Chapter 7

Scaling of the energy structure in the Lifshits tail

Summary

Using numerical simulations, we demonstrate that the 4-dimensional joint distribution function of exciton energies and transition dipole moments of the dominant ground-state-to-one-exciton and one-to-two-exciton transitions in disordered Frenkel chains obeys simple scaling behavior with the disorder strength. This combines universal scaling with the concept of the local level structure of localized one dimensional excitons. By demonstrating the scaling behavior of two-dimensional spectra, we show that the universality can be extended to the lowest two-exciton states.

7.1 Introduction

A wide variety of (quasi-)one-dimensional systems exist whose optical properties draw considerable attention. Examples are molecular J-aggregates [1, 2, 3], polysilanes (σ-conjugated polymers) [4, 5], π-conjugated polymers [6], and quantum wires and wells [7, 8, 9, 10, 11]. The primary excitations that determine the optical response of these systems are excitons, collective excitations spread over many lattice units. The interest in these systems derives from the fundamental interest in collective optical response (transitions with giant oscillator strength, narrow lineshapes, anomalous behavior) as well as from their applications in optical devices, such as light-emitting diodes and lasers. Ideally, the symmetry in these systems dictates strong selection rules, implying that a few exciton states, at precise energies, dominate the optical response. In practice, however, both the transition energies and transition dipole moments of the exciton states are spread as a consequence of disorder, either in the transition energies of individual lattice sites (diagonal disorder) or in
the interactions between lattice sites (off-diagonal disorder), imposed by the surrounding matrix, by conformational randomness, or by thickness variations (quantum wires).

These linear systems have been very fruitfully modeled by the Frenkel exciton Hamiltonian. The exact nature of the collective excitations is determined by the environment surrounding the aggregate, which gives rise to scattering of the excitations on static disorder (fluctuations in the excitation energy of the individual monomers) and on dynamic degrees of freedom (vibrations). The temperature dependence of the fluorescence Stokes shift, radiative lifetime, dephasing rate and absorption linewidth of a linear chain are surprisingly well described when the Frenkel excitons are coupled to acoustic phonons in the host medium [12, 13]. The states in the low-energy exciton band edge are mainly responsible for these optical and transport properties.

Multi-exciton states, in which several excitations are coherently shared by a number of monomers, play a crucial role to understand and describe the outcome of nonlinear optical experiments of molecular J-aggregates. Accounting for multi-exciton states theoretically requires the diagonalization of large matrices, and the consideration of a large number of transitions. It is well-known, however, that for homogeneous linear aggregates, three states dominate the third-order response, namely the ground state, the lowest one-exciton state and the lowest two-exciton state. In practice, J-aggregates suffer from appreciable disorder, which leads to localization of the exciton states. It was shown in Ref. [14] that the three-state picture still holds to a good approximation, provided that one replaces the chain length by the typical exciton localization length. This can be explained by the existence of a so-called hidden structure in the Lifshits tail of the density of states (DOS) [15, 16, 18]. In chapter 5 we showed that, indeed, the picture of three dominant states per localization segment seems to hold, by demonstrating that the pump-probe spectrum is well-fitted by the response of only those three states.

In chapter 6 we showed that the low-energy region of the joint probability distribution function \( G(\varepsilon, \mu) \) of the transition energy and transition dipole moment in disordered one-dimensional exciton systems obeys certain scaling relations. Its two-dimensional form is obtained from a universal function by a simple linear transformation that contains powers of the disorder strength.

