate the evolution of \( N_{\text{eff}} \) and \( \langle |n| \rangle \) with the help of the example introduced in Figure 3.6. From all available states we compare the bulk states corresponding to the upper band and the oscillating surface states energetically close beneath. The horizontal bars represent \( N_{\text{eff}} \) centered at \( \langle |n| \rangle \). Simultaneously, the mean
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\( N = 41 \) \( E (\text{eV}) \)

\( N = 21 \)

\( N = 11 \)

\( N = 5 \)

Figure 5.1: Behavior of the participation ratio \( N_{\text{eff}} \) and mean radial position \( \langle |n| \rangle \) of excited states in chains of different length \( N \). With circles and diamonds, \( \langle |n| \rangle \) together with the energetical position \( E \) of the states are marked; the length of the horizontal lines at each state correspond to \( N_{\text{eff}} \). For demonstration, all bulk states of the upper band (open circles) and the oscillating surface state (solid diamond) of the system introduced with Figure 3.6 are shown; the parameters are \( E_F = E_{\text{CT}} = 0 \), \( M = \epsilon_h = 0.2 \ \text{eV} \), and \( \epsilon_c = 0 \). The mean position \( \langle |n_j| \rangle \) (Eq. (5.40)) of the bulk states is found near the chain center. Since the bulk states span the whole chain, its \( N_{\text{eff}} \) is in the order of \( N \) ((a) - (c)). Due to its exponential decay, the surface state is located closer to the outermost molecules than the bulk states, and the corresponding \( N_{\text{eff}} \) stays constant ((a) - (c)). Only if the chain is sufficiently small, the tails of the surface states overlap and the exponentially damped state covers the whole chain (d)). Then, the bulk and the surface states have comparable center of mass and comparable extension (d).

Starting with the longest chain of \( N = 41 \) molecules (Figure 5.1(a)), we observe the surface states located closer to the outermost molecules than the bulk states. The effective size of the surface states is with \( N_{\text{eff}} \approx 6 \) considerably smaller than the typical bulk state which covers \( N_{\text{eff}} \approx 27 \) sites. In general, the bulk states span the whole chain and thus have an \( N_{\text{eff}} \) in the order of the chain length \( N \). The surface state, however, involves sites exclusively located very remote from the chain center, and consists therefore of two tails without overlap. The number of involved sites will not change for reduced \( N \). Such a reduction only alters the number of sites where the contribution to the surface states \( u_n \) vanishes. Hence, its size is expected to stay independently of \( N \) at a constant value in the order of unity. This can be seen if we decrease the chain length down to \( N = 11 \) sites (Figure 5.1(a)-5.1(c)). However, if we continue with even smaller chains, the bulk states and surface states do not necessarily follow their scheme anymore. In Figure 5.1(d), the chain length is reduced to \( N = 5 \) molecules. Here, both kinds of states share approximately the...
same effective size which reflects that now both states are distributed over the whole chain. The tails of the surface states overlap which lifts the degeneracy of the symmetric and the antisymmetric state.

The IPR and hence the participation ratio $N_{\text{eff}}$ can be discussed in general (see Figure 5.2). First, we consider bulk states and their effective size dependent on the chain length. Formula (5.33) for the IPR exclusively relies on the contributions $u_n$ of the molecular excitations. According to equations (3.42, 3.43), the $u_n$ of a symmetric bulk state take the form:

$$u_n = A \cosh nk \quad (3.68)$$

$$u_n = A \cos kn \quad (5.41)$$

Hence, the choice of the coupling parameters $\epsilon_e$ and $\epsilon_h$ does not play a role, because they determine the amount of the CT contributions $v_{n,\pm 1}$ and the normalization factor $A$ (cf. Eq. (5.41)):

$$\frac{1}{N_{\text{eff}}} = \sum_{n=-m}^{m} \left( \cos nk \right)^4 \left( \sum_{n=-m}^{m} \left( \cos kn \right)^2 \right)^{-2} \quad (5.42)$$

Which set of $k$ is valid for a certain value of $N$ is determined by the parameter set by means of the complicated expression (3.69). Hence, the reduction of $N$ leads to a complicated

![Figure 5.2: Dependence of the effective size $N_{\text{eff}}$ of bulk and surface states on the chain length $N = 2m+1$. In (a) the ratio $N_{\text{eff}} / N$ is surveyed for the accessible $k = [0.1, 0.9] \pi$. Apart from small deviations, the ratio is constant for a large range of $m$. Only for very small $m \leq 4$, the ratio is largely intensified. (b) Effective size $N_{\text{eff}}$ of surface states given by $\kappa R$. $N_{\text{eff}}$ is almost independent of $m$ (and hence $N$) and decreases with increasing $\kappa R$ due to the enhanced localization of the surface states. The $N$-independent curve $L = \frac{2}{\kappa R}$ displays the quantum length $L$ associated with a surface state at a particular $\kappa R$. (Note that the orientation of the axes has been changed in the right image for better visualization.)](image-url)
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tree pattern of permitted $k$. To be independent of the actual parameters, we survey $N_{\text{eff}}$ in
the complete $k$-space $k = (0, \pi)$. For convenience, we plot the ratio $N_{\text{eff}}/N$ in Figure 5.2(a). For a large variety of $N$, the effective size of the bulk states drops, apart from small fluctuations, with the chain length $N$, i.e. the ratio to $N$ remains almost constant. Reduced below a certain length $N$, the system features states whose ratio $N_{\text{eff}}/N$ differs considerably from the constant found in larger chains. Such a transition of the behavior does not take place for all states at once, but is observed for each state at an individual $N$. States nearest to $k = 0$ and $k = \pi$ lift their typical bulk behavior at earliest, with decreasing $N$ more and more states (with $k$ approaching $0.3\pi$) are involved, until finally all bulk states give up their typical bulk characteristics. Although Figure 5.2(a) is calculated from symmetric bulk states, the antisymmetric formulation yields the same overall picture.

For (symmetric) surface states, we found the coefficients $u_n$ in the form

$$u_n = A \cosh n\kappa \approx \frac{A}{2} e^{\left|n\right|\kappa R}.$$  \hspace{1cm} (5.43)

To calculate the IPR, the knowledge of $A$ is not necessary:

$$\frac{1}{N_{\text{eff}}} \equiv \frac{\sum_{n=-m}^{m} e^{4\left|n\right|\kappa R}}{\left(\sum_{n=-m}^{m} e^{2\left|n\right|\kappa R}\right)^2}. \hspace{1cm} (5.44)$$

In Figure 5.2(b), $N_{\text{eff}}$ is considered for all possible $\kappa R$ dependent on $N$. In contrast to the bulk states, the typical surface state establishes an effective size independent of the chain length $N$. The amount of $N_{\text{eff}}$ rises with smaller $\kappa R$, since smaller $\kappa R$ are related to weaker localization (Figure 5.2(b)). With the help of the example discussed above, this can be understood immediately. As the effective size only accounts for the non-vanishing contribution of $u_n$ at the ends of the chain, the number of the non-involved sites in the inner of the chain can be varied largely without affecting $N_{\text{eff}}$ at all. Viewed from this perspective, $N_{\text{eff}}$ is literally an effective size related to the surface state. It is uniquely defined by the system parameters and represents therefore an intrinsic length of the whole system. Only if $N$ becomes smaller than the intrinsic size of the surface state, both tails involve all sites and therefore the surface state cannot be considered as localized anymore. If two kinds of surface states are present, an intrinsic size has to be assigned to each surface state.

With the ansatz (5.41) for bulk states and (5.43) for surface states, the mean radial position is accessible for any possible constellation as well. Inserted into definition (5.40), $\langle |n| \rangle$ can evaluated from:

$$\langle |n| \rangle_{\text{bulk}} \overset{(5.41)}{=} \frac{\sum_{n=-m}^{m} |n| (\cos nk)^2}{\left(\sum_{n=-m}^{m} (\cos nk)^2\right)^2} \hspace{1cm} (5.45)$$

$$\langle |n| \rangle_{\text{surf}} \overset{(5.43)}{=} \frac{\sum_{n=-m}^{m} |n| (\cosh n\kappa R)^2}{\left(\sum_{n=-m}^{m} (\cosh n\kappa R)^2\right)^2} \overset{N \gg 1}{=} \frac{\sum_{n=-m}^{m} |n| e^{2n\kappa R}}{\left(\sum_{n=-m}^{m} e^{2\kappa R}\right)^2}. \hspace{1cm} (5.46)$$
Figure 5.3: Dependence of the mean radial position $\langle |n| \rangle$ of bulk and surface states on the chain length $N = 2m + 1$. The lower graph shows the ratio $\frac{\langle |n| \rangle}{N}$ for bulk states in the interval $k = [0, 1]\pi$; the upper graph the ratio $\frac{\langle |n| \rangle}{N}$ for surface states with different $\kappa_R$.

In Figure 5.3, we show the result which is plotted as ratio $\frac{\langle |n| \rangle}{N}$ to become independent of the chain length. The mean radial position is, apart from $k \lesssim 0$ and $k \gtrsim \pi$, approximately separated from the center by $1/4N$. For surface states within long chains, the corresponding separation amounts to $1/2N$. Hence, the surface states stay much closer to the outermost molecules than any bulk state. In very short chains, the position of surface states, supported by a small $\kappa_R$, are shifted away from the boundaries. Simultaneously, for certain $k$ bulk states plunge into the chain center.

With the help of both the participation ratio and the mean radial position we were able to comprehend independently that below a critical system size, both kinds of states give up their typical behavior to adapt rather similar properties.

By comparing the sizes of the critical $N$ in Figure 5.2, for which the states undergo considerable changes, we observe $N$ which are different for bulk and surface states and are correlated to the related quantum numbers $k$ and $\kappa_R$. We will see in the next section, how the critical $N$ of the surface state is related to a characteristic quantum length of the system.
5.2 Intrinsic quantum length

As observed in the previous section, the effective size of surface states is constant for sufficiently large chains. It is determined by the exponential damping of the surface states which is responsible for the formation of two non-overlapping tails:

\[ u_n \sim e^{\frac{|n|}{\kappa R}}. \quad (5.47) \]

The extension of a tail can be assigned as

\[ L = \frac{1}{\kappa R} \quad (5.48) \]

which takes the role of a decay length of the tail:

\[ u_n \sim e^{\frac{|n|}{L}}. \quad (5.49) \]

Because each state has two tails, \( 2L \) reflects the effective size of a surface state. In Figure 5.2(b), we compare the effective size \( N_{\text{eff}} \) obtained as participation ratio with the extension of the tails \( 2L = \frac{2}{\kappa R} \). As long as both tails do not overlap and thus approximation (5.47) is valid, \( 2L \) follows the curvature of \( N_{\text{eff}}(\kappa R) \). Hence the intrinsic size of the surface state can be directly defined using the value of \( \kappa R \):

\[ L = \frac{2}{\kappa R}. \quad (5.50) \]

Since \( \kappa R \) is exclusively determined by the parameter set (see Chapter 3.3.1), the characteristic quantum length under question can be assigned with the effective size \( L \) of the surface state. The quantum length \( L \) originates from the absence of CT excitations at the outermost molecules.

