Signatures of exciton-phonon coupling in linear absorption spectra of molecular aggregates

A variational polaron transformation approach

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Motivated by suggestions that exciton-phonon coupling plays an important role in determining the electronic and optical properties of molecular aggregates, in the current research project we have aimed at modeling such dynamical vibrational effects. Taking the Holstein Hamiltonian as a starting point, a new method that utilizes a variational polaron transformation was devised to calculate the linear optical response of molecular aggregates in which vibrations play a role. Focusing on small model systems containing a few to a few of tens of molecules, it was shown that this method is valid over a large range of exciton-phonon and electronic coupling strengths, as verified by comparing to a two-particle basis set approach. Not only does the current method go beyond the usual perturbative approaches by accurately probing the intermediate regime of couplings, it also provides insightful analytic expressions for linear absorption spectra at zero and finite temperatures. The computational costs of the calculation of such zero-temperature spectra were seen to be much smaller than that for two-particle method calculations. Examining absorption spectra at increasing temperature two interesting effects were observed, the first of which is a broadening of the vibrational band associated with exciton-phonon coupling, and the other being thermal destruction of exciton coherence.
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Chapter 1

Introduction

In the late 1930s, the German chemist Günter Scheibe and the UK-based researcher Edwin Jelley, working at Kodak, both did a remarkable discovery. They observed that the optical properties of a certain dye called pseudoisocyanine chloride drastically changed when its concentration in an aqueous solution was increased. Not only did the band of maximum absorption shift to lower energies, also it became narrower. Similar observations were done concerning the fluorescence yield, that turned out to be enhanced. Scheibe and his co-workers correctly attributed these effects to what they called polymerization of the dye molecules, or what we call aggregation now, signifying a clustering of molecules. [1–7] Aggregates exhibiting an absorption band that is red-shifted with respect to the monomer (single-molecule) absorption peak are termed $S$ or $J$-aggregates, after their discoverers. The type of aggregates that show an absorption peak that is shifted to higher energies (hypsochromically shifted) are named $H$-aggregates.

The shift and narrowing of the main absorption peak and the enhanced fluorescence are ascribed to result from collective electronic excitations called Frenkel excitons, i.e. excited state wavefunctions that are delocalized over several molecules of the aggregate due to coherent coupling of the molecular electronic transition dipoles [8–12]. Much of the interest in Frenkel excitons and their appearance in cyanine dye aggregates was due to their application as sensitizers in silver halide photographic films [13], but also fundamental curiosity was shown for the properties of these collective excitations and for the collective optical behavior of aggregates they were seen to cause (cf. [14] and the references therein).

Recently, the discovery of aggregate-like light-harvesting systems in photosynthetic complexes of certain bacteria and higher plants and the determination of their structure [15–18] have led to many new studies of molecular aggregates, now seen to have potential applications as nanowires and artificial light-harvesting systems. The focus lies on understanding the spectral and energy transport properties of aggregates, both within these natural systems and model systems [19–22]. The optical response of the C8S3 double-walled cylindrical aggregate system, for instance, is relatively well-understood by now; the experimentally obtained absorption spectra are explained using models in which the optical response of both walls is just superimposed, not allowing for electronic coupling between them [23–25]. It is not so well-understood, however, why the walls should be seen as uncoupled, as model calculations have shown the possibility of exciton coherence within the entire double-walled aggregate system when all resonant transfer interactions are taken into account [26]. Possibly, the presence of a dynamical environment, that is not accounted for in the model calculations, can explain these different results. Dynamic disorder caused by intermolecular vibrations, phonons in the solvent, etc. may be of the same order as the resonant transfer interactions between the two walls of the aggregate, thereby destroying the coherence. Other areas of research show that the presence of vibrations can indeed have significant effects on the optical properties of molecular system. Consider the spectral features caused by the vinyl stretch vibration that is so ubiquitous in organic molecules, for instance, or the influence of amide I vibrations on two-dimensional infrared spectra of proteins [27–29].