In this chapter we provide a detailed analysis of the stochastic properties of optically dominant ground-state to one-exciton transitions and one- to two-
7.2 Model

We consider a linear molecular aggregate of \( N \) two-level monomers with parallel transition dipoles, labeled by \( n = 1, 2, \ldots, N \). The excitation energy of monomer \( n \) is denoted by \( \varepsilon_n \). We will assume that \( \varepsilon_n \) are uncorrelated Gaussian random variables with mean \( \varepsilon_0 \) (the excitation energy of an isolated monomer) and standard deviation \( \sigma \). In this chapter, we will restrict ourselves to nearest-neighbour interactions with an excitation transfer interaction integral \(-J\). In this case the Frenkel exciton Hamiltonian is given by

\[
H = \sum_{n=1}^{N} \varepsilon_n b_n^\dagger b_n - J \sum_{n=1}^{N-1} \left( b_n^\dagger b_{n+1} + b_{n+1}^\dagger b_n \right). \tag{7.1}
\]

We will assume that \( J \) is positive (appropriate for a wide variety of exciton systems) and from now on we set \( J = 1 \), i.e., we use it as the energy unit. A small number of states in the Lifshits tail [19], just below the lower band edge at \( \varepsilon_0 - 2J \), contain almost all the oscillator strength, and dominate the optical response. The wavefunctions of these states are located on different, weakly overlapping chain segments with a typical localization length \( N^* \), and consist of (mainly) a single peak (see, for example, Fig. 2.7). By numerically diagonalizing the Hamiltonian Eq. (7.1), we calculate the exciton wavefunctions \( \sum_n \varphi_{\nu n} \) and transition energies \( \varepsilon_\nu \). The dominant optical transitions are selected according to the rule [18]

\[
| \sum_n \varphi_{\nu n} \langle \varphi_{\nu n} | \geq C_0 \tag{7.2}
\]
with $C_0 = 0.95$. This criterion selects wavefunctions that consist of mainly one peak. These states are called $s$ states, and for the remainder of this chapter $S$ will denote the set of $s$ states (see also chapters 2-5). In Fig. 7.1(a) we plotted the total oscillator strength per monomer contained in the optically dominant $s$ states in a chain of length $N$,

$$\frac{\langle \sum_{s \in S} \mu_s^2 \rangle}{N_s}$$

as a function of the disorder strength. From this figure it is seen that the $s$ states collect approximately 57% of the total oscillator strength over a very wide disorder range. Furthermore it is seen that (for infinitely long chains) any amount of disorder causes the oscillator strength to drop below this ratio for the homogeneous chain, in which the lowest state collects 81% of the total oscillator strength. When $s$ states are selected with a lower value of the selection constant $C_0$, the oscillator strength collected in the $s$-states, $\langle \mu_s \rangle$, is increased. This is shown in Fig. 7.1(b), where we plotted Eq. (7.3) for $C_0 = 0.75$. In chapter 5 used this value for $C_0$, and showed that the absorption spectrum due to $s$ states well reproduces the exact absorption spectrum, except a Lorentzian high-energy wing.

To describe the non-linear optical response, it is necessary to consider the transitions to two-exciton states, for which the molecules in the aggregate share two excitations. For one-dimensional systems in the nearest-neighbour approximation the excitations do not interact [17], and the two-exciton states can be expressed by an antisymmetric combination of two one-exciton states $|\nu_1\rangle$ and $|\nu_2\rangle$, where $\nu_1 \neq \nu_2$, and can be labeled by $|\nu_1, \nu_2\rangle$, see chapter 5, sec. 5.2. The Fermi nature of the two-exciton states in the nearest-neighbour approximation is a direct consequence of the restriction that only one excitation can exist on a single molecule.

An important finding is that the low-energy structure of the localization segments is similar to the low-energy structure of an ideal linear chain with a length $N^*$ [15, 16, 18]. The state with the lowest energy on a segment contributes dominantly to the absorption, and the second level of a segment resembles the $\nu = 2$ state of a homogeneous chain of length $N^*$, while the level spacing between the $s$ and $p$ state is comparable to the spacing of the $\nu = 1$ and $\nu = 2$ state of a homogeneous chain of length $N^*$, see chapter 5. We select the strongest one-to-two exciton transition from each $s$ state (selected
as described above). To filter out two-exciton states which consist of two $s$ type states that are localized on different segments, we also require a minimum wavefunction overlap of $\sum_n \varphi_{sn}^2 \varphi_{\nu n}^2 \geq 0.00005$. Furthermore, states that are selected as a $s$ states are not allowed to be $p$ partners in another ($sp_s$) pair. The transition dipole moment of the selected one-to-two exciton transition is denoted by $\mu_{sp_s,s}$, were the subscript $s$ in $p_s$ indicates its relation with the state $|s\rangle$. Well defined ($sp_s$) doublets are localized on the same chain segment, and form the hidden structure in the Lifshits tail of the density of states [16]. In chapter 5 we showed that these selected $s$-to-$sp_s$ transitions reproduce the exact pump-probe spectrum very well.

