CHAPTER 2

Theory of aggregate excitations

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References
2.1 Introduction

In closely packed structures like molecular crystals and aggregates, the coupling between molecules can lead to delocalization of the excited state of molecules. The delocalized excitation is called Frenkel exciton [1], and it is the main entity in the description of spectra and dynamics of optical excitations in molecular solids.

The concept of a delocalized excitation in a molecular solid has been used extensively to explain the anomalous spectral properties of coupled chromophores. Förster [2] considered the excitation transport, and Toyozawa [3] extended the theory for excitation-phonon interaction. On the basis of the theoretical foundations refinements have been made [4] to describe the transfer of excitons in solids.

Whether or not an extended state is formed depends, on the size of the intermolecular coupling ($B$) relative to the site energy differences, the so called site inhomogeneity ($\Delta$). The molecular coupling must overcome these energy differences. In Sect. (2.2), starting from a model system which consists of two coupled chromophores, the strong and intermediate coupling cases will be treated. The treatment founded on the work of Davylov [5] and Kasha [6] offers an interpretation for the observed spectra of aggregated molecules.

In the strong coupling case a band of delocalized states is formed. Along with the formation of this exciton band, the oscillator strength of the transitions is redistributed. For one and two dimensional excitons, some band states acquire a very large oscillator strength. The radiative lifetime, which is inversely proportional to the transition moment squared, is shortened for these optically allowed states.

The final section of this chapter deals with the coupling of the exciton states to lattice vibrations (phonons). The coupling between the aggregate exciton and the aggregate phonons determines the lineshape and the linewidth of the exciton transition. It will be shown that both exciton scattering and self-trapping are dependent on the strength of the exciton-phonon coupling.

2.2 Coupled chromophores

2.2.1 Dimer model

In order to obtain a better understanding of the spectra and dynamics of molecular aggregates it is useful to first consider two monomers coupled by an interaction $J$. The Hamiltonian for this system looks like:

$$H_{\text{dimer}} = H_1 + H_2 + J_{1-2},$$

(2.1)

where the subscripts refer to the individual molecules 1 and 2. The one-molecule Hamiltonians are diagonal with ground state electronic eigenfunctions $\Psi_1$ and $\Psi_2$, and energies $E_1$ and $E_2$. Provided the dimer is bound by weak van der Waals forces, the combined ground state function reads:
The ground state energy of the dimer will contain the sum of the one-molecule energies and an interaction term $D$,

$$D = \int dV_1 dV_2 \psi_1 \psi_2 J_{1-2} \psi_1 \psi_2 ,$$

which describes the binding energy or, alternatively, the van der Waals energy of the dimer. The excited state dimer wavefunction is a linear combination of singly excited states:

$$\psi_{\text{dimer}}^* = a_1 \psi_1^* \psi_2 + a_2 \psi_1 \psi_2^* .$$

The asterisk denotes which molecule is in the excited state. The coefficients $a_1$ and $a_2$ can be found by solving the eigenvalue problem $H \psi_{\text{dimer}}^* = E \psi_{\text{dimer}}^*$. The solutions are:

$$\psi^+ = 2^{-1/2}(\psi_1^* \psi_2 + \psi_1 \psi_2^*),$$

$$\psi^- = 2^{-1/2}(\psi_1^* \psi_2 - \psi_1 \psi_2^*),$$

with eigenvalues

$$E^+ = E_1^* + E_2 + D^*, \int dV_1 dV_2 \psi_1^* \psi_2 J_{1-2} \psi_1 \psi_2^* ,$$

$$E^- = E_1^* + E_2 + D^* - \int dV_1 dV_2 \psi_1^* \psi_2 J_{1-2} \psi_1 \psi_2^* .$$

The wavefunctions are the in-phase and out-of-phase combinations of the two possible excited state configurations. In fact the site basis $(\psi_1, \psi_2)$ has been transformed into a dimer basis $(\psi^+, \psi^-)$. The dimer excited state energy contains a term $E^*$, which is the single molecule excited state energy, a term $D^*$, which is the aforementioned van der Waals shift, now of the excited state, and an integral term. The integral is called dimer splitting or exciton splitting ($B$), and is a result of the excitation transfer induced by the coupling term $J$.