Motivated by these and other suggestions, the current research project is aimed at modeling the dynamical degrees within the environment and their influence on the electronic and optical
properties of molecular aggregates. We will focus on the calculation of linear absorption spectra of small model systems, consisting of a few to a few tens of molecules. The Holstein Hamiltonian, which is used to describe electronic excitations that are accompanied by phonons, giving rise to polarons, serves as the starting point: the dynamical environment is modeled by quantum harmonic oscillators that are coupled to the excitons of the aggregate [30,31]. As we are interested in the intermediate coupling regime where the electronic and exciton-phonon coupling are of the same order, the usual perturbation approaches that assume that either of these interactions is weak with respect to the other will probably break down.

We will follow an approach involving the polaron transformation [32], more specifically, a variational form of it that is combined with a mean field approach [33–37]. This allows us to take into account the average effect the vibrations have on the electronic interactions and the optical properties of the aggregate. We will show that this perturbation approach is valid over a large range of coupling strengths by comparing linear absorption spectra that result from it to predictions from a multi-particle basis set approach [27,28,38–40]. Furthermore, the influence of temperature on the aggregate system and its absorption properties will be discussed. Note that the literature on molecular aggregates that involves polaron transformations is generally aimed at understanding energy transport, not spectral properties [37,41–45].

The structure of this thesis is as follows. In the next chapter a small review of the linear optical response of molecular aggregates will be presented and attention will be paid to the coupling of electronic excitations and vibrations. Having introduced the latter, Chapter 3 proposes a polaron-transformation-based approach to calculate linear absorption spectra of a molecular aggregate coupled to vibrations. The results of this method are outlined in Chapter 4, where the focus lies on examining a large range of coupling regimes for small model systems like the molecular dimer and aggregate systems containing up to a few tens of molecules. For the dimer also the influence of disorder and thermal effects are discussed. The spectra coming from the currently-proposed method will be compared to results from a two-particle expression of the Hamiltonian. Finally, in Chapter 5 we will present the conclusions of this work.
Chapter 2

Modeling molecular aggregates

2.1 The Frenkel exciton Hamiltonian

Much of the physics of molecular aggregates, among which the shift of the absorption band upon aggregation, can be captured using a relatively simple model. In this model, each unit of the molecular aggregate, that is, each dye molecule or chromophore, is represented by an electronic energy level diagram. Within the two-level approximation that is usually applied to this level diagram, it is assumed that one of the electronic transitions dominates the others (the one having the largest transition dipole), and that it suffices to take only this transition into account when describing a molecule. See Figure 2.1 for a schematic representation of such a two-level molecule.

\[
\begin{align*}
|n\rangle & \quad \varepsilon_n \quad |g\rangle \\
\end{align*}
\]

Figure 2.1: Schematic of a two-level energy diagram that is used to represent the molecules of an aggregate. The transition of energy \(\varepsilon_n\), from the electronic ground state of the molecule to an electronically excited state, has the dominant transition dipole and it is assumed that it suffices to take only this transition into account.

The chromophores in the molecular aggregate are now seen to interact via their dominant electronic transition dipoles. Modeling this interaction is usually done by making further simplifications. For instance, the dipoles are considered in the extended–dipole scheme, where they are modeled by two point charges of opposite polarity. In the present work we will assume a simpler scenario: we model each transition dipole as a point dipole. The electronic interaction between any two aggregate molecules represented by such dipoles, say \(\vec{\mu}_m\) and \(\vec{\mu}_n\), is given by

\[
J_{nm} = \frac{\vec{\mu}_m \cdot \vec{\mu}_n}{|\vec{r}_{mn}|^3} - 3 \frac{(\vec{\mu}_m \cdot \vec{r}_{mn})(\vec{\mu}_n \cdot \vec{r}_{mn})}{|\vec{r}_{mn}|^5},
\]

where \(\vec{r}_{mn}\) is the vector pointing from one molecule to the other. Note that the interaction depends on the relative orientation of the two dipoles and it is inversely proportional to the cube of the distance between them. The essential features of the optical response of aggregates are also seen when we ignore long-range interactions, that is, electronic interactions ranging over several molecular distances. Therefore, for simplicity, we will only allow for nearest-neighbor interactions. See Figure 2.2 for a schematic representation of the aggregate described here.