**Figure 7.1:** (a) - Part of the total oscillator strength due to transitions to $s$ states according to Eq. (7.3) (circles). Part of the total oscillator strength due to transitions to $p$ states according to Eq. (7.4) (squares). The oscillator strength of $p$ states is a signature of the fact that in general the selected $p_s$ states are not perfectly antisymmetric with respect to their center. Here, the $s$ states are selected with $C_0 = 0.95$. (b) - Same, but now for $C_0 = 0.75$.

When the $s$ states are near the bare band edge, it is usually not possible to assign a $p$-like partner localized on the same segment: higher-energy states have more than one node and/or spread over segments with a size which is larger than $N^*$. Furthermore, it is also possible that (weakly overlapping) $s$-like states that fail to meet the selection criterium Eq. (7.2) are selected as a $p$-like partner. Then, the $p$ states of the selected ($sp_s$) doublets can have
significant oscillator strength $\mu_{ps}^2$. In Fig. 7.1 we plotted the dipole moment accumulated in the $p$ states,

$$\frac{\langle \sum_{s \in S} \mu_{ps}^2 \rangle}{N_s}.$$  \hspace{1cm} (7.4)

It is seen that the imperfect $p$ states carry approximately 21% of the total oscillator strength of the system for $C_0$. These states contribute to the blue wing of the absorption spectrum [18, 20]. Together, the one-exciton transitions to the $s$ and $p$ states almost completely determine the low-energy part of the linear absorption spectrum, see Fig. 7.2. When $s$ states are selected with a lower value of the selection constant $C_0$, the average Eq. (7.4) becomes smaller because less states with a high oscillator strength are available as a partner, see Fig. 7.1(b).

*Figure 7.2:* The exact absorption spectrum (solid line), the absorption spectrum calculated with $s$ states (circles), the absorption spectrum calculated with $p_s$ states (dot-dashed line), and the sum of the absorption of both the $s$ states and the $p_s$ states (dashed line). Here, the $s$ states are selected with $C_0 = 0.95$. 
7.3 Scaling of the energy structure in the Lifshits tail

The object of study in this chapter is the generalized joint probability distribution

\[ G_{sp}^{s}(\epsilon, \mu, \epsilon', \mu') = \frac{1}{N_s} \left\langle \sum_{s \in S} \delta(\epsilon - \epsilon_s) \delta(\mu - \mu_s) \delta(\epsilon' - \epsilon_{ps}) \delta(\mu' - \mu_{sp,s}) \right\rangle, \tag{7.5} \]

where the sum over \( s \) is performed over \( S \), the optically dominant one-exciton transitions of the system, \( \epsilon_s \) and \( \mu_s \) correspond to their energies and transition dipoles to the ground state, respectively. Furthermore, \( \mu_{sp,s} \) corresponds to the strongest one-to-two-exciton transition from the one-exciton state \( s \); \( \epsilon_{ps} \) corresponds to the \( s \)-to-\( sp \) transition energy \( \epsilon_{ps,s} - \epsilon_s \), and \( N_s \equiv \langle \sum_s 1 \rangle \) is a normalization constant (corresponding to the average number of localization segments in an aggregate). The angular brackets indicate the average over disorder realizations. The function \( G_{sp}^{s} \) represents the joint probability distribution of the transition energies and transition dipole moments of the \((sp)\) doublets. All the information about the stochastic variables \( \epsilon_s, \epsilon_{ps}, \mu_s, \) and \( \mu_{sp,s} \) is contained in the distribution function \( G_{sp}^{s} \). This distribution takes into account the level statistics of the \((sp)\) doublets which form the hidden level structure.