$$B = \int dV_1 dV_2 \psi_1^* \psi_2 J_{1-2} \psi_1 \psi_2^* .$$

The energy levels are depicted in Fig. (2.1). It is possible now to write down an expression for the energy differences of the possible transitions in the dimer:

$$\Delta E = (E^* - E) + (D^* - D) \pm B .$$

The first term of Eq. (2.8) is simply the single molecule excited state energy, the second term denotes the difference of the van der Waals shifts and is generally not very large. Two questions need to be answered still; what is the origin of the coupling, and what is the transition
probability between the ground state and the dimer levels.

The excited state of a molecule can be seen as an oscillating charge distribution. When an optical field is applied to an unexcited molecule, this charge distribution can resonate with the field, which leads to absorption of energy. An identical molecule, which is close to an excited molecule, can also resonate with the oscillating charge distribution of the excited molecule. This last resonance causes the coupling of molecular excited states. The two resonance processes are governed by the same molecular property: the transition moment between molecular ground and excited states. The transition moment can be limited to the point dipole–dipole interaction term of a multipole expansion. In this case the interaction is reduced to two oscillating dipoles next to one another. The magnitude of the interaction is determined by the geometry of the problem, and by the relative phases of the oscillators. The simplified exciton splitting has the form of the dipole–dipole interaction energy:

\[ B = \frac{\mu_1 \cdot \mu_2}{r^3} - \frac{3(\mu_1 \cdot \mathbf{r})(\mu_2 \cdot \mathbf{r})}{r^5} \]  \hspace{1cm} (2.9)

In the case where the two transition moments are parallel and equal in magnitude the expression for \( B \) becomes:

\[ B = \frac{\mu^2}{r^3} (1 - 3\cos^2 \theta) \]  \hspace{1cm} (2.10)

Here \( \theta \) denotes the angle between the line connecting the chromophores and the direction of the transition moments. For example, when the transition moments are aligned head to tail this angle is zero degrees.

<table>
<thead>
<tr>
<th>Table 2.1 parallel dimers</th>
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In Table (2.1), three special cases are summarized with parallel in-phase transition moments. From the table it can be seen that the energy for the card pack dimer (\( \theta=90^\circ \)) is increased by \( \mu^2/r^3 \), the energy for the head to tail dimer (\( \theta=0^\circ \)) on the contrary, is lowered by \( -2\mu^2/r^3 \). The energy change is zero at the so called "magic angle". If one realizes that the oscillating electric field has a characteristic length of one wavelength, which is much larger than the dimer separation, one concludes that the constituting monomers experience the same field. The component
of the combined transition moments that is in phase with the field carries double oscillator strength, relative to the monomer, whereas the out-of-phase component carries none. The in-phase dimer state is called superradiant because it carries double oscillator strength, and is the main entity for the understanding of the radiative properties of aggregates.

In real dimers other arrangements of transition moments than parallel exist. In that case the full expression of Eq. (2.9) must be evaluated, which results in two states that both carry nonzero oscillator strength. The energy splitting of the two states is determined by the actual geometry of the dimer and the direction of the transition moment. For example, when the transition moments are perpendicular, the interaction energy $B$ is zero; and both dimer states have equal transition moment. The only dimer feature that is apparent in this case is the van der Waals term.

In constructing this dimer model some relevant interactions have not been taken in account as, for example, differences in the static energies of the monomers at site 1 and site 2. Another neglected factor is the coupling of the electronic excitation to low frequency vibrational modes of the dimer. Despite these omissions the model explains some of the most striking phenomena in the spectroscopy of dimers.

2.2.2 Aggregates

The concept of the dimer can be extended to the case where $N$, the number of coupled monomer units, is very large. As in the dimer case, the excitation is a collective one, extending over all units. In order to extend the dimer paradigm to the case for large $N$, the whole assembly is assumed to be smaller than the wavelength of the exciting optical field. The approximate size of a dye molecule is 0.5 nanometer. Combining this with a typical visible wavelength of 500 nanometer the linear extension can be thousand units. I will show that the energy levels and the transition moments, together giving rise to the absorption spectrum, do not change significantly upon going from small to large aggregates. In Sect. (2.3) it will be shown that the radiative dynamics are more sensitive to the aggregate size.

