Chapter 3

Signature of anomalous exciton localization in the optical response of tubular J-aggregates

We demonstrate that the disorder scaling of the low-temperature optical absorption linewidth of tubular J-aggregates sharply contrasts with that known for one-dimensional J-aggregates. The difference can be explained by an anomalous localization of excitons originating from both the long-range intermolecular interactions and the quasi two-dimensional geometry of the tubes. This regime approaches the weak localization limit of the standard Anderson model. Moreover, we demonstrate that the optical properties of excitons in tubular aggregates with dipole-dipole interactions show striking similarities to one-dimensional toy models with inter-site interactions falling off with distance $r$ as $r^{-\xi}$, with $3/2 \leq \xi \leq 2$. Our results provide a simple explanation for the origin of the strong linear dichroism and weak exciton-exciton scattering in tubular J-aggregates observed in experiments.¹

¹This chapter is based on E. A. Bloemsma, S. M. Vlaming, V. A. Malyshev, and J. Knoester, in preparation.
3.1 Introduction

Self-assembled low-dimensional nanostructures of organic molecules are known to have special optical and energy transport properties, among which are enhanced spontaneous emission [20, 21], strong nonlinear susceptibilities [14–16, 18], and highly efficient energy transfer [11, 66, 133], rendering them ideal for possible use in future optoelectronic devices. Double-walled nanotubular J-aggregates formed by the synthetic amphiphilic cyanine dye CSS3 [65] are currently of particular interest: their highly uniform supramolecular structure closely resembles the natural light-harvesting antennae (chlorosomes) in green sulphur bacteria [27, 48, 68, 70, 105–107]. The strong interactions between the molecular transition dipoles result in collective (extended) optical excitations in the nanotubes, known as Frenkel excitons. Their localization (coherence) length depends on the scattering on static (and dynamic) disorder imposed by the host medium. The complex interplay between intermolecular resonance transfer interactions, static disorder, and dynamic degrees of freedom determines the fascinating optical and transport properties of the nanotubes.

In the absence of disorder, the absorption and linear dichroism spectra of tubular J-aggregates exhibit two red shifted absorption bands resulting from three allowed superradiant transitions: one polarized along the cylinder axis and one deriving from two degenerate states polarized perpendicular to this axis [62, 97, 116]. In general, disorder-induced exciton scattering results in states that have a wider range of polarization directions [134]. Remarkably, measurements of polarization dependent absorption spectra of CSS3 tubular J-aggregates reveal that, even at ambient temperatures, the optical response is still governed by transitions with preferred parallel and perpendicular orientation, despite a significant degree of disorder [69, 71]. These findings indicate that exciton localization in cylindrical aggregates is strongly suppressed. This is also consistent with recent experimental data on weak exciton-exciton scattering in molecular nanotubes, revealed by double-quantum two-dimensional electronic spectroscopy [135].

In this chapter, we study the localization properties of excitons in molecular nanotubes and how these are reflected in the linear optical response. To achieve this, we calculate the disorder scaling of the low-temperature absorption linewidth. This relation is sensitive to the particular form of the density of states (DOS) in the optically relevant region, which plays a major role in the localization properties of the excitons. In particular, we demonstrate here that the disorder scaling of the low-temperature absorption linewidth (FWHM) of CSS3 tubular J-aggregates differs substantially from what is known to date for one-dimensional (1D) molecular J-aggregates. The physical origin of this can be traced back to the long-range intermolecular interactions and quasi two-dimensional structure of the tubes, giving rise to an unusual exciton energy dispersion relation and DOS. More specifically, in the
absence of disorder, the DOS of the nanotubes vanishes near the lower exciton band edge (where the optically dominating states reside), in contrast to the divergent behavior of the DOS for 1D J-aggregates in this region [23,33,34]. The latter results in strongly localized excitons, while the nanotubes’ vanishing DOS gives rise to severely weaker scattering of the excitons. Interestingly, this regime turns out to be close to the weak localization limit in the standard Anderson model [118,136,137].