We will demonstrate that the distribution \( G_{sp}^{s} \) derives from one universal underlying function through simple scaling relations: independent of the strength of the disorder its four-dimensional form may be obtained from one universal function by simply scaling the energy and dipole axes using linear transformations that contain powers of the disorder strength,

\[ \tilde{\epsilon} = \frac{\epsilon + 2}{\sigma^{1.33}}, \tag{7.6a} \]

\[ \tilde{\mu} = \frac{\mu}{2.2\sigma^{-0.33}}. \tag{7.6b} \]

The energies \( \epsilon_s \) and \( \epsilon_{ps} \) scale with the transformation Eq. (7.6a). The constant 2 corresponds to the position of the bare exciton band edge at the energy \(-2J\), whereas the factor \( \sigma^{1.33} \) reflects the disorder induced broadening of the
exciton band along the $\varepsilon$ direction. The transition dipole moments $\mu_s$ and $\mu_{ps}$ scale with $\sigma$ according to the transformation Eq. (7.6b), which describes the decrease of the transition dipole moments with increasing disorder strength $\propto \sigma^{-0.33}$. These relations are consistent with the fact that increasing the disorder strength leads to an increase of the fluctuations in the transition energies, and a decrease of the localization size ($N_{loc}$), i.e., a decrease of the average oscillator strength per state [21]. The transformation Eq. (7.6) can be compared to the transformation Eq. (6.6) of chapter 6. The differences lies in the absence of terms which shift the energies with increasing disorder values. We drop this term because it obscures the relations between the different variables of Eq. (7.5).

For a given disorder strength $G_{sp}$ may be calculated by straightforward sampling of a sufficient number of disorder realizations. To obtain a smooth distribution, a large number of realizations are required. To obtain our results more efficiently, we calculated the eigensystem of the Hamiltonian Eq. (7.1), and tabulated $(\varepsilon_s, \mu_s, \varepsilon_{ps}, \mu_{sp_s})$ for 200 000 localization segments. We then verified whether all six possible projections of $G_{sp}$ on the parameter planes $(\varepsilon_s, \mu_s), (\varepsilon_s, \varepsilon_{ps}),$ etc., scale with Eqs. (7.6). In the subsequent sections, we will consider several of these projections, and discuss their relevance.

### 7.3.1 Dominant one-exciton transitions

First, we will consider the joint probability distribution of the one-exciton transition energy $\varepsilon_s$ and the transition dipole moment $\mu_s$ of the optically dominant $s$ states of aggregate segments, $G_s(\varepsilon, \mu)$. The latter is defined as

$$G_s(\varepsilon, \mu) = \frac{1}{N_s} \left\langle \sum_{s \in S} \delta(\varepsilon - \varepsilon_s) \delta(\mu - \mu_s) \right\rangle,$$

and can be obtained by integrating $G_{sp}$ over the energy and transition dipole moment of the $p$ states, $\varepsilon_{ps}$ and $\mu_{sp_s}$. Because the states which form $G_s$ dominate the linear optical response, many spectroscopic observables can be expressed using this distribution. Furthermore, the zero-temperature absorption band is determined for a large part by

$$A_s(\varepsilon) = \int d\mu G_s(\varepsilon, \mu) \mu^2.$$
The width of $A_s(\varepsilon)$, $\sigma^*$, is determined by the fluctuations of the transition energies of the superradiant states. The scaling of the width is related to the $\varepsilon$ scaling of $G_s(\varepsilon, \mu)$, i.e., $\sigma^* \propto \sigma^{1.33}$. This agrees well with the value that was obtained for the width of the absorption band in previous work [22].