The approach is the same as for the dimer case, starting with single particle Hamiltonians and coupling terms:

$$ H_{agg} = \sum_n H_n + \sum_{n,m} J_{nm} \tag{2.11} $$

When one assumes that the binding forces between the constituting monomers are weak and no electron delocalization takes place in the ground state, the ground state wavefunction is a product of single particle wavefunctions:

$$ \Psi_{agg} = \prod_n \Psi_n \quad \tag{2.12} $$
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The aggregate ground state energy contains a van der Waals term, \( D \),

\[
E_{\text{agg}}^0 = N E_n + D_{\text{agg}}^0.
\]  

(2.13)

Considering excited state wavefunctions, these are again linear combinations of singly excited wavefunctions such as:

\[
\Phi_a = \Psi_a \prod_{n \neq a} \Psi_n ,
\]

(2.14)

where the label \( a \) refers to the molecule that is excited. The linear combinations are:

\[
\Psi_k = N^{-1/2} \sum_a c_{ak} \Phi_a .
\]

(2.15)

As in the dimer case the basis has been transformed from site oriented wavefunctions into aggregate oriented ones. Instead of considering a long chain with one unit excited, the whole aggregate is involved. The key parameter characterizing the excitation is not the label of the excited molecule, \( n \), but the \( k \)-value, denoting the state of the whole aggregate. In order to complete the picture we have to consider the transition moments and the energies of the aggregate levels.

The interaction term \( J_{nm} \) in Eq. (2.11) is often limited to the so-called nearest neighbor terms. The coupling \( J_{nm} \) in that approximation only has nonzero values for adjoining sites, \( n=m \pm 1 \). The neglect of other coupling terms is justified by the \( 1/r^2 \) behavior of the coupling, for example, the \( n=m+2 \) term originates from a pair with distance \( 2r \), resulting in an interaction that is one eighth of the nearest neighbor term. The interaction of the monomers is assumed to be represented by dipole–dipole coupling. Using cyclic boundary conditions for the chain (circular aggregate), the energies of the band levels can be expressed as:

\[
E_k = E_a^0 + D_a^0 + 2B \left( \frac{N-1}{N} \right) \cos(\pi k/N) ,
\]

(2.16)

where \( k \) takes the values 0 to \( N \), and \( B \) is the binding energy. It is evident from this last equation that the width of the exciton band for large aggregates equals \( 4B \). The bandwidth is twice as large as for the dimer, reflecting the extra energy lowering as a result of extra delocalization. The dependence of the bandwidth on \( N \) is weak. For a cyclic aggregate of ten units the bandwidth is only ten percent smaller than for an infinitely long aggregate.

For an aggregate consisting of parallel units, the \( k=0 \) state carries all of the oscillator strength. That state can be envisioned as the in-phase combination of all separate transition dipole moments. Whether the allowed state is at the bottom of the band or at the top of the band depends on the actual alignment. The head to tail aggregate absorbs at the low energy side of the band, whereas the card pack aggregate absorbs at the high energy side. Historically, the two cases mentioned are
referred to as J- and H-bands [7], respectively.

![Diagram of energy levels](image)

Figure 2.1 Energy levels of a single chromophore (left) and an aggregate consisting of chromophores (right). The terms $D^0$ and $D^*$ denote the van der Waals shift in ground and excited states. The coupling $J$ leads to a band of exciton states with total width $4B$. The arrows indicate the allowed optical transitions.

The transition dipoles need not be parallel and can be organized in pairs, a situation that is commonly encountered. In this case both extremes of the exciton band acquire oscillator strength. The relative polarizations of the two transitions are perpendicular. From Fig. (2.2) it can be seen that the total transition dipole depends on the inclination angle and the direction of the total transition dipole depends on the relative phases. There is no necessity for the resultant total transition moment to be either parallel or perpendicular to the axis of the aggregate.

![Diagram of exciton band](image)

Figure 2.2 Exciton band for an aggregate with inclined transition moments. The phase of the transition dipoles is indicated by the direction of the small arrows. The top of the exciton band can be reached with light that is polarized vertically relative to the aggregate axis, whereas the bottom of the band can be reached by horizontally polarized light.