To further quantify the apparent relation between the disorder scaling of optical quantities, like the absorption linewidth etc., and the energy dependence of the DOS, we exploit in the last part of this chapter an artificial 1D exciton model, where the long-range inter-site interactions decay with inter-site distance $r$ according to the power law $r^{-\xi}$, where $3/2 \leq \xi \leq 2$. We demonstrate that the disorder-induced scaling laws can be derived directly from the explicit form of the disorder-free DOS in the optically relevant region. Moreover, when the 1D toy model DOS matches that of the tubular J-aggregates, we find that the absorption line shapes in both exciton models show a high degree of similarity.

This chapter is organized as follows. In Sec. 3.2 we present the theoretical model for the nanotubes and numerically obtain the disorder scaling of the absorption linewidth. In Sec. 3.3 we discuss the physical origin of this disorder scaling and apply the coherent potential approximation to explain the numerically found scaling exponent. In Sec. 3.4, using the toy model, we establish the general relation between the DOS in the optically relevant region and the disorder scaling of the linewidth, while we provide conclusions in Sec. 3.5.

3.2 Model and results

Our model of the tubular aggregate consists of a 2D sheet of molecules wrapped around a cylindrical surface. It can be shown that such an aggregate may be considered as a stack of $N_1$ equidistant rings of radius $R$, each ring containing $N_2$ uniformly distributed molecules with adjacent rings rotated relatively to each other by a helical angle $\gamma$ (i.e., see Fig. 2.2.1) [97]. Furthermore, the molecular transition dipoles follow the cylindrical symmetry and are specified by angles $\alpha$ and $\beta$ (Fig. 2.2.1); here $\alpha$ denotes the angle between the projection of the dipole vector on the ring plane and the local tangent of the ring, whereas $\beta$ gives the angle between the dipole vector and the cylinder axis [97]. Each molecule is identified by its position vector $\mathbf{n} = (n_1, n_2)$, with $n_1$ indicating the ring on which it resides and $n_2$ labeling the position in the ring.

The optical excitations of the tubular aggregate are described by a Frenkel exciton model that accounts for molecular excitation energies $E_n$ with Gaussian disorder (mean $\omega_0$ and standard deviation $\sigma$) and non-fluctuating intermolecular transfer interactions $J_{nm}$ determined by extended transition dipoles [138]. The
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Figure 3.2.1: Isotropic absorption spectrum of tubular J-aggregates for disorder strength $\sigma = 600 \text{ cm}^{-1}$ and model parameters taken from Ref. [71]: a radius of $R = 5.455 \text{ nm}$, a single-molecule transition dipole of $\mu = 11.4 \text{ Debye}$, a charge separation distance of $L = 0.7 \text{ nm}$, dipole angles $\alpha = 0^\circ$, $\beta = 47.4^\circ$ and a helicity angle of $\gamma = 6.74^\circ$.

corresponding Hamiltonian reads

$$H = \sum_n E_n |n\rangle \langle n| + \sum'_{n,m} J_{nm} |n\rangle \langle m|,$$

(3.2.1)

where $|n\rangle$ denotes the state in which molecule $n$ is excited while all others are in the ground state. The prime on the summation indicates the exclusion of terms with $n = m$.

To establish the disorder scaling of the optical linewidth, we performed numerical simulations of the absorption spectrum for tubular aggregates with diagonal (energy) disorder. The zero-temperature linear absorption spectrum is given by $A(E) = \langle \sum_q O_q \delta (E - E_q) \rangle$, where $O_q$ is the oscillator strength of the exciton state $q$, averaged over all possible orientations of the cylinder, $E_q$ gives the energy of state $q$ and the brackets $\langle \ldots \rangle$ denote the average over all random energies of the molecules (see Ref. [97] for details). The spectra are obtained by numerical diagonalization of Eq. (3.2.1) for $10^3$ disorder realizations and using the procedure outlined in Ref. [140] to minimize fluctuations in the spectra. In all calculations, we simulated cylinders of $N = 6000$ molecules to avoid finite size effects and, for explicitness, considered the set of parameters that was used in Ref. [71] to fit the
3.2 Model and results