Due to a possible presence of both oscillating and non-oscillating surface states, two \( L_{1,2} \) are found. They are equal in the case of resonance \( E_F = E_{\text{CT}} \), but differ for all other constellations. Hence, it is difficult to decide about the role of \( L \), e.g., whether it can be interpreted as radius of the mixed Frenkel-CT exciton.

The decision can only be made after the behavior of both types of surface states and the bulk states in systems smaller than the largest \( L \) found has been studied simultaneously. During the next section we will keep this question in mind.

5.3 Bulk and surface states in small chains

The mechanisms forcing the properties of the bulk and surface states to change their properties with the system size are of fundamentally different nature.

Clearly, the bulk states suffer from finite-size-effects: Generally all sites, apart from nodes in antisymmetric states, contribute with non-vanishing coefficients to the eigenstates. The coefficients ensure that the exciton wave functions vanish at the boundaries. Their reaction on the varied system size corresponds to the particle-in-a-box picture.

A change of the system size is accompanied by the redistribution of the bulk states within the Brillouin zone. The number of allowed \( k \) becomes smaller for lower \( N \). Thereby, the bulk states near the center of the Brillouin zone subsequently separate from \( k = 0 \). While the bulk states travel of into the Brillouin zone, their energy follows the dispersion of the
5.3 Bulk and surface states in small chains

Figure 5.4: Energy $E$ and fractional oscillator strength $f$ as function of the length $N$ for a chain with the parameters $E_F = E_{CT} = 0$, $M = \epsilon_h = 0.2$ eV, and $\epsilon_e = 0$ (see Figure 3.6). Shown are the bulk states with lowest $k$ for each the upper and the lower band (circles) in comparison to the oscillating and the non-oscillating surface state (both symmetric). To resolve the oscillator strength of the oscillating surface states and the lower bulk state, the curve corresponding to the oscillating surface state has been artificially shifted to smaller $f$. The quantum length $L$, retrieved from the surface state at $N = 41$, is indicated with a vertical line.

underlying excitonic bands (Figure 5.4(a)). Simultaneously, the fractional oscillator strength is redistributed to states with larger $k$. In sufficiently large chains, the overwhelming part of the oscillator strength is still concentrated in the states with lowest $k$. Thus, the fractional oscillator strength varies linearly in $N$, as shown in Figure 5.4(b) for each of these states.
For small systems, the lowest $k$ reaches the region of steepest dispersion. With any further lowering of $N$, the states with lowest $k$ within each band undergoes a large shift in energy.

The surface states behave in a different way. Surface states respond to the reduction of the system size with an altering of the internal structure caused by the damping factor $e^{-|n|\kappa R}$. Such a response is denoted, as mentioned earlier in the introduction of this chapter, as quantum confinement. In long chains, i.e., long in comparison with the extension $L$ of the surface states, the tails of the states are well separated from each other. The number $N_{\text{eff}}$ of sites which contribute to the wave function ($u_n \neq 0$) is fixed (cf. Figure 4.5) and thus independent of $N$ (illustrated in Figure 5.2(b)). Hence, the fractional oscillator strength as well as the energy of the surface states are constant; seen for both types of surface states in Figures 5.4(a) and 5.4(b). Both the symmetric and the antisymmetric states corresponding to one $\kappa$ are degenerate. If, however, the system is reduced below the quantum length, the surface states give up their typical structure. The tails start to overlap. Immediately, the energies of the symmetric and antisymmetric states split. Now, the symmetric state involve all sites of the chain and gains therefore fractional oscillator strength compared to the nearby bulk states. Especially the non-oscillating surface states profit from the new situation, since the additional contributions from the centered sites do not compensate each other in the transition dipole moment (cf. Eq. (3.86)). With all sites of the chain involved, the fractional oscillator strength of the surface states depends almost linearly on $N$. In Figure 5.4(b), especially the non-oscillating surface state turns rather fast into this behavior ($N < 10$).

It is important to note that in long chains, the bulk and surface states change their properties simultaneously but independently. The specific system size below which the finite-size effects become most severe for bulk states is initially not identical with the critical system size determined by the intrinsic size of the surface states. However, it will be explained below that the independence of bulk and surface states gets lost in small chains.

For very small chains, the terminology of bulk and surface states becomes inappropriate. In sufficiently long chains, all bulk states share an effective size in the order of the chain length. The surface states are localized at the chain ends due to the presence of an exponential damping factor, hence their effective size is independent of $N$. In small systems, however, the effective size cannot be used to distinguish between the different kinds of states anymore, because their characteristic behavior has gone. Nevertheless, exponentially damped states, although being delocalized completely, are known to appear as surface states in larger chains. Hence, we refer to exponentially damped states as surface states also in small systems, while keeping in mind that only the exponential damping provides the difference to the bulk states.

While the size of already small chains is gradually reduced, the surface state does not only give up its localized tails, but also changes its Frenkel-CT mixing ratio $\eta$. Of course, any change of $\eta$ has to be accompanied by a change of the mixing ratio of another state, for the total 'amount' of Frenkel parentage must be preserved in the whole system. Such a redistribution of Frenkel parentage happens if the surface state lies close in energy to a bulk state. Hence, the bulk states nearest to the band gap are mostly affected. While the system size is decreased, the bulk states start to redistribute their oscillator strength and thereby feeds the surface state. This is the explanation of the phenomenon which we observed while discussing the mixing ratio of bulk states in small chains (see Figure 4.4). Of course, the Frenkel parentage of the bulk state lowers with the feeding of the surface state. Hence, the mixing ratio of bulk states near the surface states becomes significantly different from the ratio predicted for the infinite chain. A bulk state found in such a constellation suffers not only from finite-size effects, but also changes its internal structure. The variation of their energy and oscillator strength is not independent of the close-by surface state anymore.
A clear distinction between quantum confinement and finite-size influence is not possible anymore.

To show the consequences of the aforementioned effects, we turn again to our demonstration example (Figure 3.6) continued in Figure 5.4. As long as long chains are considered, the contribution of the surface states to the absorption spectrum differs from the bulk states. Due to their localization, the surface states posses only a very small oscillator strength in comparison to the bulk states with lowest \( k \). The oscillating surface state in Figure 5.4(a) is energetically well separated from the upper band bulk state, hence the presence of the surface state does not affect this bulk state. Independent from each other both states keep their typical behavior down to the smallest considered system size (cf. Figure 5.4(b)). In contrast, the non-oscillating states are energetically very close to the bulk state of the lower band, hence we expect both kinds of states to affect each other significantly. The redistribution of Frenkel contribution is so strong that the non-oscillating surface state was granted almost the entire fractional oscillator strength. The bulk state reaches rapidly \( (N < 10) \) zero intensity whereas the surface state entirely adopts the linear scaling \( f(N) \) which was characteristic for the bulk state in large chains (Figure 5.4(a)). If we track further the distribution of fractional oscillator strength versus energy while we reduce \( N \), we observe even for a positive dispersion of the lower band\(^1\) that the center of fractional oscillator strength is shifted toward higher energies, at the position of the surface state.

The largest \( L \) found serves as an upper estimation to justify the application of an infinite chain model. A system larger than \( L \) has two bulk states close to \( k = 0 \) which accumulate the oscillator strength. The ratio of oscillator strength of the upper bulk state with respect to the lower bulk state is already comparable to the corresponding ratio found in the infinite system. The surface states are supposed to have a very small oscillator strength. Hence, the information necessary to forecast the electronic spectrum is almost completely provided by the infinite chain description.

Any system smaller than the largest \( L \) already exhibits pronounced changes in the properties of the corresponding surface state. In systems where both surface states occur, the reduction of \( N \) below the smaller \( L \) ensures distinctive quantum confinement effects for both surface states.

### 5.4 Weak localization - Large radius surface states

Only if the quantum length is too small \((< \) two lattice constants), a discussion of quantum confinement effects is not reasonable anymore. Distinctive quantum confinement effects are expected in systems where the surface states are weakly localized and hence the quantum length is rather large. It is worth asking in general for which systems we can expect a minimum localization and whether such a minimum exists at all.

According to (5.50), the localization of the surface state is given by the inverse of \( \kappa_R \) (without loss of generality we assume \( \kappa_R > 0 \)). The smaller \( \kappa_R \) the more the surface state penetrates the chain. With equation (4.23), the \( \kappa_R \) are expressed by the system parameters. The variable \( Z \) was introduced as \( Z = e^{-\kappa} \). To achieve a minimal \( \kappa_R \), we need a \( Z \) with \( |Z| \approx 1 \). Hence, we have to investigate \( Z \) given by formula (4.23) for the limiting case \( |Z| = 1 \). Under four conditions, \( |Z| \) derived from formula (4.23) can exactly take the value unity. These conditions correspond to equations (4.44) which now have been further evaluated.