In the preceding sections on dimers and aggregates the basic factors determining the delocalization of excitation have been discussed. Though
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many factors were ignored, the description offers a model for aggregate excitations. This model will often be referred to in the rest of this thesis. The key elements of the model are the weak van der Waals binding of the units, and the excitation transfer in the excited state. The weak binding implies that no delocalization takes place in the ground state. Only the excited state basis must be transformed into a delocalized one.

One of the most interesting results is the direct link between energy levels and transition moments. The transition dipole moments are directly linked to the observed absorption strength. The comparison of monomer, dimer, and aggregate absorption spectra with each other provides information about interaction and delocalization of the excited state.

The total oscillator strength does not change upon the coupling of monomer units, because $N$ participating units carry $1/N$ part of the total excitation. The transition moment of the optically allowed aggregate state, however, is enhanced by a factor $\sqrt{N}$. This last enhancement drastically changes the radiative properties of the aggregate, as will be shown in Sect. (2.3). The treatment of transition dipoles which can add up, only works as long as the transition dipoles stay in phase, which means that no dephasing of the transitions of the units inside the aggregate should occur. If the transition dipoles do dephase, the radiative properties of the aggregate will change. The description of aggregates in the above way is therefore called coherent. The incoherent description is used for cases where the correlation between the monomers is totally lost. The transfer term in that last limit only results in a random hopping of the excitation.

2.3 Optical lineshape of molecular excitons

2.3.1 Exciton–phonon coupling

The treatment of the previous section leads to a description in terms of a band of energy levels and delocalized exciton wavefunctions. The goal of this section is to identify the factors that determine the dynamics of the delocalized excitation. The term dynamics refers to both the dephasing rate of the optical excitation and to the lifetime of that excitation.

The linewidth of a transition to a pure isolated exciton $k$–state is determined solely by lifetime broadening ($T_1$). When the influence of other molecular degrees of freedom is incorporated in the model, other factors determine the optical properties as well. The Hamiltonian of Eq. (2.11) can be extended with terms accounting for the coupling of the delocalized excitation to low frequency lattice modes (phonons) [8,9]. The total Hamiltonian takes the following form:

$$H_{tot} = H_{agg} + H_{ph} + H^{(1)}_{ex-ph} + H^{(2)}_{ex-ph}.$$  \hspace{1cm} (2.17)

The terms $H_{agg}$ is the aggregate Hamiltonian that was previously used. The terms in that Hamiltonian are made more explicit using creation and annihilation operators:
In this equation $\varepsilon_n$ is the single particle (monomer) energy, directly related to the single particle Hamiltonian $H_n$. The term $D$ is the van der Waals shift that was also previously encountered. This shift is now characterized by a parameter $R$, and must be evaluated at the equilibrium position $R=0$, because the phonon modes modify the distances between monomers, and consequently also the coupling of the monomer wavefunctions. $a_n^+$ and $a_n$ are the Bose creation and annihilation operators that create or annihilate an excitation on a site with label $n$. It is important to realize that these operators are strictly site based. The intersite coupling term $J$ is, like $D$, characterized by the equilibrium value at $R=0$. The summation extends over all sites for which $n \neq m$, but is often limited to nearest neighbor interaction, $m=n\pm1$.

The phonon Hamiltonian is given by:

$$H_{ph} = \sum_{q} \hbar \omega_{q} (b_q^+ b_q + 1/2) .$$

(2.19)

The creation and annihilation operators $b_q^+$ and $b_q$ refer to phonons with wavevector $q$ and frequency $\omega_q$. The important difference relative to the electronic excitations created by $a_n$, is that the phonons are delocalized lattice excitations with a wavevector instead of excitations localized on a particular site. The phonon Hamiltonian gives the energy of the phonon, without mixing electronic and lattice motions.