Figure 3.2.2: Numerically obtained linewidths (FWHM) $W_{\|}$ (symbols) of the energetically lowest absorption band of the tubular aggregate for various disorder strengths $\sigma$ together with the best power law fit $W_{\|}(\sigma) \propto \sigma^{2.83}$ (straight line). The tubular aggregate parameters are identical to those used in Fig. 3.2.1, and are summarized in Table 3.2.1 as Structure I.

measured absorption spectrum of the inner wall of CSS3 aggregates. That is, we take a radius of $R = 5.455$ nm, a single-molecule transition dipole of $\mu = 11.4$ Debye, a charge separation distance of $L = 0.7$ nm, dipole angles $\alpha = 0^\circ$, $\beta = 47.4^\circ$ and a helicity angle of $\gamma = 6.74^\circ$. This parameter set is summarized in Table 3.2.1 as Structure I.

In Fig. 3.2.1, we present the simulated absorption spectrum for disorder magnitude $\sigma = 600$ cm$^{-1}$. The spectrum reveals the signatures characteristic for tubular J-aggregates; that is, there are two narrowed superradiant exciton transitions red shifted compared to the monomer spectrum (we take $\omega_0 = 0$). Here, the lowest energy J-band ($E_{\|} = -2450$ cm$^{-1}$) stems from transitions polarized mainly along the tube axis and lies at the lower exciton band edge, while the other band ($E_{\perp} = -2000$ cm$^{-1}$) is mainly polarized perpendicular to this axis and is located above the band edge.

To calculate the width (FWHM) of the energetically lowest absorption line, we first decompose the spectrum into the sum of two Lorentzian lineshapes to filter the contribution of the high energy absorption band to the width of the low energy absorption peak. The width of the energetically lowest absorption band is then taken as the FWHM of the corresponding Lorentzian. The results
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Figure 3.2.3: Numerically obtained linewidth scalings (best power law fit [straight lines] of the data points [symbols]) of the energetically lowest absorption band for four distinct sets of parameters for the tubular aggregate geometry (see main text for details), summarized in Table 3.2.1: (a) the dipole orientation $\beta$ (Structure II), (b) the cylinder radius $R$ (Structure III), (c) the helicity angle $\gamma$ (Structure IV), and (d) the commensurability $N_2$ (Structure V).

for different disorder values in the interval of $\sigma = 425 - 700$ cm$^{-1}$, shown as symbols, together with the best power law fit $W_\parallel(\sigma) \propto \sigma^B$ (straight line) of the data points, are displayed in Fig. 3.2.2. We point out that the disorder interval is bound from below due to finite size effects and from above because of overlap between the two absorption bands. The observed trend that $W_\parallel(\sigma)$ increases for larger $\sigma$ stems from the fact that the number of dye molecules that coherently share an excitation decreases if $\sigma$ increases. The resulting power law exponent $B = 2.83$ implies that the rate at which the line broadens differs drastically from that of 1D molecular J-aggregates, where (assuming nearest-neighbor interactions) $W_{1D} \propto \sigma^{4/3}$ [33, 34, 132].

To corroborate further on the obtained power law exponent, we calculated the disorder scaling of the linewidth for several other molecular arrangements, in ad-
3.3 Discussion

3.3.1 Physical origin: self-consistent approach

In general, the disorder scaling of optical quantities, like the linewidth, is closely related to the localization of excitons. The latter may be estimated by comparing the size scaling of energy spacings $\delta E$ (i.e., the DOS) of exciton states in the bare ($\sigma = 0$) exciton spectrum with the size scaling of the disorder-induced scattering rate $\sigma_{\text{eff}} = \sigma/N^{1/2}$ between them. Here the scattering rate reflects the effect of exchange narrowing: due to their delocalized nature, exciton states feel an effective disorder $\sigma_{\text{eff}}$ which is smaller than the bare disorder value $\sigma$ [23]. If $\sigma_{\text{eff}} \ll \delta E$, the exciton states will be mixed weakly and, therefore, remain delocalized over the entire system. In this case, the absorption linewidth scales linearly with $\sigma$. On the