\(^1\)For positive dispersion the bulk state is shifted towards lower energies.
with respect to the sign of $\tilde{\Delta}$:

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<thead>
<tr>
<th></th>
<th>$Z_1$</th>
<th>$Z_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>a) $\beta = \alpha$</td>
<td>$\frac{\tilde{\Delta}}{1+\alpha} - \frac{1+\alpha}{1+\alpha} - 2\alpha$</td>
<td>$1$</td>
</tr>
<tr>
<td>b) $\beta = -\tilde{\Delta} + \alpha$</td>
<td>$\frac{\tilde{\Delta} - 1 - \alpha}{1+\alpha} - \frac{1+\alpha}{1+\alpha} - 2\alpha$</td>
<td>$1$</td>
</tr>
<tr>
<td>c) $\beta = -\alpha$</td>
<td>$1$</td>
<td>$-\frac{\tilde{\Delta}}{1+\alpha} + \frac{1+\alpha}{1+\alpha} - 2\alpha$</td>
</tr>
<tr>
<td>d) $\beta = -\tilde{\Delta} - \alpha$</td>
<td>$1$</td>
<td>$\frac{\tilde{\Delta}}{1+\alpha} - \frac{1+\alpha}{1+\alpha} - 2\alpha$</td>
</tr>
</tbody>
</table>

In these equations, all solutions have been assigned such that, without loss of generality, always $Z_1 > Z_2$. Each constellation (a)-(d) yields a further $Z$ which still contains $\tilde{\Delta}$. At $\tilde{\Delta} = 2$ or $\tilde{\Delta} = -2\alpha$, respectively, the absolute value of this $Z$ becomes unity, too. In Figure 5.5, we display the constellations relevant for $\tilde{\Delta} < 0$ in the corresponding $(\alpha, \beta)$ phase diagram.

Of course, the condition $|\beta| < \alpha$ does not allow surface states with $|Z| = 1$. However, systems with parameters close to the constellations above posses at least one type of surface states which is weakly damped. If additionally $\alpha$ is much larger than $|\tilde{\Delta}|$, e.g., if $M$ becomes rather small, the absolute value of both $|Z|$ approaches unity. Then, both types of surface states are weakly damped.

Thus, we find systems with weakest localization of surface states for $|\beta| \approx \alpha$ or $\beta = -\tilde{\Delta} \pm \alpha$. Systems with almost perfectly balanced charge transport integrals but a rather large overall Frenkel - CT coupling with respect to the Frenkel transfer integral are best candidates to observe pronounced quantum confinement effects.
Figure 5.5: Parameter constellations favoring weak localization of oscillating surface states ($\tilde{\Delta} < 0$). The desired combinations of $\alpha$ and $\beta$ are found in zones (shaded grey) close to $\beta = \alpha$ (dashed line). Near the planes $\beta = -\alpha$ and $\beta = -\tilde{\Delta} - \alpha$ (straight lines), non-oscillating states occur. If moreover $\tilde{\Delta} = 2$, the states close to $\beta = -\alpha$ are weakly localized as well. Also for $\tilde{\Delta} = -2\alpha$ close to $\beta = -\tilde{\Delta} - \alpha$, the non-oscillating states are weakly damped.
In this chapter, we return to the quasi-one-dimensional materials introduced in Chapter 1. The instrument to describe the electronic transitions in these materials has been derived in Chapters 3 and 4. The only step remaining to apply the model to real substances is to equip Hamiltonian (3.1) with the correct parameters which contain the knowledge about the monomer excitation and the possible mutual molecular interactions. For two representatives of the PTC-derivatives, MePTCDI and PTCDA, the required values are available from model proposals which utilized the strong coupling between Frenkel and CT excitons. In the first section, we collect the current knowledge about these two substances which are necessary to motivate the parameterization.

6.1 MePTCDI and PTCDA

The isolated molecules of the PTC-derivatives, displayed in Figure 1.1 in Chapter 1, behave very similar. Their optical properties are governed by the $\pi$-electron system which extends over the whole perylene tetracarboxylic acid core [11, 12, 13].

The spectra of dilute solutions of MePTCDI and PTCDA are shown in the upper panels of Figure 6.1. These spectra are related to monomers and serve in good approximation as the absorption spectra of isolated molecules.

The relationship between the low energy absorption observed and the molecular structure is well understood. The lowest transition, assigned as $S_0 \rightarrow S_1$ transition [43]. The vibronic progression observed is a result of the coupling of the electronic state $S_1$ to several vibrational modes of the molecule. Combined studies with IR and Resonant Raman Spectroscopy [98, 99] revealed a rich manifold of vibrational modes. Among them, as demonstrated in reference [100], two in-plane modes of comparable energy contribute with large oscillator strength to the absorption. As a result, the vibronic substructure is treated as one effective mode. Hence, the spectrum is assigned as the electronic transition with the vibronic progression of this effective mode.

The solid state phases consists almost exclusively of crystallites in which the interaction of the molecules is much weaker than intramolecular interactions, e.g., between the covalently bound atoms. Thus, the low energy electronic states in the condensed phase are expected to preserve the electronic structure known from the single molecules to a large degree. Indeed, as a inspection of the UV/VIS absorption spectra of thin vapor-deposited films (lower panels in Figure 6.1) and of the materials in solution (upper panels of Figure 6.1) verifies, the thin
films absorb roughly in the same energy interval as the isolated molecules.

However, the intermolecular interactions present in both materials alter the electronic structure considerably. A direct comparison of thin film and solution absorption spectra in the UV/VIS range (cf. Figure 6.1) indicates that the nature of isolated molecules cannot be transferred to the aggregate to achieve a sufficient description of the electronic structure.

Moreover, the thin film spectra differ strongly with the material; not only for MePTCDI and PTCDA but systematically for several further PTC-derivatives (an overview is given in reference [101]). Obviously, the actual alignment of the molecules with respect to each other crucially determines the interactions between the molecules. The molecular plane-to-plane alignment in the crystal suggests that the intra-stack interactions are much larger than interactions between molecules of different stacks. This gives rise to expect a pronounced anisotropy in the material properties which, e.g., has been found indeed in the optical prop-
properties of single crystals of α-PTCDA [102]. The individual interactions have been quantified with several theoretical approaches. As will be shown in the next section, the applied model descriptions combine the properties known from the isolated molecule with estimations of the relevant intermolecular interactions.

Single crystals provide the best conditions for basic studies. However, thin films are technologically relevant. Vapor-deposited thin films of PTC-derivatives typically form polycrystalline or amorphous layers [103]. With the choice of evaporation conditions, e.g. the substrate, the ‘quality’ of the films can be tuned. Reports in literature range from highly ordered epitaxial growth [104, 105] on single crystalline metal substrates, polycrystalline highly textured films on semiconductor surfaces [15], or nearly isotropic polycrystalline films on quartz glass [106]. The observed growth modes are surveyed more detailed in Section 6.4 below.

In crystalline films, PTCDA occur in two solid state modifications. In both phases, the crystal structure is monoclinic, classified as space group $P2_1/c$, with two molecules per unit cell. The structure of the first modification, assigned as α-PTCDA in reference [107], was obtained by Lovinger et al. In Figure 1.1, the structure of the α-phase is visualized by the projections onto the (100) plane (Figure 1.1(c)) and the (010) plane (Figure 1.1(e)), respectively (see Chapter 1). With $a = 3.72 \, \text{Å}$, the lattice constant along the a-axis is considerably smaller than the molecular extension of 11.3 Å which corresponds to the separation of the O-atoms along the large molecular axis (cf. Figure 1.1(a)). Taking into account the tilt angle of the molecules in respect to the a-axis, the plane-to-plane separation of two neighbors in the stack is 3.37 Å (Figure 1.1(e)). The second polymorph, β-PTCDA, is very similar to the α-phase, except for the inclination of the stacking axis with respect to the molecular planes [107]. Later, the structure of both modifications have been refined in reference [108]. In typical thin films, both modifications appear simultaneously.

For MePTCDI, only one modification has been observed so far. The structures published in reference [11] and in references [109, 110] slightly differ in the lattice spacings and in the monoclinic angle. Relying on the data published in reference [11], the projections of the crystal on (100) plane and (010) plane are shown in Figures 1.1(d) and 1.1(f). Similar to PTCDA, the close stacking along the a-axis (lattice constant $a = 3.87 \, \text{Å}$) separates the planes of neighboring molecules by 3.40 Å which is small in comparison with the molecular extension of 14.35 Å (cf. Figures 1.1(b) and 1.1(f)).

For our studies, we concentrate on the molecular stacks formed along the a-axis. The most crucial interactions are expected to occur within the molecular stacks. The individual interactions have been quantified with several theoretical approaches. As will be shown in the next section, the applied model descriptions combined the properties known from the isolated molecule with estimations of the relevant molecular interactions.
6.2 Available model descriptions

For the crystals MePTCDI and PTCDA, a number of parameter sets is available which are required for the Hamiltonian (3.1). To explain experimental findings, such as absorption spectra [53, 54, 78, 80, 111, 112], electro-absorption spectra [78, 80, 111], and emission spectra [78, 112], the model Hamiltonians cover a variety of effects which are neglected in our purely electronic, one-dimensional model.

Our model Hamiltonian (3.1) represents, apart from the boundary conditions, a sub-problem which is shared by all proposals. Hence, we can retrieve complete sets of parameters to determine our Hamiltonian. In Table 6.1, we gathered the electronic parameters of the available models. We give them both in the notation used in the corresponding references and in the notation of our work. The electronic parameter sets are taken from more complex model situations. Introduced into our model, a reduced set will not yield statements which can be directly used to verify experiments. However, we can describe the consequences for the underlying electronic problem. Once the full problem is considered, effects caused by the electronic constellation can be clearly separated.

Neither independent measurements nor theoretical calculations were able to provide all required parameters to correctly predict the optical and electro-optical properties of both materials so far. Therefore, all recent approaches in literature involve the fitting of uncertain degrees of freedom in the model backbone to the experimental spectra. The need for independent parameters constantly pushed forward the quality of theoretical calculations [53, 81, 111, 114]. However, remaining uncertainties in the case of MePTCDI and PTCDA reduce the application of these parameters to estimate the reliability of the fitted results.

In the following, we briefly review the background of the models registered in Table 6.1. The main emphasis is laid on the specific circumstances which induced the most remarkable differences in the parameter sets. We additionally show for each model the corresponding excitonic bands and the surface states in Figure 6.2 (PTCDA) and in Figure 6.3 (MePTCDI).

All model Hamiltonians descent from the MERRIFIELD-Hamiltonian [75]. They have been adjusted to a problem-related number of CT states and contain the possibility of exciton-phonon coupling. Among them are the strong vibronic coupling Hamiltonians [53, 80, 111] that involve basis functions in which excitations of internal phonons at electronically excited sites are allowed. Since the vibrational excitation has to stick with the electronic excitation, the terminology strong vibronic coupling was chosen. Alternatively, this limiting case has also been considered as molecular vibron model, introduced in reference [112], where the authors intend to underline that internal phonons are not allowed to occur at molecules found in their electronic ground state.