Figure 7.3, left column, shows $G_s(\varepsilon, \mu)$ for three values of $\sigma$. At first sight, the three distributions look very different. With increasing value of $\sigma$, the distribution shifts down and broadens along the $\varepsilon$ direction and also shifts towards lower dipole moment. The right column in Fig. 7.3 shows the same distributions, after applying the scale transformations Eq. (7.6). It is clear that after these transformations the distributions indeed are (almost) the same, and demonstrate that the transformations properly scale, respectively, the $\varepsilon_s$ and $\mu_s$ parameters of the distribution $G_{sp_s}$.

**Figure 7.3:** Left column: Gray-scale representation of the joint probability distribution $G_s(\varepsilon, \mu)$, calculated for nearest-neighbour interactions and diagonal disorder, using three different disorder strengths $\sigma$ given in the panels. Right column: Contour plots of the same distributions, except that the transformations (7.6) with the constants given in the text have been applied to rescale both axes. After rescaling, the distribution lies close to the point $(0,1)$. Contours are given in steps of 10% of the peak value of the distribution.
When comparing these distributions with the joint distribution function of the energies and the dipole moments of all one-exciton transitions, \( G \) (see chapter 6), it is seen that \( G_s \) forms the low-energy “head” of \( G \). Furthermore, note that the used scaling parameters are identical.

7.3.2 Dominant one-to-two-exciton transitions

Next, we consider the scaling of the \( s \)-to-\( sp_s \) transition energies \( \varepsilon_{ps} \) and the corresponding transition dipole moment \( \mu_{sp,s} \), i.e., the dominant two-exciton transitions. Their joint probability distribution is defined as

\[
G_{ps}(\varepsilon, \mu) = \frac{1}{N_s} \left\langle \sum_{s \in S} \delta(\varepsilon - \varepsilon_{ps}) \delta(\mu - \mu_{sp,s}) \right\rangle ,
\]

and can be obtained by integrating \( G_{sp,s} \) over the energy and transition dipole moment of the \( s \) states.

Figure 7.4, left column, shows the distribution \( G_{ps}(\varepsilon, \mu) \) for three values of \( \sigma \). Similar to the scaling of \( G_s \) the distribution shifts down and broadens along the \( \varepsilon \) direction and also shifts towards lower dipole moment. The right column in Fig. 7.4 shows the same distributions, after applying the scale transformations Eq. (7.6). It is clear that after these transformations the distributions, indeed, appear very similar. From this we conclude that the scaling transformations Eq. (7.6) can also be applied to the transitions between the one-exciton manifold and the two-exciton manifold. Furthermore, this demonstrates that \( G_{sp,s} \) also properly scales with respect to \( \varepsilon_{ps} \) and \( \mu_{sp,s} \).

7.3.3 Level repulsion

We now focus on the level repulsion between the \( s \) and the \( p \) states. The correlation between the energy of the \( s \) state and the corresponding \( p \) state is revealed by considering the distribution

\[
\mathcal{E}(\varepsilon, \varepsilon') = \frac{1}{N_s} \left\langle \sum_{s \in S} \delta(\varepsilon - \varepsilon_s) \delta(\varepsilon' - \varepsilon_{ps}) \right\rangle .
\]

This distribution can be derived from \( G_{sp,s} \) by integrating over the transition dipole moments. The left column of Fig. 7.5 shows the numerically generated
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Figure 7.4: Same as in Fig. 7.3, calculated for $G_{ps}(\varepsilon, \mu)$, i.e., the distribution of the energy and transition dipole moment of the dominant one-to-two exciton transition from the $s$ states.

distribution $E(\varepsilon, \varepsilon')$ for three values of $\sigma$. The major part of the distribution lies above the diagonal, which reflects the quantum mechanical level repulsion of the states of the $(sp_s)$ doublets, which are localized on the same segment [16, 18]. The right column in Fig. 7.5 shows the same distributions, after applying the scale transformation Eq. (7.6a). Again, the transformed distribution result in a universal function $\tilde{E}(\tilde{\varepsilon}, \tilde{\varepsilon}')$ for arbitrary strength of the diagonal disorder. This demonstrates that the $G_{sp_s}$ also properly scales with respect to $\varepsilon_s$ and $\varepsilon_{ps}$.
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Figure 7.5: Same as in Fig. 7.3, calculated for $\mathcal{E}(\varepsilon, \varepsilon')$, showing the correlations between the transition energy of $s$ states and their corresponding $p$ states. The distribution in the upper left panel is barely visible on this scale.