<table>
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<th>Model</th>
<th>$R$ (nm)</th>
<th>$N_2$</th>
<th>$\beta$ (degrees)</th>
<th>$\gamma$ (degrees)</th>
<th>scaling exponent $B$</th>
</tr>
</thead>
<tbody>
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<td>2</td>
<td>47.4</td>
<td>6.74</td>
<td>2.83</td>
</tr>
<tr>
<td>II</td>
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<td>2</td>
<td>$-1.1$</td>
<td>16.7</td>
<td>3.29</td>
</tr>
<tr>
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<td>2</td>
<td>45.3</td>
<td>10.1</td>
<td>3.15</td>
</tr>
<tr>
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<td>5.410</td>
<td>2</td>
<td>43.1</td>
<td>93.4</td>
<td>2.83</td>
</tr>
<tr>
<td>V</td>
<td>5.428</td>
<td>53</td>
<td>51.6</td>
<td>3.0</td>
<td>2.84</td>
</tr>
</tbody>
</table>

Table 3.2.1: Summary of the sets of model parameters used for the various tubular aggregate structures discussed in this chapter. The parameters that were changed drastically in each model are printed in bold.
other hand, if $\sigma_{\text{eff}} \gg \delta E$, disorder-induced scattering between the states will result in their localization with typical size given by $N_{\text{coh}}$. The latter may be interpreted as the effective number of coherently bound molecules.

In order to estimate $N_{\text{coh}}$, we use the concept of a hidden structure in the Lifshits tail [128, 132], the existence of which has been confirmed explicitly for 1D localized Frenkel excitons by numerical simulations [128, 131, 141]. It consists of several, almost non-overlapping, segments of typical size $N_{\text{coh}} \ll N$, each segment containing two (or more) localized states that resemble low energy homogeneous Bloch states undergoing level repulsion with an effective energy separation $\delta E^*$. The latter can be estimated from the bare level spacings by replacing $N$ with the typical localization size $N_{\text{coh}}$. Similar, the effective mixing between states on the same segment is given by $\sigma_{\text{eff}}^* = \sigma/\sqrt{N_{\text{coh}}}$. For a disorder strength $\sigma$, $N_{\text{coh}}$ is determined from a competition between $\delta E^*$ and $\sigma_{\text{eff}}^*$. If $\sigma_{\text{eff}}^* > \delta E^*$, the scattering between the states tends to further reduce $N_{\text{coh}}$, thereby effectively increasing $\delta E^*$ at a higher rate than $\sigma_{\text{eff}}^*$. When $\sigma_{\text{eff}}^* < \delta E^*$, disorder is of perturbative nature and results in the increase of $N_{\text{coh}}$, where now $\sigma_{\text{eff}}^*$ increases faster than $\delta E^*$. Estimation of $N_{\text{coh}}$ thus follows in a natural way from the equality $\delta E^* = \sigma_{\text{eff}}^*$ [128, 132]. The absorption linewidth, being determined by the typical energy spacing in the Lifshits tail set by $N_{\text{coh}}$, is then given by $W = \sigma/\sqrt{N_{\text{coh}}}$. In the standard 1D Anderson model (assuming nearest-neighbor interactions only) the bare level spacings near the band edge diminish with increasing system size as $\delta E \approx 4\pi^2N^{-2}$, i.e., the DOS diverges as $D(E) \propto |E - E_0|^{-1/2}$. Thus, in the thermodynamic limit ($N \to \infty$) the equality $\sigma_{\text{eff}} \gg \delta E$ always holds, resulting in strongly localized exciton states. From the above explained self-consistency arguments, we find the well-known relations for the coherence number $N_{\text{coh}}^{1\text{D}} \approx (4\pi^2)^{2/3}\sigma/|J|^{-2/3}$ and the disorder scaling of the linewidth $W_{1\text{D}} \approx (4\pi^2)^{-1/3}\sigma/|J|^{4/3}$ [132]. In two dimensions, the Anderson model with nearest-neighbor coupling leads to a level spacing in the optically relevant region that decreases linearly with system size, i.e., $\delta E \approx 4\pi^2N^{-1}$, resulting in a constant DOS near the exciton band edge. Because the exciton separation in the 2D case diminishes with increasing $N$ at a lower rate than for the 1D model, excitons in two dimensions are more extended than those in one dimension, for the same disorder strength. This is directly reflected in the coherence number $N_{\text{coh}}^{2\text{D}} \approx (4\pi^2)^{2}(\sigma/|J|)^{-2}$. Consequently, we find the following disorder scaling of the linewidth $W_{2\text{D}} \approx (4\pi^2)^{-1}(\sigma/|J|)^{2}$. Comparison of the linewidths in one and two dimensions shows two important features. First, for the same disorder strength the linewidth is typically smaller in two dimensions, which results from the weaker localization of the excitons. Second, the disorder scaling exponent of the linewidth in 2D is larger, which indicates that
here the line broadening is more sensitive to variations of the disorder strength $\sigma$. We point out that this dimensionality dependence of the optical response is not confined to the cases discussed above. In fact, a 3D model with nearest-neighbor coupling reveals a cubic disorder scaling of the linewidth and even weaker localization of the excitons compared to two dimensions [33,142].