Considering the total aggregate some more assumptions are made. We will only take into account resonant excitation transfer interactions, describing the transfer of an excitation from one molecule to an other. This interaction mixes the excited states of the separate molecules.
The *non-resonant transfer interactions* are neglected, so that no mixing occurs between the total ground state of the aggregate and multi-exciton states. This is called the *Heitler-London approximation*. The electronic ground state of the molecular aggregate is thus seen to be the product of single-molecule ground states.

In the current project we will focus on the linear optical response of molecular aggregates. This means that we only look at processes in which a single photon is absorbed in the material under study at a time and, thus, only one electronic excitation can reside in it. That is, we only for so-called *one-exciton states*. Note that we will assume such an excitation, being an electron-hole pair, to be tightly bound and to sit on one molecule, so that it is of the Frenkel exciton type. Only allowing for one-exciton states, in which only one quantum of energy is absorbed, does not mean that the excitations can not spread over several molecules. On the contrary, we can still have superpositions of states in which one molecule is excited, leading to a certain probability to find the excitation there. This allows for interesting features like *exciton delocalization*, that emerges upon aggregation when the resonant transfer interaction is strong enough (that is, larger than the energy difference between the excited-state levels of the molecules involved).

The Hamiltonian that describes the singly-excited states of an \( N \)-molecule aggregate in the scheme just sketched, is given by

\[
H = \sum_{n=1}^{N} \epsilon_n c_n^\dagger c_n + \sum_{n \neq m}^{N} J_{nm} c_n^\dagger c_m. \tag{2.2}
\]

In this Hamiltonian, the first term describes the excited states of the molecules making up the aggregate. Their transition energies are denoted by \( \epsilon_n \). We explicitly allow for inhomogeneity in the transition frequencies of the molecules, taking into account possible shifts due to the different local solvent environment the molecules are in. The second term describes the transfer of an excitation from one molecule to an other. The resonant transfer interaction, \( J_{nm} \), between any two molecules \( n \) and \( m \) is taken to be of the point-dipole type mentioned previously, only taking into account nearest-neighbor interactions. We will mostly refer this interaction as the *electronic interaction*.

The notation of the electronic states involves the Pauli creation (\( c_n^\dagger \)) and annihilation (\( c_n \)) operators for an excitation on molecule \( n \). As we speak of electronic excitations, these operators are fermionic in nature and they obey anticommutation relations on each molecule. Furthermore, double (de)excitations are not allowed. We thus have

\[
\{c_n, c_m^\dagger\} = c_n c_m^\dagger + c_m^\dagger c_n = 1, \quad c_n c_m = c_m^\dagger c_n^\dagger = 0. \tag{2.3}
\]

The Pauli operators for different molecules do commute. Note that the Pauli operator notation and Dirac’s bra-ket notation for an excitation at molecule \( n \) are related via

\[
|n\rangle = c_n^\dagger |g\rangle, \tag{2.4}
\]

where \( |g\rangle \) is used to denote the electronic ground state of the total aggregate, which, as mentioned, is seen to be the product of single-molecule ground states. The properties of the Pauli excitation operators are summarized in Appendix A.1.
2.2 Exciton states and energies

The Hamiltonian given above is expressed in terms of molecular excitations and their interaction. The physical response of the system, however, follows from the electronic eigenstates of the Hamiltonian, which can differ from the molecular wavefunctions. These eigenstates can be found by diagonalizing the Hamiltonian. This is easily done when the Hamiltonian is expressed in the matrix representation (taking the molecular excitations as the basis),

$$H_{nm} = \epsilon_n \delta_{nm} + J_{nm}(1 - \delta_{nm}).$$

(2.5)

Labeling the electronic eigenstates (exciton states) with $k$, we can express them as a superposition of molecular wavefunctions using the coefficients from the diagonalization (labeled $\phi_k(n)$):

$$|k\rangle = \sum_n \phi_k(n)|n\rangle = \sum_n \phi_k(n)c_n^g|g\rangle,$$

$$\sum_n |\phi_k(n)|^2 = 1.$$  

(2.6)

Here, the sum over $n$ is (implicitly) taken to run over all aggregate molecules, $n = 1, 2, \ldots, N$.