The two exciton–phonon coupling terms are the ones that are relevant for dephasing and localization of the exciton. The expression for the first coupling term is:

$$H_{ex-ph}^{(1)} = \sum_{q} \sum_{n,m} F_{nm}^q \hbar \omega_{q} (b_{-q}^+ b_{q} + b_{q}^+ b_{-q}) a_{n}^+ a_{m} .$$

(2.20)

This term represents the influence of the phonons on the coupling between sites. The summation extends over the two different site indices ($n$ and $m$), and is connected to the intersite coupling term $J$. Actually, this contribution can be treated as the change of the intersite coupling caused by interaction with lattice modes. $F$ stands for the coupling strength of the phonons with respect to the intersite interaction.

The second exciton–phonon term $H^{(2)}$, describes the change of the energy on one particular site $n$ caused by interaction with phonons:

$$H_{ex-ph}^{(2)} = \sum_{q} \sum_{n} \chi_{n}^q \hbar \omega_{q} (b_{-q}^+ b_{q} + b_{q}^+ b_{-q}) a_{n}^+ a_{n} .$$

(2.21)

The electronic creation and annihilation operators now refer to the same site $n$. This term can be envisioned as a change of the van der Waals shift term $D$. $\chi$ is the coupling strength for this particular part of the exciton–phonon interaction.

The two exciton–phonon terms can be differentiated by the noted local and intersite character. $H^{(1)}$ can be named the intersite term and $H^{(2)}$
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can be named the local term. The effect of the two parts of the exciton-phonon coupling is quite different. The local part \( \mathcal{H}^{(2)} \) describes the fluctuation of the site energy caused by phonons. From theoretical work [9] it can be concluded that this last term leads to fluctuations of the energy of the exciton states. The states do not mix as a result of the coupling and the lineshape is not influenced. The intersite term does have an effect on the exciton states, the term causes the scattering of exciton \( \mathbf{k} \)-states by phonons. The modulation of the coupling between the units mediated by the intersite coupling term mixes the pure exciton states, and causes \( \mathbf{k} \) to \( \mathbf{k}' \) scattering.

The scattering of the exciton state as described by the intersite term \( \mathcal{H}^{(1)} \) is essentially a lifetime limiting or \( T_1 \) process. A scattering event always leads to a change of the exciton state. For an infinite circular aggregate only the transition to one \( \mathbf{k} \)-state is optically allowed. After excitation this initially prepared state scatters from \( \mathbf{k} \) to \( \mathbf{k}' \) and from \( \mathbf{k}' \) to \( \mathbf{k}'' \) and so on. Because there are many \( \mathbf{k} \)-states accessible, it is not likely that an exciton returns to the initially prepared state. The homogeneous line shape of the exciton state therefore reflects the rate at which the optically allowed level is depopulated caused by the interaction with phonons.

The influence of the the local exciton-phonon term \( \mathcal{H}^{(2)} \) modifies the zero-order wavefunctions. The new basis set consists of mixed exciton-phonon states, the so-called polaron states. A polaron is an exciton that is accompanied by a phonon induced deformation.

The behavior of an excitation will differ dramatically depending on which of the two exciton-phonon coupling terms dominates. In the limit where the intersite terms are negligible, a polaron is formed. If the local term can be ignored the excitation is better described as an exciton state that is scattered by phonons \( (\omega_{\mathbf{q}}, \mathbf{q}) \) at certain times, changing the exciton \( \mathbf{k} \)-state from \( \mathbf{k} \) to \( \mathbf{k}'+q \).

The equations above follow from a perturbative approach, considering linear exciton-phonon coupling only. The resulting eigenstates are exciton \( \mathbf{k} \)-states. A different approach to the interaction of the exciton with the lattice modes is the so called Haken-Strobl model [10]. In this model the phonons are not treated explicitly, but handled together with all other lattice modes as random fluctuations of \( \varepsilon \) and \( J \). The principal results of Haken and Strobl [10] are:

\[
\langle \varepsilon_n(t) \varepsilon_n(t') \rangle = \hbar \gamma_{\text{loc}} \delta(t-t') \tag{2.22}
\]

\[
\langle J_{nm}(t) J_{nm}(t') \rangle = \hbar \gamma_{\text{int}} \delta(t-t') \tag{2.23}
\]

\[
\langle \varepsilon_n(t) \rangle = \varepsilon_n \tag{2.24}
\]

\[
\langle J_{nm}(t) \rangle = J_{nm} \tag{2.25}
\]