We now address the effects of the long-range dipole-dipole interaction (LRI) on the absorption linewidth. In 1D, accounting for these interactions beyond the nearest neighbor, this leads to a slight decrease of the linewidth (for fixed disorder strength) and, moreover, results in a minor increase of the disorder scaling exponent [34,128,131,143]. These effects, although present, do not significantly change the optical response in 1D. For the standard 2D Anderson model with dipolar LRI, the energy spacing in the optically relevant region scales as $\delta E \propto N^{-1/2}$ (consequently, the DOS vanishes linearly with energies approaching the band edge) [144].

In this case, $\sigma_{\text{eff}}$ and $\delta E$ scale similarly with system size $N$, indicating a special regime of localization. This situation is known as the marginal regime or the weak Anderson localization limit [118, 136, 137]. The self-consistency arguments predict that in this case the scaling exponent of the linewidth approaches infinity [145]. These arguments, although no longer sufficient to determine the explicit value of the scaling exponent in this regime, do reveal that, unlike the 1D case, the presence of dipolar LRI in two dimensions has more pronounced effects on the optical linewidth and disorder scaling. In particular, the existence of weakly localized excitons yields typically very narrow absorption lines which are highly sensitive to changes in the disorder.

The self-consistent approach presented here qualitatively explains the numerically found large linewidth scaling exponent of tubular aggregates (i.e., see Sec. 3.2). That is, its origin can be traced back to the quasi two-dimensional structure of the tubes and the presence of long-range intermolecular interactions. In the following Section, we will adapt a more formal approach, known as the coherent potential approximation. This semi-analytical approach yields a direct relation between the value of the disorder scaling exponents of the absorption linewidths and the explicit form (i.e., energy dependence) of the DOS in the optically relevant energy region.

### 3.3.2 Formal approach: the coherent potential approximation

To gain insight into the value of the numerically obtained scaling exponent of the tubular aggregate absorption linewidth, we apply the coherent potential approximation (CPA), thereby closely following the procedure outlined in Ref. [142]. The
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Figure 3.3.1: (a) Numerically calculated DOS $D(E - E_0)$ in the absence of disorder for the tubular aggregate with parameters identical to those used in Fig. 3.2.1 (Structure I in Table 3.2.1). Exciton energies are binned into intervals of length $\delta = 140 \text{ cm}^{-1}$. (b) Disorder-free DOS (symbols) near the lower band edge together with the best power law fit $D(E - E_0) \propto |E - E_0|^{0.44\pm0.06}$ (straight line).