2.2.1 The dimer

The simplest aggregate system, that forms a model system for collective behavior, is the molecular dimer, the system consisting of two interacting molecules. When we allow for inhomogeneity in the transition frequencies of the molecules ($\epsilon_1 \neq \epsilon_2$), this system is called the inhomogeneous dimer or the heterodimer. A schematic representation of it is shown in Figure 2.3.

![Figure 2.3: Schematic representation of the inhomogeneous molecular dimer.](image)

Using the molecular excited state wavefunctions as a basis, the dimer Hamiltonian can be represented using a matrix as

$$H = \begin{bmatrix} \epsilon_1 & J \\ J & \epsilon_2 \end{bmatrix}.$$  

(2.7)

Solving for the electronic energy levels of this system (the eigenvalues of the above matrix), we obtain

$$E_k = \epsilon_1 + \epsilon_2 \pm \sqrt{(\epsilon_1 - \epsilon_2)^2 + J^2}.$$  

(2.8)

The nature of the eigenstates of the system depends on the amount of inhomogeneity ($|\epsilon_1 - \epsilon_2|$) being present with respect to the interaction strength ($|J|$). In the limit of large inhomogeneity, they reduce to the single-molecule wavefunctions, accompanied by energy levels given by the original molecular transition energies. The limit of small inhomogeneity (that is, the homogeneous limit) makes for a more interesting analysis, for then the wavefunctions are (approximately) given by the symmetric and antisymmetric combinations of molecular wavefunctions, which are labeled using $k = +$ and $k = -$, respectively. Formulawise, these are given by (also stating the eigenfunction energies),

$$|\pm\rangle = \frac{|1\rangle \pm |2\rangle}{\sqrt{2}}, \quad E_{\pm} = \epsilon_0 \pm |J|.$$  

(2.9)
Here, \( \epsilon_0 \) is just the average of the two (almost equal) single-molecule transition energies. Note that when these transition energies are exactly equal, the dimer is called homogeneous. For explicitness, in this limit where the symmetric and antisymmetric wavefunctions are (approximate) eigenstates of the system, the coefficients of Equation (2.6) are given by

\[
[\phi_k(n)] = [\phi_{nk}] = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & 1 \\ 1 & -1 \end{bmatrix}.
\] (2.10)

The possibility of having the (anti)symmetric wavefunctions expresses the fact that the resonant transfer interaction causes exciton delocalization, i.e. both molecules have a non-zero probability to be excited when the energy of the incoming light is tuned to either of the eigenenergies (\( E_k \)) of the system.

### 2.2.2 Larger aggregates

The above analysis for the small model system of the dimer extends straight-forwardly to larger aggregate systems. Here, we will consider a chain-like systems only: the linear aggregate. For simplicity, we will assume that all molecular transition frequencies are equal, not allowing for disorder. Also we will only take into account nearest-neighbor interactions. A schematic representation of such an aggregate is shown in Figure 2.4.

![Schematic representation of a homogeneous aggregate consisting of N molecules, including only nearest-neighbor interactions. The transition energies are assumed equal for all molecules.](image)

Figure 2.4: Schematic representation of a homogeneous aggregate consisting of \( N \) molecules, including only nearest-neighbor interactions. The transition energies are assumed equal for all molecules.

For a linear aggregate, the electronic eigenstates \( |k\rangle \) are usually labeled \( k = 1, 2, \ldots, N \). For the homogeneous aggregate with nearest-neighbor interactions only, these eigenstates and their energies can be expressed as [14]

\[
|k\rangle = \sqrt{\frac{2}{N+1}} \sum_n \sin(\frac{2\pi nk}{N+1})|n\rangle, \quad E_k = \epsilon_0 + 2J \cos(\frac{\pi k}{N+1}).
\] (2.11)

For inhomogeneous systems or descriptions admitting long-range interactions one has to resort to numerical methods to find the eigenstates and energies of the aggregate (cf. [46], for instance).