The model 4 which relies on the smallest basis set was presented by HOFFMANN et al. in references [53, 54]. The one-dimensional Hamiltonian incorporates three vibronic sublevels of the Frenkel exciton and one symmetry-adapted A_g-CT exciton. For the CT and the Frenkel exciton share the same vibrational ground state, the coupling of the Frenkel states with the CT state can by expressed by the electronic matrix elements $\epsilon_e$ and $\epsilon_h$, which were multiplied by the Franck-Condon overlap between the vibrational ground state and the excited vibronic state. By fitting, the resulting excitonic states at $k = 0$ were assigned to the energetical positions and the oscillator strength of the four prominent peaks found in the absorption spectra. After applying the fitting procedure to spectra taken for different polarizations of the incident light, the differences found in the peak energies and intensities were explained with Davydov-Splitting: Due to the interaction of the non-equivalent molecules in the unit cell, all states observed in the strictly quasi-one dimensional treatment split in energy. Remarkably,
<table>
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<tr>
<th></th>
<th>① Holstein&lt;sup&gt;a&lt;/sup&gt;</th>
<th>② Holstein dimer</th>
<th>③ molecular vibron model</th>
<th>④ molecular vibron model</th>
<th>⑤ + vibronic overlap</th>
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<tbody>
<tr>
<td></td>
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<td>[112]</td>
<td>[78], Table 1</td>
<td>[111, 80]</td>
<td>[53, 54]</td>
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<td></td>
<td></td>
<td></td>
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<td></td>
<td>[113]</td>
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### PTCDA

<table>
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<td>$E_R$</td>
<td>2.330</td>
<td>$\Delta_{CT}$</td>
<td>2.270</td>
<td>$\Delta_{CT}$</td>
<td>2.270</td>
<td>$\Delta_{CT}$</td>
<td>2.270</td>
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<tr>
<td>$E_F$ (eV)</td>
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<td>$E_B$</td>
<td>2.200</td>
<td>$\Delta_{0F}$</td>
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<td>$\Delta$</td>
<td>0.126</td>
<td>$W$</td>
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<td>$W$</td>
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<tr>
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<td>$\tilde{J}_F$</td>
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<td>$\tilde{t}_b$</td>
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<td>$\tilde{J}_F$</td>
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<td>$\tilde{J}_F$</td>
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<tr>
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### MePTCDI

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<tbody>
<tr>
<td>$E_{CT}$ (eV)</td>
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<tr>
<td>$\epsilon_h$ (eV)</td>
<td>$\tilde{t}_b$</td>
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</table>

**Table 6.1:** Electronic parameters retrieved from available model proposals for PTCDA and MePTCDI. In brackets we give the notations from the corresponding publications if they differ from the notation of this work. The vibronic overlap $S_0$ in ⑤ has been taken from Ref. [54, p. 101].

<sup>a</sup>Due to a misprint in Ref. [112, Sec. V], the parameter indicated as t has to be read as 2t.
for any considered spectrum the fitting procedure yield an on-site CT energy $E_{CT}$ which was lower than the Frenkel on-site energy $E_F$. From the spectra, only the value of $\epsilon_+ = \epsilon_e + \epsilon_h$ was accessible. The decomposition into $\epsilon_e$ and $\epsilon_h$ presented utilized the estimation of $\epsilon_e$ and $\epsilon_h$ obtained from quantum chemical calculations with the semi-empirical method ZINDO/S [45, 53, 54].

Parameter set ❼ is directly related to model ⪀. The electronic interaction parameters have been corrected by the Franck-Condon overlap given in reference [54, p. 101] between the vibrational ground state and first the vibronic level. The parameters generated in this way already contain corrections due to intramolecular vibrations. The adjustment allows us to extend the electronic parameters to a set which describes the lowest energy states quantitatively more correctly [115].

Proposal ⪁ originates from the work of MAZUR et al. The authors address the explanation of electro-absorption spectra. References [80, 111] contain the explanation of the spectra of PTCDA published in reference [116]. A proposal for MePTCDI has been added in reference [111]. Electro-absorption spectroscopy has been proven as a standard technique to investigate charge transfer induced effects in the electro-optical properties. A model was required which is capable of reproducing the shape, the amplitude, and the directional peculiarities of the spectra. In particular, the reproduction of the absolute signal and the

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**Figure 6.2:** Excitonic bands (solid lines) and the surface states (triangle) of PTCDA according to the model proposals dealing with infinite chains (cf. overview in Table 6.1). The left panel contains the experimental thin film absorption spectrum to which the parameters of all proposals have been fitted.
directional properties is very challenging. To account for differences in the spectra caused by electric fields applied in different directions with respect to the molecular planes, further inter-stack CT states cannot be neglected initially. Owing to their large permanent dipole moment, they may significantly contribute to the signals. Such a background constellation requires the application of a three-dimensional Hamiltonian which explicitly contains inter-stack interactions. The Hamiltonian for infinitely extended crystal is automatically diagonal with respect to the wave vector \( k \). The electrically induced changes in the optical absorption are entirely determined by the states at \( k = 0 \). Thus, the actual decomposition of \( \epsilon_\perp \) into \( \epsilon_\mathrm{e} \) and \( \epsilon_\mathrm{h} \) is not relevant. Accompanying theoretical calculations suggested only a small difference between \( \epsilon_\mathrm{e} \) and \( \epsilon_\mathrm{h} \). Hence, it was convenient to set \( |\epsilon_\mathrm{e}| = |\epsilon_\mathrm{h}| \) which reduced the number of fitting parameter by one. The final determination of still adjustable parameters of the model requires a fitting to experimentally obtained electro-absorption characterizations of PTCDA and MePTCDI. The experimental results available in literature are rather limited. For comparison with theoretical predictions, sufficient information is provided for PTCDA \([116, 117]\). The published electro-absorption spectra of MePTCDI \([118]\) lack indispensable information to retrieve the absolute signal amplitude. Hence, for serious comparison only the absorption spectrum could be used. For our purposes, one of the main results is that the estimation of inter-stack influences on the electro-absorption spectra of PTCDA now justifies the application of one-dimensional approaches. Although only the absorption spectrum was available for MePTCDI, the strong relationship between both materials suggested by the structure and by theoretical estimations, motivated the authors to suggest a parameter set for MePTCDI as well.

With the introduction of Holstein Hamiltonians \([78, 112]\), the formulation of the coupling between internal phonons and excitons allow the formation of phonon clouds which cover more than the site of the electronic excitation. Those Hamiltonians act in a Lang-Firsov basis where phonon excitations at sites different from the electronically excited states are enabled. So far, only strictly one-dimensional considerations are available. Model \( \mathcal{O} \) is based on the description presented in Hennessy et al. which considered a pair of PTCDA molecules (dimer) \([78]\). The original Holstein Hamiltonian which contains exclusively molecular excitations, has been enriched with further CT excitations which are allowed to couple to the molecular excitations. Already at this stage, the shape of the absorption spectra could be reproduced rather well. The absolute values of the CT transfer integrals were initially set equal \( (|\epsilon| = |\epsilon_\mathrm{e}| = |\epsilon_\mathrm{h}|) \); the relative signs have been fixed from independent AM/1 calculations. The magnitude of \( |\epsilon| \), the Frenkel-CT on-site separation, and the Frenkel transfer \( M \) were adjusted to the absorption and emission spectrum. The incorporation of the red-shifted emission spectrum gave rise to a notably large value of the adjusted Frenkel transfer integral \( M = 0.18 \) eV.

The work of Hoffmann et al. \([112]\) continues to utilize the Holstein Hamiltonian to determine the lowest excited states. The authors proceed from the dimer to finite linear aggregates with periodic boundary conditions. This treatment provides us the parameter set \( \mathcal{O} \). They aim to generate accurate absorption spectra which can be compared one-to-one to real experimental absorption spectra. Any experimentally obtained absorption coefficient \( \alpha(E) \) contains both the index of refraction \( n \) and the extinction \( k \). To obtain \( n(E) \) and \( k(E) \), the knowledge of the complex dielectric function \( \epsilon \) is required:

\[
\epsilon = \epsilon_1 + i \epsilon_2 = (n + i k)^2 .
\]  

In reference \([112]\), the eigenstates of the Holstein Hamiltonian were used as the starting point to construct the dielectric function. They mainly enter the imaginary part \( \epsilon_2 \) which
most essentially determines the shape of the spectra. The dielectric function, eventually formulated for MePTCDI and PTCDA, points out a significant influence of the strongly varying refractive index $n$ on the absolute value of $\alpha(E)$ in the low energy range. Earlier proposals, e.g. in references [80, 111], neglect any dispersion $n(E)$ in the spectral region of interest. Not surprisingly, the parameters mirror the non-negligible influence of $n$, most obviously in the Frenkel transfer integrals $M$. The values obtained are systematically an order of magnitude smaller than the $M$ proposed by models which do not regard the full dielectric function.

For each proposal, we determine the intrinsic quantum length $L$ with the help of the surface states. The knowledge of $L$ allows us to estimate the cluster size which justifies the application of the infinite chain description. In the framework of the corresponding model, the electronic sub-problem of the cluster is sufficiently described by an infinite aggregate.

A comparison between the models, in particular with respect to the expected quantum length $L$, must be carried out very cautiously. To guarantee conclusions which span all proposals, all desired quantities must be stable with respect to such varying parameter sets.

Figure 6.3: Excitonic bands (solid lines) and the surface states (triangle/diamond) of MePTCDI according to the model proposals dealing with infinite chains (cf. overview in Table 6.1). The left panel contains the experimental thin film absorption spectrum to which the parameters of all proposals have been fitted.
6.3 Extraction of the intrinsic quantum length

The models \(1 - 5\) were proposed to explain absorption spectra, where \(3\) mainly concentrates on electro-absorption spectra. These experimental techniques rely on excitation with light. Hence, only transitions into states with \(k = 0\) can be induced. As we already mentioned in Section 4.1, at \(k = 0\) only knowledge of the sum \(\epsilon_+ = \epsilon_e + \epsilon_h\) is necessary. The decomposition into \(\epsilon_e\) and \(\epsilon_h\) introduces a further degree of freedom which cannot be fixed with the absorption data alone. Therefore, the proposals \(1 - 3\) aim to determine a correct \(\epsilon_+\) for which the assumption \(\epsilon_e = \epsilon_h\) is convenient. The correct fine structure of \(\epsilon_+\) can be resolved if further experimental information about states with \(k \neq 0\) becomes available. In proposal \(4\), where already different \(\epsilon_e\) and \(\epsilon_h\) are given, additional information from independent quantum chemical calculations is introduced [45]. The artificial setting \(\epsilon_e = \epsilon_h\) in models \(1 - 3\) limits statements concerning surface states. The perfectly balanced situation \(\alpha = \beta\) immediately suppresses one oscillating state.