The spectral line shape in this case is given by

$$L(E) = \frac{1}{\pi} \frac{\text{Im}[V(E)]}{(E - \text{Re}[V(E)])^2 + (\text{Im}[V(E)])^2},$$

(3.3.1)

where $\text{Re}[V(E)]$ and $\text{Im}[V(E)]$ are the real and imaginary parts, respectively, of the energy dependent coherent potential $V(E)$ representing the line shift (half width) of the spectrum. They can be found by solving a self-consistent equation, which, in the weak disorder limit, takes the form

$$V(E) = \sigma^2 G(E - V(E)).$$

(3.3.2)

Here $G(E) = N^{-1} \sum_k [E - E_0 - E_k]^{-1}$ is the disorder-free exciton Green function. The energies $E_k$ are obtained from diagonalizing Eq. (3.2.1) (for $\sigma = 0$) and $E_0$ introduces a shift of the energy spectrum such that its zero point lies at the bare exciton band bottom.

To solve Eq. (3.3.2), the Green function is separated into its real and imaginary parts, $G(E) = \text{Re}[G(E)] + i\text{Im}[G(E)]$, where we explicitly assume that the real part $\text{Re}[G(E)]$ is a constant. The imaginary part $\text{Im}[G(E)]$ can be identified with the disorder-free DOS, defined as $D(E) = N^{-1} \sum_k \delta(E - E_k)$. In
3.4 Relation to one-dimensional toy models

Fig. 3.3.1, we display the numerically calculated DOS (shown as squares) of the tubular aggregates near the lower exciton band edge together with the best power law fit $D(E) \propto |E - E_0|^{-P}$ (straight line) for the same parameters used to generate Fig. 3.2.2, i.e., those of Structure I given in Table 3.2.1. The results reveal that the DOS falls off near the band bottom, approximately in a square root dependent fashion ($P = 0.44 \pm 0.06$). This behavior of the DOS leads to weak scattering of the exciton states in this region, which can hold even for a moderate disorder strength.

From the above, it follows that the Green function can to good approximation be expressed as $G(E) = -C + iD |E - E_0|^{1/2}$, where $C, D > 0$. Inserting this into Eq. (3.3.2) and solving the resulting self-consistent equation yields the coherent potential near the band bottom $V(E_0)$. To lowest order in $\sigma$, it is given by

$$V(E_0) = -C\sigma^2 + iC^{1/2}D\sigma^3.$$  

(3.3.3)

From the CPA approximation, we thus find a $\sigma^3$ dependence on the linewidth. This is in good agreement with the numerically found disorder scaling of the low energy absorption linewidth ($W_{||} \propto \sigma^{2.83}$) for the tubular aggregates based on the parameter set of Structure I (shown in Fig. 3.2.2).

3.4 Relation to one-dimensional toy models

The above results confirm that there exists a relation between the energy dependence of the disorder-free DOS and the disorder scaling of the optical absorption band at low temperature. We will now further quantify and generalize this apparent relation by means of a simple one-dimensional toy model. It consists of a 1D lattice of $N$ sites with uncorrelated site energies drawn from a Gaussian distribution with mean zero and standard deviation $\sigma$, and non-fluctuating couplings between sites $n$ and $m$ of the form $J_{nm} = J/|n - m|^{\xi}$, where $J$ denotes the nearest-site coupling strength. In the absence of disorder, the eigenstates of this model (assuming periodic boundary conditions) are Bloch waves $|K\rangle = N^{-1/2} \sum_n \exp(iKn) |n\rangle$, with $K = 2\pi kN^{-1}$ denoting the normalized wave number. The energy dispersion relation reads $E_K = -2 |J| \sum_{n>0} \cos Kn/n^{\xi}$, where we explicitly take $J < 0$ to ensure that the optically active state (i.e., the state labeled by wave number $K = 0$) has the lowest energy. Near the lower band edge ($K \to 0$), the energies may be approximated by $(1 < \xi < 3) E_K \simeq E_0 + |J| A_\xi K^{\xi - 1}$ [145, 146]. Here $E_0 = -2 |J| \zeta(\xi)$ is the lower band edge in the thermodynamic limit ($N \to \infty$), $\zeta(\xi)$ the Riemann zeta function and $A_\xi$ a positive constant of the order of unity [147, 148].