When one assumes periodic boundary conditions, essentially linking both ends of the linear aggregate to each other, so-called Bloch wavefunctions can be introduced [46],

\[
|k\rangle = \frac{1}{\sqrt{N}} \sum_n e^{2\pi i kn/N}|n\rangle.
\] (2.12)

Allowing for nearest-neighbor interactions only and taking \( N \) odd, the accompanying energies are

\[
E_k = \epsilon_0 + 2J \cos(2\pi k/N).
\] (2.13)

We note that these energies come in degenerate pairs \( E_{\pm k} \). Due to this symmetry, the eigenstates are labeled \( k = 0, \pm 1, \pm 2, \ldots \). It depends on the number of molecules (and thus eigenstates) and the type of aggregate where the top of the band lies. Looking at a \( J \)-aggregate: for odd \( N \), the top of the band is shared by the states \( k = \pm \frac{N-1}{2} \). For an even number of molecules the top of the band resides at the energy \( E_k = E_N \), showing separate states at either side of the
2.3 Linear absorption spectra

Now that we have looked at the electronic structure of molecular aggregates, we can turn to their optical behavior. Several spectroscopic techniques – in which photons are used to illuminate a molecular system and detect its response – exist to experimentally determine this optical behavior. As we assume one-exciton states only, we consider linear techniques here, meaning that only one photon is involved in the interaction with the aggregate at a time. Two-dimensional techniques, like pump-probe spectroscopy, are, thus, out of the scope of the current work.

Some of the linear probing techniques are sensitive to polarization of the aggregate, by exciting it with polarized light, for example, linear dichroism (LD) or circular dichroism (CD). Others ignore polarization information, just exciting isotropic mixtures of a certain molecular aggregate. In the present report we focus on the (theoretical) calculation of linear absorption spectra, ignoring polarization, meaning that we try to find in what frequency range radiation energy is absorbed in a molecular aggregate (exciting electronic states in the process).

In linear spectroscopy we assume the interaction of the radiation field and the molecular system to be small with respect to the inter- and intramolecular interactions. Fermi’s Golden Rule then leads to the following expression for the absorption spectrum as a function of the frequency of the incoming light, $\omega$.

$$A(\omega) = \sum_f \sum_i \mathcal{P}_i \left| \langle f | \vec{M} \cdot \vec{e} | i \rangle \right|^2 \delta(E_f - E_i - \omega). \quad (2.14)$$

The first sum runs over all possible excited states of the system under consideration. These excited states are labeled $|f\rangle$ and they have energies $E_f$. Correspondingly, the sum over $i$ extends over the initial states, which are denoted by $|i\rangle$, having energies $E_i$. Each initial state is weighed by a Boltzmann factor, expressing the probability to find the system in that state in the first place, assuming it is in thermal equilibrium,

$$\mathcal{P}_i = \frac{\exp(-\beta E_i)}{\sum_i \exp(-\beta E_i)}. \quad \beta \equiv \frac{1}{kT}. \quad (2.15)$$

The actual argument of the sum is the square of certain matrix elements. These are the transition dipole moments of the molecular aggregate, projected along some polarization direction of the incoming light, $\vec{e}$. Their squared magnitude is referred to as the oscillator strength of the transition involved.

Note that in determining the total dipole moment of the aggregate, we assume that the total dipole operator is just the sum of single-molecule dipole operators,

$$\vec{M} = \sum_n \vec{\mu}_n (c_n^\dagger + c_n). \quad (2.16)$$

We thus apply the dipole approximation, for which it is necessary to assume that the total aggregate is small compared with respect to the wavelength of the incoming radiation (more precise: the typical exciton delocalization length should be small w.r.t. this wavelength).

A final note concerning the formula for the absorption spectrum concerns the Dirac delta function. It indicates that the absorption spectrum consists of sharp peaks, each representing a transition at a certain energy, it is a stick spectrum. The height of the peaks is determined by the (sum of the) oscillator strength at a certain energy. In reality, of course, the peaks in a spectrum are never infinitely sharp. Rather, they have a linewidth, dictated by the finite lifetime of a transition and the amount of disorder that is present in the system. These effects we do not
model, but for convenience and easy interpretation of spectra, we will take into account some homogeneous broadening by convoluting each peak with a Gaussian envelope.

Now, when speaking of molecular aggregates, it is unlikely to find such a system in an electronically excited state at room temperature as optical transition energies typically are too large: $E_f - E_i \gg kT_{room}$. Therefore, we can take as initial state the electronic ground state of the aggregate, $|i\rangle = |g\rangle$, and leave out the Boltzmann factor altogether.