7.4 Two-dimensional spectroscopy

In this section, we consider the two-dimensional spectrum which results from the transitions between the states in individual $(sp_s)$ doublets, and compare the obtained spectra with the exact spectrum. Two-dimensional spectroscopy is a recently developed third-order optical technique [23, 24] which is related to the pump-probe spectrum which we discussed in chapter 5. The two-dimensional spectrum consists of an $x(y)$-axis which can be interpreted as the energy of the pump (probe) beam [25]. It accumulates the response of the system which is pumped with one frequency, and probed with another frequency. This spectrally resolved pump-probe spectrum allows for a more detailed study of the transitions involved in the nonlinear optical response as compared to the ordinary short-pulse pump probe spectrum, which can be obtained from the two-dimensional spectrum by integrating the two-dimensional spectrum over the pump frequencies. A detailed treatment of this technique is beyond the scope of this chapter, for details see Refs. [23, 24, 25] and references therein.
In this section we present the rephasing (or photon-echo) spectrum at zero temperature, neglecting homogeneous line broadening, assuming that there is zero time delay between the pump and the probe pulses. The goal of this section is two-fold. First, we want to study if the scaling relations Eq. (7.6) can be extended to the exact two-dimensional absorption spectrum. Second, we want to examine how well the transitions within the $(sp_s)$ doublets reproduce the exact spectrum.

![Figure 7.6](image-url): Top row: Two-dimensional spectra calculated using the selected $(sp_s)$ doublets, for three different disorder strengths $\sigma$ indicated above the panels. Here, the $x$-axis corresponds to the pump frequencies, and the $y$-axis to the probe frequencies. The transformation Eq. (7.6a) has been applied to rescale both axes. The peak above the diagonal is positive and represents induced absorption. The peak below the diagonal and the diagonal itself corresponds to bleaching and stimulated emission processes. Contours were drawn at $\pm 25\%$, $\pm 20\%$, $\pm 15\%$, $\pm 10\%$, and a $\pm 5\%$ of the maximum of the induced absorption peak. Bottom row: Same as the top-panels, but now for the exact two-dimensional correlation spectra.

Figure 7.6, top row, shows the two-dimensional spectrum resulting from
the transitions within the \((sp_s)\) doublets for three values of \(\sigma\). Here the energy axes have been scaled with Eq. (7.6a). It is seen that the transformation results in spectra that appear (almost) the same. The narrow diagonal peak for equal pump and probe frequencies represents the negative bleaching and stimulated emission processes of the one-exciton transitions to the \(s\) and \(p_s\) states. The positive peak above the diagonal represents positive contributions of the blue-shifted induced absorption from the \(s\)-to-\(sp_s\) transitions, as well as negative contributions involving the \(|s\rangle\langle p_s|\) and \(|p_s\rangle\langle s|\) coherences as the system’s state created by the pump pulse. The low energy part of the positive peak in the spectrum is for a large part the result of \(s\)-to-\(sp_s\) transitions.

The weak negative peak below the diagonal involves positive contributions of the red-shifted induced absorption from the \(p\)-to-\(sp_s\) transitions, as well as negative coherent contributions. For the homogeneous chain the one-exciton states can be found analytically [17], reading

\[
|\nu\rangle = \sum_n \sqrt{\frac{2}{N+1}} \sin \frac{\pi \nu n}{N+1} b_n^\dagger |g\rangle
\]

with energies

\[
\varepsilon_\nu = \varepsilon_0 - 2J \cos \frac{\pi \nu}{N+1},
\]

and the \(p\) state corresponds to the \(\nu = 2\) state. In this case, the transition from the ground state to the state \(|2\rangle\), and the \(|2\rangle\)-to-\(|1,2\rangle\) transition does not have a dipole moment. Therefore, this peak is absent for the homogeneous chain. For disordered aggregates, the transitions to \(p_s\) states, and the \(p\)-to-\(sp_s\) can have a transition dipole moment. These transitions are typically much weaker compared to the ground-state-to-\(s\) states or the \(s\)-to-\(sp_s\) transitions, which explains the weakness of the signal. Figure. 7.7 schematically depicts the level structure of an \((sp_s)\) doublet, and the positions and magnitude of contributions of the transitions involving these states.