The extraction of the intrinsic quantum length \(L\) requires full knowledge of the surface states. From all five parameters given in Table 6.1, a certain part of the information is necessary to decide whether surface states occur or not. As pointed out with the phase diagrams (Figure 4.8) in Section 4.3, the separation of \(E_F\) and \(E_{CT}\) given by \(\bar{\Delta}\), the combined amount of charge transfer integrals \(\alpha\), and the balance \(\beta\) of the charge transfer integrals, all with respect to the Frenkel transfer \(M\), are required. We list them together with all corresponding formal solutions \(Z_{1,2}\) in Table 6.2. For any valid \(Z\), the properties of the associated surface states are shown as well.

The variety found within the parameter sets immediately allows each scenario of surface state combinations (cf. also Figures 6.2, 6.3): The Holstein dimer model \(2\) and the model proposed by Mazur et al. \(3\) forbid surface states in PTCDA completely. Albeit the parameters originate from rather different points of view, both models are very closely situated within the parameter space \((\bar{\Delta}, \alpha, \beta)\), the phase diagram for \(\bar{\Delta} < 0\) (Figure 4.8(a)) may serve as a guide. With \(\beta = \alpha\) \((Z_2 = -1)\) and additionally \(-\bar{\Delta} < 2\alpha\) \((Z_1 > 1)\), both possible \(Z\) are ruled out. For the same material, all remaining models \(1, 4, 5\), and yield a non-oscillating surface state. In phase diagram 4.8(a), the parameter constellation of the Holstein model corresponds to \(-\bar{\Delta} \approx \alpha = \beta\), whereas the parameter relationships in \(4\) and \(5\) correspond to \(\bar{\Delta} \approx \alpha > \beta\) in phase diagram 4.8(c). The intrinsic quantum length extracted from the non-oscillating states reacts very sensitively on the choice of \((\bar{\Delta}, \alpha, \beta)\); a sensitivity which allows the formation surface states of similar properties starting from the most opposite parameter sets \(1\) and \(4\).

The overall picture obtained for MePTCDI is as inhomogeneous as for PTCDA. Model \(1\) and \(3\) predict a non-oscillating surface state with a huge quantum length \(L\). Referring to equation (5.51(a)), condition \(\bar{\Delta} \leq -2\alpha\) together with \(\alpha = \beta\) represents one precondition which enable very weakly localized states. However, already a very small translation along \(\alpha = \beta\) leads to totally different circumstances, as can be seen from the comparison between MePTCDI and PTCDA in case \(3\). The intrinsic quantum lengths predicted with \(4\) and \(5\) are very similar, \(L \approx 1.3\), but originate from states of different oscillation type. The derived quantum length is systematically smaller as the \(L\) taken from the models with perfectly balanced CT integrals.

It remains the question whether the lifting of the condition \(\epsilon_e = \epsilon_h\) will destroy the picture obtained for the models \(1 - 3\). Already the slightest deviation from \(\beta = \alpha\) prompt the occurrence of an additional oscillating surface state. As long as this deviation is not to large, e.g., \(\beta = 0.9\alpha\) (cf. Figure 4.6), the parameter constellation favors a large \(L\), as we have
already learned in Chapter 5.4. However, such a weakly damped oscillating surface state has a vanishing oscillator strength and no bulk state with considerable oscillator strength is located near $k = \pi$ either. As discussed in Chapter 5.3, such a surface state will not play an active part in the absorption spectrum. Hence, we will neglect the influence of the quantum length provided by such a surface state.

The inhomogeneity of the surface state properties found provides a very dangerous ground for the consideration of quantum confinement. Except in cases ① and ③ for MePTCDI, the intrinsic quantum length is rather small. Systems have to contain less than three molecules to observe quantum confinement. Hence, quantum confinement effects originating from an intrinsic length can hardly be observed. For PTCDA in particular, we can conclude that the application of the corresponding infinite chain models is justified already for systems with more than four molecules.
### Table 6.2: Formal solutions $Z$ for surface states (cf. Eq. (4.23)), surface state energies, and resulting quantum length $\mathcal{L}$ for available model proposals for PTCDA and MePTCDI; derived with the dimensionless parameters $\tilde{\Delta}$, $\alpha$, $\beta$.

<table>
<thead>
<tr>
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<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
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<tr>
<td>Holstein</td>
<td>Holstein</td>
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<td>molecular vibron model</td>
<td>molecular vibron model</td>
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<td>dimer</td>
<td>3D infinite crystal</td>
<td>1D infinite chain</td>
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#### PTCDA

<table>
<thead>
<tr>
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<th>3</th>
<th>4</th>
<th>5</th>
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</thead>
<tbody>
<tr>
<td>$\tilde{\Delta}$</td>
<td>-2.310</td>
<td>-0.700</td>
<td>-0.722</td>
<td>0.642</td>
<td>1.658</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>2.048</td>
<td>0.245</td>
<td>0.187</td>
<td>0.681</td>
<td>1.761</td>
</tr>
<tr>
<td>$\beta$</td>
<td>2.048</td>
<td>0.245</td>
<td>0.187</td>
<td>0.191</td>
<td>0.493</td>
</tr>
<tr>
<td>$Z$</td>
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<td>0.414</td>
<td>-1.000</td>
<td>1.169</td>
<td>-1.045</td>
</tr>
<tr>
<td>$\Delta_{CT}$</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$\mathcal{L}$</td>
<td>-2.267</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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</tbody>
</table>

#### MePTCDI

<table>
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<tr>
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<th>3</th>
<th>4</th>
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</tr>
</thead>
<tbody>
<tr>
<td>$\tilde{\Delta}$</td>
<td>-5.217</td>
<td>-0.600</td>
<td>-0.600</td>
<td>0.693</td>
<td>1.676</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>3.125</td>
<td>0.405</td>
<td>0.405</td>
<td>0.532</td>
<td>1.287</td>
</tr>
<tr>
<td>$\beta$</td>
<td>3.125</td>
<td>0.405</td>
<td>0.405</td>
<td>0.340</td>
<td>0.821</td>
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<tr>
<td>$Z$</td>
<td>-1.000</td>
<td>0.750</td>
<td>-1.000</td>
<td>0.851</td>
<td>-1.098</td>
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<tr>
<td>$\Delta_{CT}$</td>
<td>-5.468</td>
<td>-</td>
<td>0.750</td>
<td>-</td>
<td>0.448</td>
</tr>
<tr>
<td>$\mathcal{L}$</td>
<td>-6.942</td>
<td>-</td>
<td>12.354</td>
<td>-</td>
<td>1.253</td>
</tr>
</tbody>
</table>
6.4 Available experimental observations of finite size effects

Due to the strong dependence of the surface state energies on the parameters $\alpha, \beta, \tilde{\Delta}$ and $M$, the spectroscopy of surface excitons can make a contribution to elucidate the nature of the Frenkel and CT exciton mixing in molecular chains. Of course, significant contribution of the surface states can be expected only in experimental investigations of absorption spectra of rather short chains. From the viewpoint of our model, the intrinsic quantum lengths extracted in the preceding section rule out the occurrence of quantum confinement effects. However, the presence of surface states in small aggregates might be important. The role the surface state is playing in absorption spectra is comprehended in Figures 5.4. As already argued in Section 5.3, a surface state acquires oscillator strength from an energetically close-by bulk state. If we concentrate on the lower band bulk state with smallest wave-vector $k$, we expect the state to transfer oscillator strength by and by to the surface state with reducing the system size $N$. Since the surface state lies always at higher energies than the bulk state, the low energy part is dominated by the surface state as soon it was granted more fractional oscillator strength than the bulk state. We exemplarily illustrate this process in the viewgraphs in Table 6.3(b,c) for model case 5 of MePTCDI. In the electronic spectrum we would effectively observe a shift of the lowest excited state towards higher energies which is, remarkably, independent of the actual dispersion of the lower band. Table 6.3(a) collects for all model proposals of Table 6.1 the energies of the surface states in the smallest available chain ($N = 3$) and the bulk state within the lower excitonic band at $k = 0$ (limit of long chains). If the ratio $f_s/f_b$ in the small chain is considerably larger than unity, the separation of the surface state and the lower band edge at $k = 0$ can be recognized as a blue-shift in the electronic spectrum (cf. also Table 6.3(b)). Judging from the results in Table 6.3(a), in the framework models 4 and 5 the surface state becomes indeed relevant for the consideration of the electronic spectra.

Hence, we seek for experiments in which the dependence of absorption with respect to the system size was studied. As an important requirement we must be able to identify our chain length $N$ with the system size. Just the application of organic molecular beam deposition [119, 120, 121] opened an interesting perspective for such studies.

In literature, the relationship between optical properties and the film thickness has been investigated for PTCDA and MePTCDI layers on different substrates, starting from very thin films, a few Angstroms thick, to bulky layers consisting of several hundreds of Angstroms.