Taking as final states the eigenstates of the Hamiltonian considered, as given in Equation (2.6), the transition dipole of the transition to exciton state $k$ (parallel to the polarization of the incoming field) can be expressed in the molecular dipoles as

$$\vec{\mu}_k \cdot \vec{e} = \langle k | \vec{M} | g \rangle = \mu \sum_n \phi^*_k(n) \phi_n(n).$$

Here, the expression on the right-hand side follows from the following simplification (which we will assume in all that follows): the molecular dipoles are taken to have equal magnitude, $\mu$, and are seen to be oriented parallel. The incoming field is also taken to be directed along the dipoles. When one wants to consider polarization-dependent spectroscopic techniques or one wants to the study an isotropic mixture of aggregates, the direction of polarization (or its average) should be taken into account.

Now, collecting all of the above results, we can express the normalized absorption spectrum as a sum of oscillator strengths (squared magnitude of the above transition dipoles) as follows.

$$A(\omega) = \frac{1}{N \mu^2} \sum_k |\vec{\mu}_k \cdot \vec{e}|^2 \delta(E_k - \omega) = \frac{1}{N} \sum_k \left( \sum_n \phi_k(n) \right)^2 \delta(E_k - \omega).$$

### 2.3.1 The dimer spectrum

Let us now focus on the optical response of the dimer model system. As electronically speaking there are two interesting limits in which to look at the dimer, also these limits are considered here. When the inhomogeneity (disorder) is small with respect to the electronic coupling, the symmetric and antisymmetric wavefunction of Equation (2.9) describe the system. As it turns out, in this limit the symmetric state contains all the oscillator strength, as can be calculated using the expression for the wavefunction coefficients in Equation (2.10). When considering fluorescence, this phenomenon is referred to as cooperative spontaneous emission or exciton superradiance. The antisymmetric state does not radiate and is called dark. For a $J$-aggregate such optical response is shown in the characteristic spectrum in Figure 2.5a. There the energy spacing between the symmetric and antisymmetric eigenstate is marked on the horizontal axis. This energy spacing is referred to as the exciton band width and for the dimer it is $W = 2|J|$. When the disorder increases, the so-called coherence between the two molecules is destroyed, and we end up with the spectrum in Figure 2.5b, that consists of the sum of the two single-molecule spectra.

### 2.3.2 Spectra of larger aggregates

Extending the system to a linear aggregate with parallel dipoles and nearest-neighbor couplings of strength $J < 0$, a typical spectrum as shown in Figure 2.6a can be calculated. A homogeneous system is considered here, for which the oscillator strengths are given by [14]

$$|\vec{\mu}_k|^2 = |\langle k | \vec{M} | g \rangle|^2 = \frac{1-(-1)^k}{2} \frac{2 \mu^2}{N+1} \cot^2\left( \frac{\pi k}{2(N+1)} \right).$$

The totally symmetric eigenstate ($k = 1$) contains most of the oscillator strength, being superradiant. The rest of the oscillator strength is distributed over the other odd-numbered eigenstates. All even-numbered states are dark. The exciton band width grows to $W = 4|J|$ when the number of molecules within the aggregate is increased.

It turns out that assuming periodic boundary conditions is rather convenient, for then the totally symmetric eigenstate, $k = 0$, contains all oscillator strength. A typical spectrum is shown in Figure 2.6b.
Figure 2.5: Calculated absorption spectra for the dimer in (a) the homogeneous limit and (b) the limit of large inhomogeneity. For clarity, the spectral peaks have been broadened by Gaussian line shapes of standard deviation $\sigma = 0.28$. The area under each spectrum, representing the total oscillator strength of the system per contributing molecule, is unity.

Figure 2.6: Calculated absorption spectra for the homogeneous octomer assuming (a) open boundary conditions and (b) periodic boundary conditions. Only nearest-neighbor interactions were taken into account. For clarity, the spectral peaks have been broadened by Gaussian line shapes of standard deviation $\sigma = 0.14$. The area under each spectrum, representing the total oscillator strength of the system per contributing molecule, is unity.