The contribution of the \(s\)-to-\(sp_s\) transitions to the induced absorption peak in the two-dimensional spectrum is described by the distribution

\[
\mathcal{I}_{sp_s}^{2D}(\varepsilon, \varepsilon') = \int d\mu d\mu' G_{sp_s}(\varepsilon, \mu, \varepsilon', \mu') \mu^2 \mu'^2
\]

Because the pump-probe spectra presented in chapter 5 are reasonably well
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Figure 7.7: (a) - Schematic level diagram of the transitions involved in an \((sp_s)\) doublet. In this figure the subscript \(s\) on the index \(p_s\) has been omitted for clarity. (b) - The positions and contributions of these transitions to the two-dimensional spectrum. Here, the radii of the circles schematically represent the magnitude of the response. Furthermore, open circles correspond to a positive contribution, and closed circles correspond to a negative contribution.

described by only the \(s\)-to-\(sp_s\) transitions, one might also expect that the main features of the two-dimensional spectrum are well-described by the spectra resulting from the \((sp_s)\) doublets, in particular the low-energy induced absorption part. This comparison is useful to explain the observed two-dimensional spectra.

Figure 7.6, lower row, shows the complete two-dimensional spectra, where the energy axes have been scaled with Eq. (7.6a). It is clearly seen that these spectra are almost identical after rescaling, demonstrating that not only the transitions within the \((sp_s)\) segments, but all involved two-exciton transitions can be scaled with Eq. (7.6a). Although the induced absorption above the diagonal appears similar to the approximated spectra, this peak is more intense for the exact spectrum. To correctly retrieve the peak intensity, it is necessary to take into account other one-to-two-exciton transitions. When the induced absorption contribution from \(s\)-to-\(ss'\) transitions is added to the spectra involving only the transitions within the \((sp_s)\) doublets, i.e. transitions from \(s\)
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states to other (weakly overlapping) $s$ states $s'$, we obtain an almost complete agreement for the low-energy part of the induced absorption. The negative feature below the diagonal is much more pronounced as compared to the spectra of the $(sp_s)$ states. The nature of this peak is more subtle; to retrieve the spectral shape contributions of all two-exciton transitions in the bottom of the exciton band need to be taken into account.

7.5 Conclusion

In this chapter, we have considered the dominant ground-state-to-one-exciton and one-to-two-exciton transitions in disordered linear Frenkel chains. The dominant one-exciton transitions - $s$ states - are found in the low-energy part of the joined distribution function of transition energy and dipole moment of the exciton states, $G(\epsilon, \mu)$ introduced in chapter 6. An $s$ state forms a local level structure with a $p_s$ states that is localized on the same segment. We examined the joint probability distribution $G_{sp_s}(\epsilon, \mu, \epsilon', \mu')$ of the transition energies and the transition dipole moments of the $(sp_s)$ doublets. We have demonstrated that for one-dimensional exciton systems with diagonal Gaussian disorder, this distribution derives from one universal underlying function through simple scaling relations. The scaling relations are equal to the scaling of the low-energy region of the complete exciton band, see chapter 6, which shows that, surprisingly, the scaling properties of one-exciton transitions also applies to the local level structure and two-exciton transitions. Although the transitions involving only the selected $(sp_s)$ pairs play an important role in the third-order optical response, they are not sufficient to reproduce the exact two-dimensional spectrum. The scaling of the exact two-dimensional spectrum unambiguously demonstrates the generality of the scaling-laws.

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