Here the brackets denote averaging over time, and \( \gamma_{\text{loc}} \) and \( \gamma_{\text{int}} \) are the associated with the rate of the fluctuations of local energies and intersite couplings respectively. The total homogeneous linewidth of the exciton transition assuming nearest neighbor interaction only, is expressed as:
The importance of this result is that the linewidth contains a contribution caused by the local energy fluctuation of Eq. (2.22). In the linear exciton–phonon coupling model the only process that influences the linewidth is the scattering to other k-states. In the Haken–Strobl model this scattering is incorporated in the term $\gamma_{\text{int}}$. The local fluctuation leads to a contribution to the linewidth of the exciton that is not accompanied by a change of state, in other words, a pure dephasing process. This dephasing process has consequences for the radiative behavior as will be shown in Sect. (2.3.3).

The incorporation of lattice motions into the description of excitons is necessary in order to understand the shape of exciton lines. If one considers linear exciton–phonon coupling only, the two extreme cases are an exciton scattered by phonons, and a polaron, depending on the magnitudes of the coupling terms. The interaction with phonons in this approximation does not lead to pure dephasing. Starting from the Haken–Strobl model the pure dephasing of the exciton transition can be understood. Equivalent to the local energy fluctuation formalism (Eq. (2.22), one can evaluate higher order exciton–phonon coupling terms of the Hamiltonians Eq. (2.20) and Eq. (2.21).

2.3.2 Influence of site inhomogeneity

The basic exciton Hamiltonian Eq. (2.11) incorporates the coupling term $J_{nm}$, that no matter how small, totally delocalizes the excited state wavefunction. This fact is caused by the identity of all single particle Hamiltonians $H_n$ for all monomers that form the aggregate. The resulting energy levels are sharply defined, and the width of the transitions is only determined by lifetime broadening. In most liquids and solids the width of transitions of dopant molecules is determined predominantly by site to site energy differences. If these energy differences change rapidly as in room temperature liquids, a time dependent description must be adopted. The site energies in that limit are characterized by time correlation functions. In solids at low temperature the correlation time is infinite. This means that the site contribution to the total energy is static.

The static site energy $\Delta_n$, can directly be incorporated in the aggregate Hamiltonian:

$$H_{\text{agg}} = \sum_n (H_n + \Delta_n) + \sum_{n} \sum_{m} J_{nm}.$$  \hspace{1cm} (2.27)

In general the inhomogeneities are distributed randomly, according to a Gaussian distribution with width $\sigma$.

Noninteracting monomers have an absorption spectrum centered around the eigenvalue of $H_n$, with the aforementioned width $\sigma$. When the monomers combine to aggregates, different situations arise depending on the relative sizes of the coupling $J$ and the spread of the inhomogeneity.
Without inhomogeneity delocalization will occur, independent of the size of the coupling. Introducing the site dependent energy \( \Delta_n \) leads to a competition between this energy and the site to site coupling. A large inhomogeneity totally inhibits any delocalization, whereas a small inhomogeneity leads to almost total delocalization.

When the coupling term is large enough to overcome the inhomogeneities, the linewidth of the aggregate changes drastically. The excitation extends over a large number of units and consequently the inhomogeneity that can be assigned to the total excitation is some average of the monomer inhomogeneities. This effect is known as exchange narrowing, or motional narrowing. Knapp [11] has considered aggregates with a Gaussian spread of the site inhomogeneity. In that limit the linewidth scales with the root of \( N \). The scaling with the root of \( N \) indicates that the inhomogeneities average quadratically, and that the resulting absorption line has the root–mean–square value as compared to monomer. Quadratic averaging can be anticipated because the coupling term that connects neighboring sites must overcome energy differences \( \Delta_n - \Delta_{n+1} \), where the deltas are distributed according to a Gaussian. For cases where the coupling \( J \) and the inhomogeneity \( \sigma \) are comparable, the narrowing effect is less pronounced.