In experiments done by So et al. [122], thin alternating layers of PTCDA (10 - 1000 Å) and NTCDA have been grown. In the multiple hetero-structures, the thickness of all PTCDA layers was constant. X-Ray investigations revealed that the films sandwiched between two NTCDA layers suffer a very small strain and therefore almost keep their bulk structure. The planar PTCDA molecules, i.e., the molecules in the (102) crystal plane (cf. Figure 1.1(e)), lie flat on the NTCDA layer beneath. Hence, the molecules in the layer are stacked perpendicular to the NTCDA layer. With the distance of 3.22 Å between the (102) planes, a thickness of 10 Å roughly correspond to three monolayers (ML). Since the absorbing regions of PTCDA and NTCDA have almost no overlap, the contribution from both components to the absorption of the hetero-structure could be clearly distinguished. The low energy absorption was thereby attributed to PTCDA. When the thickness of the PTCDA layers was reduced from 31 to 3 ML, the lowest absorption maximum of the whole structure was gradually shifted towards higher energies by an amount of 200 cm$^{-1}$. 
6.4 Available experimental observations of finite size effects

(a) proposed energy shifts $\Delta E$

<table>
<thead>
<tr>
<th>model</th>
<th>$N \to \infty$ $E_b$ (eV)</th>
<th>$N = 3$ $E_s$ (eV)</th>
<th>$\Delta E$ (meV)</th>
<th>$\Delta E$ (cm$^{-1}$)</th>
<th>$\frac{f_s}{f_b}$</th>
<th>$\frac{f_s}{f_b}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTCDA</td>
<td>2.200 2.207</td>
<td>2.214 2.224</td>
<td>2.233 2.243</td>
<td>7 58</td>
<td>9 74</td>
<td>11 86</td>
</tr>
<tr>
<td>MePTCDI</td>
<td>2.117 2.121</td>
<td>2.149 2.153</td>
<td>2.097 2.106</td>
<td>3 28</td>
<td>4 29</td>
<td>9 75</td>
</tr>
</tbody>
</table>

(b) MePTCDI: energy shift

(c) MePTCDI: $E(N)$ and $f(N)$

Table 6.3: Competition of bulk and surface states in small chains of PTCDA and MePTCDI. Table (a) contains the energy of the surface state $E_s$ in chains with 3 molecules, the energy $E_b$ of the lower band state at $k = 0$, and the resulting shift $\Delta E = E_s - E_b$ which result from the various model proposals of Table 6.1. Whether this shift can be recognized in the electronic spectrum, is decided with the ratio of the surface state oscillator strength $f_s$ with respect to the bulk state intensity $f_b$. The ratio is shown for $N = 3$ and for comparison also for a long chain $N = 21$. Calculated for model case ⑤, the lower figures show for MePTCDI the position of the surface state of the $N = 3$ chain with respect to the lower excitonic band (b), and between the bands (inset (b)), respectively, and the dependence of the energy and the fractional oscillator strength for both the surface state and the close-by bulk state with largest $f$ (c).
Later, these experiments were taken up by Leonhardt et al. [123]. They investigated the growth of PTCDA on amorphous quartz glass and on single alkali halide crystals. The absorption spectra of films with gradually reduced thickness revealed peak shifts similar to the shifts observed in the hetero-structures. With combined investigations of absorption and fluorescence, the authors proved that the shifts observed in absorption can be indeed attributed to PTCDA. While the layer thickness was reduced from 80 ML to 3 ML, the lowest absorption peak was shifted towards higher energies. The authors offer a convincing explanation: Instead of finite size effects, the occurrence of the two PTCDA modifications are responsible for the peak shift. The absorption spectra of the $\alpha$- and the $\beta$- phase slightly differ, the lowest absorption maximum of the $\beta$-phase lies $\approx 600 \text{ cm}^{-1}$ below the corresponding peak of the $\alpha$-modification. With decreasing film thickness, the ratio of $\alpha$- to $\beta$-phase increases and the absorption spectrum of the $\alpha$-phase continuously gains dominance.

The structure and morphology of films grown from PTC-derivatives depend strongly on the substrate and the growing conditions chosen. Remarkably, the molecules of PTCDA arrange almost always flatly on the substrate, no matter amorphous, polycrystalline, or single crystalline substrates have been chosen [15, 124]. The (102)-plane known from the crystal was found parallel to the substrate independently of the substrate temperature and the sublimation rate. However, the surface roughness and the grain size of polycrystalline films remain strongly dependent on substrate, substrate temperature and sublimation rate. This fact should be kept in mind: In most cases, the nominal thickness, calculated from the amount of material evaporated, is given which allows us no conclusion about the thickness distribution.

The structure of the MePTCDI films is much more sensitive to the evaporation conditions than PTCDA. The most important influence on the growth behavior is the choice of the substrate. On alkali halides (KCl, [125]) and on a bi-axially stretched polymer film (polyethylene terephthalate, [54]), a considerable amount of molecules were oriented flatly on the substrate. However, in all cases the quality of orientation is not as perfect as for PTCDA. Only a fraction of the crystallites share the same orientation. According to the crystal structure, in these crystallites the (102)-plane is oriented parallel to the substrate surface. The results of X-ray diffraction measurements in references [54, 125] are supported by investigations using Infra-Red (IR) spectroscopy [99]. Even in films of 2000 A thickness grown on NaCl, a large degree of stacks aligns perpendicular to the substrate. A comparison of Resonant Raman (RRS) spectra [99] suggests the same orientation of MePTCDI molecules grown on quartz glass. Interestingly, also completely different molecular alignment of MePTCDI on quartz was reported [109]. Here the molecules are cofacially stacked perpendicular to the substrate. Such a stack orientation was also found for films grown on indium tin oxide (ITO) [125]. However, if no special effort is made, the crystallites show an almost random orientation [124].

A thorough investigation of the dependence of optical and electrical properties on the growth conditions has been presented in reference [126]. Absorption spectra of MePTCDI films on quartz glass taken in-situ during the growth show a pronounced red-shift of the lowest absorption minimum with increasing film thickness. Between 20 A and 100 A nominal thickness a shift of 182 cm$^{-1}$ was observed. A observation of the film morphology revealed an island formation within the films (Volmer-Weber growth) with islands up to 100 A in height. The authors assumed further that the planes of the first molecules arriving at the substrate during the evaporation lie parallel to the substrate surface. With this assumption in combination with growth mode observed, they attribute the overall changes in the spectra with increasing film thickness to the increased formation of aggregates in which the large
interaction between stacked molecules is established.

The same material-substrate combination was chosen in reference [106], but no particular effort has been made to get well ordered films. A film thickness variation from 500 Å to 15 Å was accompanied by a blue-shift of the lowest energy minimum in transmission. Even though the minima in transmission are not directly related to maxima in absorption, their shift of about 400 cm\(^{-1}\) should correspond to a blue-shift in absorption in the same order of magnitude. However, also in this experiment the thickness distribution is broad. In the thinnest films the thickness error can reach 50%. As a possible contribution to the shift, the influence of the microscopical polarizability with respect to the macroscopic dielectric function \(\epsilon\) of material (classical local field contribution) which differs for very thin and thick films, was estimated. Without knowledge of the microscopical composition of the crystallites the authors were only able to show that such a model is in principle able to predict line shifts in the desired order of magnitude.

All experiments discussed above consistently demonstrate that a reduction of the layer thickness leads to the shift of the lowest absorption maximum towards higher energies. However, it is very difficult to assign the chain length \(N\) to the layer thickness. In all PTCDA layers as well as in some MePTCDI layers investigated [126], the (102) plane is oriented parallel to the substrate plane. The stacks are formed perpendicular to the substrate as desired. The height of a single stack can therefore be assigned with the chain length. For such an isolated chain, the theoretical proposals forecast a blue-shift in the correct order of magnitude (cf. Table 6.3). However, the thickness distribution of these samples has to be taken into account. Furthermore, the electronic spectra cannot reflect the continuous energy shift over tens of lattice constants. To cover the behavior of the absorption spectra, the transitions into the excitonic states obtained from the model have to be assigned with finite line width (e.g., as done in reference [85]). Such necessary extensions point towards the application of the dielectric background function, e.g., as described in reference [112]. In conclusion, the surface state can contribute to a considerable change of the absorption spectrum with changing layer thickness. In comparison to the other mechanisms mentioned, this contribution is not of leading importance, since also presumably randomly oriented samples exhibit a pronounced blue-shift [106].

To perform a better comparison of experimentally obtained data with predictions using a model as presented here, experiments are required which allow a clear separation of finite size effects from effects originating, e.g., from morphology. Therefore, the combination of absorption measurements with structural characterization incorporating precise determination of the film thickness is of crucial importance. To ensure further that the chain length can be assigned with the film thickness, very smooth films, i.e., films with a narrow thickness distribution, are needed. Therefore, the best way to realize these requirements would be the investigation of highly ordered films grown in a layer-by-layer fashion on well defined substrates. This can be archived by the epitaxial growth of ultrathin organic films on surfaces of single crystalline substrates, such as PTCDA on Au(111) [120, 127] and PTCDA on MICA [121].

6.5 Beyond the ideal chain: Adjustments at electronic level

Several effects have to be included to provide a serious basis for the discussion of experimental results. One can think of a several approaches with which the idealized problem can be adjusted to more realistic formulations. In Figure 2.1, we indicated below the idealized
model two major extension paths. Already within the purely electronic description, it is necessary to drop the assumption of ideal chains. The on-site energies and interactions may change with the number of molecules involved. In the framework of our exciton model, the properties of the system are encrypted by the parameters which are assigned to each site.

In a first step, we assume that the on-site energies $E_F$ and $E_{CT}$ depend on the site $n$ in a free standing chain and thus on the separation from the surface $|m - n|$. The lack of an equivalent nearest neighbor should affect at least the boundary sites $|m|$. The molecular excitation energy $E_F$ is expected to be different from the bulk value and to be closer to the monomer excitation energy in vacuum. On the simplest adjustment level, $E_F$ at the outermost sites $|m|$ has to be chosen different from the bulk sites. It is more realistic to assume that the value $E_F$ drops continuously towards the bulk value with increasing distance from the chain end. An estimation of the $E_F$ site distribution for PTCDA or MePTCDI is not available so far.

The on-site energy $E_{CT}$ of a localized charge transfer excitation depends on the neighborhood in the crystal. In particular, the contributing polarization energy is very sensitive to the environment of the charged molecules. In references [81, 114], the electronic contributions to the polarization were calculated by taking into account a non-uniform charge distribution within the single molecule. The electrostatic influences of the surrounding molecules on a pair of oppositely charged molecules were estimated in the zero-overlap approximation. In this approximation, the electron and the hole, sitting on different molecules, cannot be transferred to other molecules, since the charge transfer integrals are neglected. Embedded in a cluster of molecules, the CT energy is stabilized with increasing size of the clusters, i.e., $E_{CT}$ is decreased. The calculations for PTCDA in reference [81] predict a change in the order of tens of meV. If the cluster is considered as an ellipsoid with the same number of molecules along each crystal axis, as assumed in [81], we can estimate the number of molecules within the central stack which contains the molecular ions: For the nearest stack neighbor CT, the stabilization energy increases by $\approx 10$ meV if the stack height was reduced from 10 to 5 molecules. To regard this effect in our model, one has to equip each site with an energy $E_{CT}(N)$ dependent on the chain length.