2.4 The Holstein Hamiltonian

So far, only isolated aggregates and their electronic structure were considered. It is clear, however, that in reality there are many more degrees of freedom than just the transitions between electronic ground and excited states. Consider, for instance, the host medium (solvent) and its influence on the aggregate in it. Effective descriptions of such an influence exist in the framework described in the previous sections. One can, for instance, include a site-dependent (Gaussian) solvent shift (also called diagonal disorder), $\Delta_n$, in each of the molecular transition energies, $\epsilon_n = \epsilon_0 + \Delta_n$, or allow for deviations from a regular aggregate geometry by including interaction disorder (off-diagonal disorder) [46].

When other effects, like the presence of certain molecular vibrations, are considered, it seems
unlikely, however, that the electronic description outlined previously is sufficient. It is the aim of this section to introduce a model that includes any such dynamical effects and allows for thermal effects to be included. One such a model consists of the following idea: all degrees of freedom that are of other nature than the electronic excitations, i.e. the vibrational degrees of freedom, are modeled by a bath consisting of quantum harmonic oscillators that are coupled to the excitons of the aggregate. This gives rise to combined electronic-vibrational excitations called \textit{polarons}. The harmonic oscillators can represent intramolecular vibrations, phonons in the medium, etc.

A specific form of this model was proposed by Holstein at the end of the 1950s \cite{30,31}. In his model, each molecule possesses a single vibrational degree of freedom. These harmonic oscillator vibrations are described by their momenta $p_n$, coordinates $x_n$ and their frequencies $\omega_n$. A unit mass is assumed for each of the oscillators.

It is assumed that the coupling between electronic excitations and vibrations, the exciton-phonon coupling, is linear in the phonon coordinate and diagonal in the electronically excited states. The effect of this coupling is modeled as follows. Both the electronic ground and excited state of each molecule are seen to be accompanied by a harmonic oscillator. The potential well of the electronically excited state is taken to be shifted with respect to the ground state potential well, however, such as to model the change in the molecular electronic configuration upon excitation. This shift is denoted by $d_n$. A schematic representation of a molecule in the Holstein model is shown in Figure 2.7.

\begin{equation}
\begin{split}
H &= \sum_{n=1}^{N} \epsilon_n |n\rangle \langle n| + \sum_{n \neq m}^{N} J_{nm} |n\rangle \langle m| \\
&\quad + \frac{1}{2} \sum_{n=1}^{N} \left( \frac{1}{2} \sum_{n=1}^{N} \left( p_n^2 + \omega_n^2 x_n^2 \right) |g\rangle \langle g| + \frac{1}{2} \sum_{n=1}^{N} \left( p_n^2 + \omega_n^2 (x_n + d_n)^2 \right) \right) |n\rangle \langle n|.
\end{split}
\end{equation}

(2.20)

Using the Dirac bra-ket notation for the electronic states, the Holstein Hamiltonian can be expressed as the following extension of the exciton Hamiltonian in Equation (2.2),

\begin{equation}
\begin{split}
x_n &= \sqrt{\frac{1}{2\omega_n}} (a_n + a_n^\dagger), \\
p_n &= -i \sqrt{\frac{\omega_n}{2}} (a_n - a_n^\dagger).
\end{split}
\end{equation}

(2.21)
Rewriting the Hamiltonian in terms of these vibrational ladder operators and again using the operator notation for the electronic levels, we obtain

$$H = \sum_n (\epsilon_n + \omega_n \lambda_n^2) c_n^\dagger c_n + \sum_{n \neq m} J_{nm} c_n^\dagger c_m + \sum_n \omega_n (a_n^\dagger a_n + \frac{1}{2})$$

$$+ \sum_n \omega_n \lambda_n (a_n^\dagger + a_n) c_n^\dagger c_n,$$  \hspace{1cm} (2.22)

where with each oscillator a unitless characteristic called the Huang-Rhys factor is involved, given by

$$\lambda_n^2 = \frac{\omega_n}{2} d_n^2.$$  \hspace{1cm} (2.23)

These Huang-Rhys factors also determine the coupling strength between an exciton and its associated vibrations, which is \(\omega_n \lambda_n\).

What is important to note, is that for each molecule the energy of the transition from the (vibrationless) electronic ground state to the electronically excited state has changed due to the coupling with phonons. Also vibrational quanta are excited in the latter state, which leads to a new transition energy called the vertical energy. It is the sum of the adiabatic energy, \(\epsilon_n\), and the relaxation energy, \(\omega_n \lambda_n^2\).