Knapp [11] especially considered the effect of intersite correlation of the energies in the aggregate. It is plausible that two monomers which are next to each other in an aggregate have comparable environments. The linewidth in that case does not scale with the root of \( N \), but contains an extra variable \( \beta \) that gives the amount of intersite correlation. Summarizing, the aggregate linewidth in the strong coupling limit \( (J \gg \Delta) \) reads:

\[
W_{\text{agg}} = N^{-\frac{1}{2}} W_{\text{monomer}} ,
\]

and with implementation of correlation,

\[
W_{\text{agg}} = N^{-\frac{1}{2}} \left( \frac{1+\beta}{1-\beta} \right)^{-\frac{1}{2}} W_{\text{monomer}} , \beta<1
\]

where \( \beta=0 \) implies no correlation and \( \beta=1 \) infinite correlation. The treatment shows that in the limit of infinite correlation of inhomogeneities the monomer linewidth is recovered.

### 2.3.3 Aggregate superradiance and dephasing

For the analysis of the optical dynamics of molecular aggregates it is important to know the connection between the radiative properties of the monomer units and the aggregate as a whole. An exciton can show \( N \)-fold enhancement of the radiative rate. This full enhancement is not reached when the interactions with the host environment of the exciton are incorporated. In Sect. (2.2) it was shown that for an infinite circular aggregate only one \( k \)-state carries oscillator strength. The transition dipole moment of this exciton level is enhanced by a factor \( \sqrt{N} \), and since the radiative rate is proportional to the square of the transition
moment, that rate is enhanced by a factor \( N \). This phenomenon is the superradiant enhancement.

Grad et al. [12] made the first attempt to describe interaction of this superradiant exciton with the environment. The interaction of the exciton and the lattice modes was modeled according to the Haken–Strobl model, ignoring the intersite (scattering) term. An effective Hamiltonian is formulated that contains the damping of the excitation explicitly in the form of an imaginary part:

\[
H_{\text{eff}} = H_{\text{agg}} - \frac{\gamma}{\pi} i \Gamma \quad .
\]  

(2.30)

The most important point is that the superradiant damping \( \Gamma \) of the aggregate is much smaller than the coupling energy \( B \) of the monomers. For example, the radiative lifetime of an aggregate excitation can be of the order of tens of picoseconds (approximately 1 cm\(^{-1} \) in energy units), and the exciton coupling strength can be 1000 cm\(^{-1} \). The fluctuations introduced by the environment Eq. (2.22) compete with the radiative decay, without affecting the delocalization of the excitation.

The approach outlined here was extended by Spano and Mukamel [13] using a Liouville operator method. Their result can be summarized as follows. Homogeneous dephasing is caused by fluctuations:

\[
\langle \varepsilon_n(t) \varepsilon_{n}(t') \rangle = \Gamma_{\text{dep}} \delta(t-t') \quad ,
\]  

(2.31)

as in the Haken–Strobl model. The damping of the excitation is in direct competition with the superradiant decay,

\[
\Gamma_{\text{tot}} = N\gamma + \Gamma_{\text{dep}} \quad .
\]  

(2.32)

Next to the acceleration of the superradiant decay expressed in Eq. (2.32), another decay process with a time constant much longer than the monomer decay results from the treatment. Upon going to the limit of fast dephasing \( \Gamma_{\text{dep}} \gg N\gamma \), the decay of the superradiant exciton consists of a fast initial component determined by the dephasing, and a slow decay determined eventually by the monomer rate \( \gamma \).

A last remark should be made about the nature of the dephasing. The term dephasing as it is used here refers to the fluctuations of the monomer transition frequencies. The dephasing of the optically allowed exciton which is probed by homogeneous linewidth measurements is connected to this monomer dephasing, but it is not necessarily the same.