However, the argumentation above suggests that the CT energy will vary with the position of the localized CT with respect to a surface and thus with the site $n$. To our best knowledge, no estimations of this effect in the context of PTC-derivatives have been published. For other materials the correlation between the energy and the location of the CT has been considered. In three-dimensional C$_{60}$ clusters, the surface CT energy has been obtained from self-consistent polarization field SCPF calculations [128]; a technique which was applied also in reference [114]. The localized CT at the surface is significantly destabilized by $\approx 0.1$ meV with respect to a bulk CT state. Moreover, this destabilization grows linearly with increased cluster size.

Another way of looking at the problem is the actual geometry of the clusters. So far, the parameters have been acquired under the condition that the underlying geometrical alignment of the molecules exactly matches the crystal structure. However, near the boundaries the molecules very likely give up the optimum geometry of the bulk. To give an qualitative illustration, we conducted a small numerical experiment: Consider a stack of PTCDA molecules in which the molecules initially have the bulk alignment. We now allow the separation of all sites along the stack axis to vary, i.e., we drop the rigid lattice assumption. In doing so, only the variation of the center-of-mass distance $r$ was allowed to vary, as in-

\[^{1}\text{We refer to the notation introduced for odd } N \text{ chains (Figure 3.4)}\]
6.5 Beyond the ideal chain: Adjustments at electronic level

Figure 6.4: Site separation of PTCDA molecules in stacks of the height \( N = 2m + 1 \).

While indicated in the inset of Figure 6.4, whereas the tilt angle of the molecules with respect the stacking axis was kept as in the bulk. With the aid of an atom-atom potential method [129] which utilizes the universal force field parameterization [130] of a Lennard-Jones potential, the distance \( r \) between all nearest-neighbor sites has been optimized for chains of arbitrary length. We display in Figure 6.4 the dependence of the (non-uniform) site separation on the given number of molecules \( N = 2m + 1 \) and the position within the chain \( |m - n| \).

Independently from the total length, we observe a decline of the site spacing with an increasing distance from the chain end. The outermost molecule is slightly more separated (ca. 0.01 \( \text{Å} \)) from its neighbor than a typical bulk molecule. Even the closely following molecule recognizes the chain end, but the resulting difference to the bulk separation is negligible. The saturation spacing which is rapidly reached in the curve presented, does not exactly meet the experimentally observed bulk value. This deviation can be easily explained with the neglect of influences of molecules of neighboring stacks, electro-static interaction, and the non-optimized choice of force field parameters, respectively. If further effects are incorporated, probably more molecules may arrange not as close as in the bulk. The predicted distances may also saturate closer to the experimentally obtained bulk separation. Nevertheless, the viewgraph qualitatively mirrors the most important fact: The relevant changes of the molecular separation are observed between the outermost molecules and their nearest neighbor. Transferred into a semi-finite crystal, it means that the outermost layer is more separated from the layer beneath than the typical bulk layer spacing. By adjusting the parameters of our rigid-lattice-model, we can account for this effect indirectly. The molecular separation sensitively enters the coupling parameters \( M(|m|, |m-1|) \), \( \epsilon_e(|m|, |m-1|) \), and \( \epsilon_h(|m|, |m-1|) \) between the outermost molecules. The direction in which the value of parameters has to be varied correlates with the overlap of the molecular wave functions.
Whether an increasing or a decreasing of the total overlap has to be expected is difficult to decide, since the molecular arrangement causes very complicated interpenetration pattern of the π-type wave functions [26].

According to the studies of Müller et al., a variation of $E_F$ at the outermost molecules and the variation of the related couplings to them gives rise to surface states of TAMM-type [74]. They arise, similar to the surface states obtained in our idealized picture (cf. Section 4.3), from the ‘imperfect’ neighborhood of the outermost molecules. The occurrence of these surface states is sensitively dependent on the relationship between the parameters at the boundaries and in the bulk [74]. Generalized to the full Frenkel-CT problem, the adjustment of all matrix elements in Hamiltonian (3.1) which involve outermost molecules opens an additional source for surface states which are equipped with their specific intrinsic quantum length.

It is obvious that effectively three absorbing states are not sufficient to describe a broad spectrum with more than three significant features. The coupling to internal phonon modes, even in the strong coupling regime, plays an important role. The incorporation of the coupling is beyond the scope of our work. The general Holstein formalism for finite chains, in particular for a non-ideal electronic sub-problem, cannot be handled analytically anymore, has thus to be carried out numerically. Only in a few limiting cases a partially analytical treatment is possible. However, in combination with the dielectric model function, the Holstein Hamiltonian provides excellent premises to tackle the broad featured, thickness dependent absorption spectra obtained in references [120, 121]. Such considerations are currently under way.
Conclusions

7.1 Summary and conclusions

We offer a concept to predict and comprehend the electronic excited states in regular aggregates formed of quasi-one-dimensional organic materials. The tight face-to-face stacking of the molecules allowed us to idealize the crystals and clusters as weakly interacting stacks with leading effects taking place within the columnar sub-structures. Thus, we adopted the concept of the small radius exciton theory in linear molecular chains to examine the excitonic states.

In the model presented, the excited states are composed of molecular excitations and nearest neighbor charge transfer (CT) excitations. The coupling between the molecular and the localized CT excitations is permitted. We analyzed the structure and properties of the excited states which result from the coupling of Frenkel and CT excitons of arbitrary strength in finite chains. The boundary conditions adopted describe idealized free ends: At each outermost molecule, only one nearest neighbor CT is permitted, but interactions involving these molecules are kept exactly equal to interactions between molecules with two equivalent neighbors.

With this work, we provide a partially analytical approach to determine the excitonic states of mixed Frenkel CT character. The initial Schrödinger equation has been expressed in the basis of localized Frenkel and nearest neighbor CT excitations. In this basis set, the Schrödinger equation has temporarily the form of a set of equations. The main step to reformulate this system of equations is the introduction of a complex wave vector $\kappa$. The usage of a wave vector naturally opens the opportunity to compare the results obtained with systems described by periodic boundary conditions. In such cyclic chains, $\kappa$ becomes automatically purely imaginary and Im($\kappa$) plays the role of a quasi-momentum $k$ in the limit of infinite chains.

Formulated with the help of the wave vector $\kappa$, the original set of equations was transformed into two central equations which determine the set of valid $\kappa$ for symmetric and antisymmetric states, respectively, and equations determining the eigenstate energies dependent on $\kappa$. The sole step which involves numerical calculations is the solution of the central equations which determine the valid $\kappa$. In the presence of the boundary conditions, this equations yield a discrete set of non-equally spaced $\kappa$. Two main types of states can be distinguished with the help of their wave vector $\kappa$.

The majority of states are bulk states with purely imaginary $\kappa = ik$. They correspond to the excitonic states of the infinite chain. In consequence, the dispersion relation $E(k)$ of these state matches exactly the dispersion relation known from the infinite chain. In the limit of long chains, the bulk states inherit the Frenkel-CT ratio from the underlying band
state. Hence, the internal structure of the excitons in infinite chains is directly transferred to the bulk states in finite chains. The effective size $N_{\text{eff}}$ of a bulk state is always in the order of the chain length $N$.

TAMM-like *surface states* belong to the second class of states. They are characterized by a wave vector either in the form $\kappa = \kappa_R$ or $\kappa = \kappa_R + i\pi$. The real part $\kappa_R$ is responsible for a damping factor $e^{-|n|\kappa_R}$, which localizes the wave function of the surface states at the outermost molecules. Energetically such states are limited to occur within the band gap opened by the excitonic bands of the infinite chain. Compared to the bulk states, surface states are predominantly of CT character. The internal structure is determined by the mixing ratio and the decay length given by the damping factor. The decay length is exclusively determined by the parameter set and is independent of the system size. It can therefore be assigned as a characteristic quantum length which plays a vital role for the understanding of system-dependent behavior of the states. A brief summary of the main features of bulk and surface states are collected in Table 7.1.

The occurrence of surface states is very sensitive to the parameterization, i.e., the relation between on-site energies and intermolecular couplings. We were able to derive general conditions for the occurrence of surface states. Based on these conditions, we constructed phase diagrams with which we can determine for each possible choice of parameters the number and properties of the surface states occurring.

The different nature of bulk and surface states leads to distinct quantum confinement effects. We have to distinguish between two regimes: In case of weak confinement ($\mathcal{L} \ll N$), both kinds of states arrange with the system size according to their nature. Derived from the excitonic states of the infinite chain, the bulk states preserve their quasi-particle character in these large systems. They are extended over the whole chain with their effective size $N_{\text{eff}}$ being in the order of the chain length $N$. Considered as a quasi-particle confined in box, they change their energy with the system size according to the particle-in-a-box picture.

The surface states feature a characteristic quantum length, which determines the effective size of the state. This intrinsic length is defined as decay length $\mathcal{L} = 2/\kappa_R$ of the wave function, which is damped by a factor $e^{-|n|\kappa_R}$. For $\mathcal{L} \ll N$, the effective size is fixed and hence independent of the system size. In this regime, the surface states do not react to a change of the chain length $N$ at all. It is worth noticing that the appearance of surface states itself is a consequence of confinement, because surface states are completely unknown in infinite chains.

If the states are strongly confined, a regime which is entered when $\mathcal{L} \approx N$, they give up their typical behavior and influence each other strongly. As soon as $N$ reaches the intrinsic length, the tails of the surface states overlap each other so that the states effectively extend over the whole chain. With an effective size comparable to the system size, they become sensitive to the actual chain length. Moreover, bulk states close-by in energy are strongly affected. These bulk states transfer Frenkel character to the surface states and thus increase the oscillator strength of the latter.