The disorder-free DOS in the vicinity of the lower band edge for this toy model yields the following power law behavior

$$D(E) \propto |E - E_0|^{1/\xi - 1}.$$  

(3.4.1)
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1.1
1.2
1.3
1.4
1.5

0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6

σ/|J|

ξ = 19/10
B_ξ = 2.12 ± 0.04

ξ = 9/5
B_ξ = 2.36 ± 0.1

ξ = 5/3
B_ξ = 2.86 ± 0.1

ξ = 8/5
B_ξ = 3.35 ± 0.13

Figure 3.4.1: Numerically obtained absorption linewidths (FWHM) \( W_\xi (\sigma) \) (symbols) in the 1D toy model for different values of the interaction exponent \( \xi \) and for various disorder strengths \( \sigma/|J| \). The best power law fits \( W_\xi (\sigma) \propto \sigma^{B_\xi} \) are shown as straight lines.

This relation shows that the DOS is very sensitive to the value of \( \xi \): we find divergent \((2 < \xi < 3)\), constant \((\xi = 2)\) or vanishing behavior \((1 < \xi < 2)\) near the band bottom. We point out that \( \xi = 3/2 \) corresponds to the marginal (weak localization) regime. Below this value, both the DOS and its derivative vanish resulting in the existence of extended states (even at moderate values of the disorder) that exhibit a localization-delocalization transition with respect to the disorder strength \( \sigma \) [148]. Henceforth, we will focus on values of \( \xi \) in the interval \( 3/2 \leq \xi \leq 2 \); here, the DOS itself vanishes, although all states remain localized.

An approximate solution for the coherent potential near the band bottom \( V(E_0) \) for the DOS in Eq. (3.4.1) can be obtained from Eq. (3.3.2) in a similar way as before. Keeping only lowest order terms in \( \sigma \), it now reads

\[
V(E_0) = a_\xi \sigma^2 + ib_\xi \sigma^{\frac{2}{\xi-1}},
\]

where \( a_\xi, b_\xi \) are constants that depend on \( \xi \). Thus, the CPA gives a disorder-induced linewidth scaling \( W_\xi \propto \sigma^{2/(\xi-1)} \) which shows strong dependence on \( \xi \), ranging from a \( \sigma^2 \) behavior (for \( \xi = 2 \)) to a \( \sigma^4 \) dependence (for \( \xi = 3/2 \)). In Fig. 3.4.1 we present the results of the numerically calculated absorption linewidths (symbols) for interaction exponents \( \xi = 8/5, 5/3, 9/5, 19/10 \) and various disorder values \( \sigma = 1/|J| - 3/2 |J| \), together with the power law fits \( W_\xi (\sigma) \propto (\sigma/|J|)^{B_\xi} \).
3.4 Relation to one-dimensional toy models

Figure 3.4.2: Absorption spectra of the tubular aggregate (parameters identical to Fig. 3.2.1) for disorder values $\sigma = 450 \text{ cm}^{-1}$ and $\sigma = 625 \text{ cm}^{-1}$ together with the corresponding spectra of the 1D toy model for interaction exponent $\xi = 5/3$ and disorder strengths $\sigma = 0.8 |J|$ and $\sigma = 1.1 |J|$, respectively. Due to rounding errors in $\sigma/|J|$, the latter spectra have been shifted by 5 cm$^{-1}$ (for $\sigma = 0.8 |J|$) and 18 cm$^{-1}$ (for $\sigma = 1.1 |J|$) to match the exact position of the tubular absorption peak.

Figure 3.4.1 shows that, for each $\sigma$, the linewidths broaden with increasing value of $\xi$. This trend is consistent with the fact that the typical localization length decreases for higher values of $\xi$, resulting from diminishing strength of the long-range interactions. Furthermore, the calculated linewidth scaling exponents together with their CPA predicted values (given in brackets) are $B_{8/5} = 3.35 (3.33)$, $B_{5/3} = 2.86 (3.0)$, $B_{9/5} = 2.36 (2.5)$ and $B_{19/10} = 2.13 (2.22)$, which show overall good agreement. We note that the slight discrepancy observed between our numerical findings and the CPA predicted values are due to neglecting higher orders of $\sigma$ in Eq. (3.4.2). This has been verified explicitly by limiting $\sigma$ to both smaller and larger values. For smaller values, this yields scaling exponents that get closer to the expected CPA values, while in the opposite case the exponents slowly tend towards linearity, as expected for completely localized exciton (i.e., single molecule) states.