2.3.4 Polarons and self-trapping

In Sect. (2.3.1) it was shown that in the approximation of linear exciton–phonon coupling two coupling terms exist. The intersite coupling term leads to scattering of the phonon and the local coupling term leads to a new mixed state: the polaron. The delocalization of a molecular exciton is counteracted by the presence of site inhomogeneities. The coupling of units must overcome the random energy differences, \( J \gg \Delta \). In this limit a delocalized exciton is formed which leads to motional
narrowing of the absorption lineshape. If the local exciton-phonon coupling term (Eq. 2.21) dominates the Hamiltonian can be transformed to [14,15]:

\[
H_{\text{pol}} = \sum_n \left[ e_n + D(\alpha) + \Delta_n - \sum_q |\chi_n^q|^2 \hbar \omega_q \right] A_n^+ A_n + \sum_{n,m} J_{nm} A_n^+ A_m^+ ,
\]

where \( A_n^+ \) and \( A_n \) refer to polaron creation and annihilation operators. An important difference relative to the exciton is the lowering of the energy expressed by the term \( \Sigma_q |\chi^q|^2 \hbar \omega_q \). This means that because of exciton-phonon coupling the energy is lowered by a certain amount. Another difference is the change of the intersite coupling \( J \); the local lattice distortion at site \( n \) will reduce that coupling. As long as this renormalized coupling is larger than the inhomogeneity, a delocalized polaron is the eigenstate of the coupled system. However, when the reduction of the intersite coupling is very large and that coupling can no longer overcome the inhomogeneity, trapping will occur.

In Fig. (2.3) the situation is sketched for the active phonon coordinate. The coupling between units leads to the formation of a band of exciton states. The excitation will be delocalized as long as the bandwidth is larger than the inhomogeneity. The coupling with the lattice phonons leads to energy stabilization \( \Sigma_q |\chi^q|^2 \hbar \omega_q \) along the phonon coordinate. The reduction of the coupling between the sites to \( J \) is indicated by the small bandwidth of the deformed state.

**Figure 2.3 Schematic energy potential for exciton and polaron states.** On optical excitation an exciton (E) is formed, the deformation along the phonon coordinate leads to a new energy minimum (P). The presence of an energy barrier (B) depends on the actual geometry of the system.

The actual dynamical behavior of the initially formed excitation depends on the system studied. Theoretical work by Rashba [16,17] on the
barrier formation in the process of self-trapping indicates that for one
dimensional excitons no barrier is found. For pure electronic
self-trapping the stability criterion for the free exciton state reads:

\[ \frac{2d}{\pi^2} N^{(2/d-1)} g < 1 \]  

(2.34)

Here \( d \) denotes the dimensionality, \( N \) is the number of participating
monomers, and \( g \) is the coupling strength. When \( N \) is large the inequality
always holds for \( d=3 \). This implies that a stable free exciton state
exists next to the self-trapped state. The two states are separated by a
barrier. In the case of a one dimensional exciton system, the free
exciton is unstable, indicating the absence of a barrier. The local
exciton-phonon interaction in a one dimensional system will always lead
to an exciton which relaxes to a trapped state. For the \( d=2 \) case the
formation of a barrier depends on the size of the coupling strength.

In low dimensional molecular systems a barrier can be present that is
caused by motions of the molecules in the lattice. In that case
self-trapping is not an electronic effect but is caused by changes in the
lattice. For example, the excitation can become localized in a one
dimensional chain when an exited state dimer (excimer) is formed. The
motion of the molecules can involve a repulsive energy that is not
connected to the energetics of the polaron itself. The repulsive energy
term leads to the formation of a barrier for self-trapping.

References

Quantum Chemistry", vol. 3, pg 93, ed. O. Sinanoglu (Academic Press,
New York).
5. A.S. Davydov, "Theory of molecular excitons" (Plenum Press, New York,
1971).
6. M. Kasha, H.R. Rawls and M. Ashraf El-Bayoumi, Pure Appl. Chem. 11,
371 (1965).
7. The terminology for the bands in dye solutions is not based on a
strict system: M-band stands for Molecular or Monomer absorption,
D-band refers to Dimer absorption, H-band refers to Hypsochromic
(blue shifted) absorption, and J-band refers to Jelley, one of the
discoverers of aggregate bands in pseudo-iso-cyanine. In some German
publications the term S-band or S-aggregates can be encountered, here
S refers to Scheibe who independently from Jelley also described the
aggregate band in pseudo-iso-cyanine.
9. D.M. Burland and A.H. Zewail, "Coherent Processes in Molecular
Crystals", Advances in Chemical Physics vol. XL, pg. 369, eds, I.
2. Theory of aggregate excitations