The purely electronic states provide an excellent starting point to understand excitonic states in finite chains of more general constitution. For typical problems which involve more effects to account for realistic scenarios, an analytical non-perturbative treatment is not possible. However, the basis set provided by the idealized system is an excellent tool to analyze the results from perturbative approximations as well as from purely numerical calculations.
### 7.1 Summary and conclusions

<table>
<thead>
<tr>
<th>bulk states</th>
<th>surface states</th>
</tr>
</thead>
<tbody>
<tr>
<td>• correspond to excitonic states of the infinite chain</td>
<td>• exist exclusively in finite systems</td>
</tr>
<tr>
<td>• either mixed Frenkel-CT states or pure CT states</td>
<td>• predominantly of CT character</td>
</tr>
</tbody>
</table>
| • purely imaginary wave vector $\kappa = i k$ | • complex wave vector $\kappa$  
  $\kappa = \kappa_R$ (non-oscillating state) or  
  $\kappa = \kappa_R + i \pi$ (oscillating state) |

### energetical alignment with respect to the infinite chain

<table>
<thead>
<tr>
<th>bulk states</th>
<th>surface states</th>
</tr>
</thead>
<tbody>
<tr>
<td>• aligned on excitonic bands</td>
<td>• within the band gap</td>
</tr>
</tbody>
</table>

### wave functions

<table>
<thead>
<tr>
<th>bulk states</th>
<th>surface states</th>
</tr>
</thead>
<tbody>
<tr>
<td>• span the whole chain</td>
<td>• feature damping factor $e^{-</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>effective size $N_{\text{eff}}$</th>
<th>weak confinement $\mathcal{L} \ll N$</th>
<th>strong confinement $\mathcal{L} \geq N$</th>
</tr>
</thead>
<tbody>
<tr>
<td>• on the order of the chain length $N$</td>
<td>• dependent on chain length according to particle-in-a-box picture</td>
<td>• states close in energy to surface states do not preserve their Frenkel CT mixing ratio $\eta$</td>
</tr>
<tr>
<td>• determined by the intrinsic quantum length $\mathcal{L} = \frac{1}{\kappa_R}$</td>
<td>• not affected by chain length</td>
<td>• delocalized over the whole chain; mixing ratio altered by Frenkel contribution from close-by bulk states</td>
</tr>
</tbody>
</table>

**Table 7.1:** Summary of the main features of bulk and surface states. For the visualization of the wave functions, the distribution of $u_n$ is shown for the non-oscillating surface state and the bulk state with lowest $k$ in a chain of $N = 41$ molecules with $E_F = E_{\text{CT}} = 0$, $M = \epsilon_h = 0.2$ eV, and $\epsilon_c = 0$ (see Figure 3.6).
The basis set is of great value in several applications: One possible problem is given by the need to adjust the situation at the outermost molecules. The influence of necessary adjustments of parameters can be evaluated in perturbation theory on the basis of the states of the idealized system. In a semi-infinite tight-binding problem, this strategy has been successfully used in reference [74]. In the framework of coupled electronic and vibronic excitations, a transformation from the initial basis, e.g., the LANG-FIRSOV basis, into a basis containing the electronic states of an ideal chain provides a classification of states. The origin of surface states, either from the electronic boundary conditions or from the exciton phonon coupling, as described in reference [93], can be clearly distinguished.

7.2 Outlook

The establishment of a one-to-one correspondence between quantum chemical calculations of whole aggregates and calculations in the framework of small radius excitons is still an open, but very desirable point. Both points of view overlap for chains of PTCDA and MePTCDI which are of the size of their intrinsic quantum length (cf. Figure 2.1 in Chapter 2).

Both approaches can be formulated using the same terminology of molecular and CT excitations. However, in reality, or more precisely, in the reality of commercially available packages featuring semi-empirical methods, the objects introduced in both approaches as localized excited states do not coincide. The standard implementations of semi-empirical methods act within a non-orthogonal basis set and disregard the overlap between the basis elements. The overlap, which nevertheless plays an important role, is introduced indirectly by overlap dependent parameterizations of interactions.

As soon as the quantum chemical calculations have been carried out with orthogonal basis elements, the constructed localized excitations necessary for a further analysis form an orthogonal basis set as well. Then, also the resulting effective Hamiltonian corresponds to a small radius exciton model Hamiltonian. All matrix elements relevant for a discussion in the framework of a simplified model as presented in thesis, namely the Frenkel transfer and charge transfer integrals, can be immediately extracted. A comparison to the effective Hamiltonian reveals the order of magnitude of adjusted on-site energies and interactions which have not been regarded throughout this work. Among them, the next nearest neighbor CT on-site energies, Frenkel transfer integrals, and the site dependent distribution of Frenkel on-site energies are interesting quantities.

After the gap between quantum chemical methods and the small radius exciton treatment has been bridged, each result of a quantitatively accurate description can be immediately analyzed with a formalism suggested by this work to reveal the leading structure-related effects.
Bibliography


[36] see Ref. [35], p. 129.


[65] see Ref. [34], p. 28.


[83] see Ref. [50], p. 56.


K. Akers, R. Aroca, A.M. Hor, R.O. Loutfy, ‘Molecular organization in perylenetetra-

K. Akers, R. Aroca, A.M. Hor, R.O. Loutfy, ‘Molecular organization in perylene

M. Elstner, M. Sternberg, Th. Frauenheim, ‘Resonant Raman spectroscopy of 3,4,9,10

G. Klebe, F. Graser, E. Hädicke, J. Berndt, ‘Crystallochromy as a solid-state effect:
Correlation of molecular conformation, crystal packing and colour in perylene-3,4:9,10-

M.I. Alonso, M. Garriga, N. Karl, J.O. Osso, F. Schreiber, ‘Anisotropic optical prop-
erties of single crystalline PTCDA studied by spectroscopic ellipsometry’, Organic

B.A. Gregg, ‘Evolution of photophysical and photovoltaic properties of perylene
bis(phenethylimide) films upon sovent vapor annealing’, J. Phys. Chem. 100 (1996)
852.

T. Schmitz-Hübsch, T. Fritz, F. Sellam, R. Staub, K. Leo, ‘Epitaxial growth on 3,4:9,10

bined LEED and STM study of PTCDA growth on reconstructed Au(111) and Au(100)

absorption of ultrathin organic molecular films: The thickness dependence of the ab-

M. Möbus, N. Karl, T. Kobayashi, ‘Structure of perylene-tetracarboxylic-dianhydride

T. Ogawa, K. Kuwamoto, S. Isoda, T. Kobayashi, and N. Karl, ‘3,4:9,10-
Perlenetetraoxycarboxylic dianhydride (PTCDA) by electron crystallography’, Acta Cryst.

M. Hasegawa, N. Sato, ‘Correlation of molecular orientations ar the interface of organic

N. Sato, ‘X-ray structure report, MePTCDI crystal data’, (1994), private communica-
tion.

G. Mazur, Stany z przeniesieniem ładunku w organicznych kryształach molekularnych

M. Hoffmann, Z.G. Soos, ‘Optical absorption spectra of the Holstein molecular crystal


List of Abbreviations

We list here an overview of the most important abbreviations and symbols which were used in this work:

\( H \) \hspace{1cm} Hamiltonian; s. Eq. (3.1)
\( \langle \ldots |(\ldots) \rangle \ldots \) \hspace{1cm} antisymmetrized product state, Slater determinant
\( |.. \rightarrow .. \rangle \ldots \) \hspace{1cm} excited singlet state
CI \hspace{1cm} Configuration Interaction
ZINDO \hspace{1cm} Zerner’s Intermediate Neglect of Differential Overlap

\( N \) \hspace{1cm} number of molecules/sites
\( n \) \hspace{1cm} site index
\( \hat{B}, \hat{B}^\dagger \) \hspace{1cm} creation/annihilation operator for molecular excitations; s. Eq. (3.1)
\( \hat{C}, \hat{C}^\dagger \) \hspace{1cm} creation/annihilation operator for charge transfer excitations; s. Eq. (3.1)

\( E_F \) \hspace{1cm} on-site energy of molecular excitation; s. Eq. (3.1)
\( E_F \) \hspace{1cm} on-site energy of charge transfer excitation; s. Eq. (3.1)
\( M \) \hspace{1cm} nearest neighbor Frenkel transfer integral; s. Eq. (3.1)
\( \epsilon_e \) \hspace{1cm} electron transfer integral; s. Eq. (3.1)
\( \epsilon_h \) \hspace{1cm} hole transfer integral; s. Eq. (3.1)

\( p \) \hspace{1cm} transition dipole moment; s. Eq. (3.83)
\( F \) \hspace{1cm} oscillator strength; s. Eq. (3.82)
\( f \) \hspace{1cm} fractional oscillator strength; s. Eq. (3.86)

\( \kappa \) \hspace{1cm} complex wave vector; s. Eq. (3.41)
\( \kappa_R \) \hspace{1cm} real part of complex wave vector; s. Eq. (3.58)
\( k \) \hspace{1cm} quasi-momentum, or wave vector; s. Eq. (3.13)
\( E_j \) \hspace{1cm} energy of an eigenstate with index \( j \)
\( |j\rangle, |\psi_j\rangle \ldots \ldots \) \hspace{1cm} eigenstate with index \( j \); s. Eq. (3.9)
\( |\text{ME}_n\rangle \ldots \ldots \) \hspace{1cm} basis function molecular excitation; s. Eq. (3.6)
\( |\text{CT}_{n,\pm1}\rangle \ldots \ldots \) \hspace{1cm} basis function charge transfer excitation; s. Eq. (3.6)
\( u_n \) \hspace{1cm} coefficient of the molecular excitation
\( v_{n,\pm1} \) \hspace{1cm} coefficient of the charge transfer excitation
\( \Delta_{CT} \) ............. energetical separation from CT on-site energy \( E_{CT} \); s. Eq. (3.44)
\( \tilde{\Delta} \) ............. Frenkel charge transfer separation parameter; s. Eq. (3.44)
\( \alpha \) ............. ratio combined charge transfer coupling to Frenkel transfer integral; s. Eq. (3.45)
\( \beta \) ............. balance parameter; s. Eq. (3.45)

\( Z \) ............. damping factor \( e^{-\kappa R} \); s. Eq. (4.21)
\( N_{\text{eff}} \) ............. participation ratio; s. Eq. (5.33)
\( \langle |n| \rangle \) ............. mean radial position; s. Eq. (5.39)
\( \mathcal{L} \) ............. quantum length; s. Eq. (5.50)

MePTCDI ....... \( N,N' \)-dimethyl-3,4,9,10-perylenetetracarboximide [11, 109]
PTCDA ........... 3,4,9,10-perylenetetracarboxylic dianhydride [15, 14]
\( \epsilon \) ............. dielectric function
\( \alpha(E) \) ........... absorption coefficient
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Versicherung

Hiermit versichere ich, dass ich die vorliegende Arbeit ohne unzulässige Hilfe Dritter und ohne Benutzung anderer als der angegebenen Hilfsmittel angefertigt habe; die aus fremden Quellen direkt oder indirekt übernommenen Gedanken sind als solche kenntlich gemacht. Die Arbeit wurde bisher weder im Inland noch im Ausland in gleicher oder ähnlicher Form einer anderen Prüfungsbehörde vorgelegt.

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(Karin Schmidt)