We now turn our attention to the case $\xi = 5/3$, for which the DOS [Eq. (3.4.1)]
vanishes as $E^{1/2}$. The observed scaling exponent $B_{5/3} = 2.86$ is nearly identical to that obtained for the tubular aggregates ($W_\parallel \propto \sigma^{2.83}$), due to the fact that DOS energy dependence of both systems is similar. This demonstrates that the toy model can in principle mimic the optical features of this complex system very well. To corroborate on this further, we show in Fig. 3.4.2 the absorption spectra of the tubular aggregates for two disorder values $\sigma = 450 \text{ cm}^{-1}$ and $\sigma = 625 \text{ cm}^{-1}$ together with the corresponding two spectra of the toy model ($\sigma = 0.8 |J|$ and $\sigma = 1.1 |J|$). The disorder values for the toy model were obtained in the following way. We first calculated the redshifts of the exciton absorption bands relative to the single-site transition in the homogeneous limit ($\sigma = 0$). The value of $|J|$ then followed from the equality of the redshifts (i.e., we find $|J| = 520 \text{ cm}^{-1}$). Next, we calculated the disorder-induced shift of the cylinder absorption band for both values of the disorder. The corresponding toy model disorder values are those for which the disorder-induced shifts of both systems are equal. The results in Fig. 3.4.2 reveal a high degree of similarity concerning both the absolute value of the width as well as the overall lineshape, which provides final support that the optical responses of both systems are similar.

### 3.5 Conclusions

Summarizing, we have investigated theoretically the disorder scaling of the linewidth (FWHM) of tubular J-aggregates at low temperature. We found numerically that the disorder scaling exponent of the FWHM is drastically increased compared to that of 1D molecular J-aggregates. In addition, this exponent is almost independent on specific details of the structural parameters of the tubular aggregate, like the radius, dipole orientation, helicity, and commensurability. We have shown that the large value of the scaling exponent originates from the combination of the quasi two-dimensional geometry of the cylinders and the anisotropic long-range intermolecular dipolar interactions. This gives rise to an unusual exciton energy dispersion and corresponding DOS in the optically relevant region (close to the bare exciton band edge); the DOS vanishes roughly in a square-root dependent fashion, thus reducing substantially the exciton scattering. As a result, the exciton localization is strongly suppressed in tubular aggregates and approaches the weak localization limit of the standard Anderson model. Furthermore, we have established a general relation between the specific form of the vanishing DOS and the disorder-induced scaling relations. As a result, the exciton model for tubular J-aggregates can be mapped onto one-dimensional toy models with highly similar optical features, provided that the behavior of the DOS close to the band edge is identical. This correspondence may provide a helpful tool for future research concerning the optical and exciton coherence properties of disordered nanotubes.
To end, we like to emphasize that our results provide an explanation to the origin of the strong linear dichroism of C8S3 tubular J-aggregates observed in experiments. Specifically, measurements of polarization dependent absorption spectra reveal that, despite a significant degree of disorder, the optical response is still governed by transitions with preferred parallel and perpendicular orientation [69,71], as dictated by the optical selection rules in the absence of disorder. Also, we have already shown in the previous chapter that, even if the disorder value exceeds the intermolecular interaction strengths, the selection rules still remain valid to a good approximation. These features indicate that the exciton states should remain quite extended at large disorder. Our findings strongly support that exciton localization is indeed severely suppressed in cylindrical J-aggregates and provide a deeper understanding of the localization mechanism in these systems. In addition, they also shed light onto the recently observed weak exciton-exciton scattering in cylindrical aggregates using double-quantum two-dimensional electronic spectroscopy [135]. Finally, we point out that the suppression of disorder-induced localization is expected to lead to enhanced excitation energy transport, which is advantageous for application in artificial light harvesting.
Signature of anomalous exciton localization in the optical response of tubular J-aggregates