In what follows, all the oscillators are seen as replicas so that they have the same Huang-Rhys factors, \(\lambda_n^2 = \lambda^2\), and frequencies, \(\omega_n = \omega_0\).

The basis set of the exciton Hamiltonian can be extended to include the vibrational degrees of freedom. This is done by introducing wavefunctions \(|N_n\rangle\), which denote the state in which the oscillator coupled to molecule \(n\) contains \(N\) vibrational quanta. \([33]\)

$$|n\rangle \prod_m |N_m\rangle = c_n^\dagger |g\rangle \prod_m \frac{1}{\sqrt{N_m}} (a_m^\dagger)^N_m |0_m\rangle = c_n^\dagger |g\rangle \prod_m \frac{1}{\sqrt{N_m}} (a_m^\dagger)^N_m |0\rangle.$$  \hspace{1cm} (2.24)

In this formulation, \(|0\rangle\) is used to denote the total vibrational ground state of the aggregate. Note that these basis states do not in general form the eigenstates of the Holstein Hamiltonian.

As a final remark, note that the model with a general bath (containing an unspecified number of discrete modes or a continuous set of modes, that are allowed to couple to any exciton) is detailed in Appendix C.

### 2.5 Linear absorption spectra revisited

As was noted before, the eigenstates of an aggregate system determine its optical behavior. The question now is what the eigenstates of the Holstein Hamiltonian are in terms of the basis states just discussed. It is not uncommon to tackle this problem using perturbation theory, in which it is assumed that a certain term in the Hamiltonian only has a small effect on its eigenstates.

Looking at the Holstein Hamiltonian, two perturbative limits are easily identified. When the exciton-phonon coupling is small with respect to the electronic coupling, the eigenstates can be approximated by a Born-Oppenheimer product of electronic wavefunctions (specifically those treated in Equation (2.6)) and vibrational wavefunctions. On the other hand, the opposite limit in which the exciton-phonon coupling is large with respect to the electronic coupling, leads us to the case in which the latter can be ignored. So-called shifted oscillator states can be introduced as approximate eigenstates. We will see an example of this below, when speaking of a system consisting of one molecule.

Being able to select appropriate eigenstates in certain limits is convenient. It is unlikely, however, that their range of applicability is such that they are still valid in an intermediate regime of coupling in which the electronic and exciton-phonon coupling are of the same order. There, the above perturbative limits no longer hold probably. Let us turn to a short analysis of the weak electronic coupling limit, nonetheless, before we return to a discussion about the intermediate regime of couplings.
2.5.1 The monomer spectrum and vibrational progression

When regarding the single-molecule system, we are automatically led to limiting behavior of the Holstein model as electronic coupling between chromophores plays no role then. The Hamiltonian for a single molecule can be written

\[ H = (\epsilon_0 + \omega_0 \lambda^2)c^\dagger c + \omega_0 (a^\dagger a + \frac{1}{2}) + \omega_0 \lambda (a^\dagger + a)c^\dagger. \]  

(2.25)

This Hamiltonian can be diagonalized by shifting the phonon operators,

\[ a \rightarrow \tilde{a} = a - \lambda c^\dagger c, \]
\[ a^\dagger \rightarrow \tilde{a}^\dagger = a^\dagger - \lambda c^\dagger c, \]  

(2.26)

which leads to the following Hamiltonian, in which the electronic excitation and the vibrational mode are no longer coupled. Note that this Hamiltonian can be and is expressed in the old phonon operators.

\[ H = \epsilon_0 c^\dagger c + \omega_0 (a^\dagger a + \frac{1}{2}). \]  

(2.27)

The eigenstates of this Hamiltonian are the so-called shifted oscillator states, which are simple product eigenstates of an electronic excitation on the single molecule and vibrations on the oscillator to which it is coupled,

\[ |e\rangle|M\rangle = c^\dagger |g\rangle \frac{1}{\sqrt{M!}} (a^\dagger)^M |0\rangle. \]  

(2.28)

As we will see, when shifting the phonon operators, also the excitation creation and annihilation operators are affected. They are dressed with the phonon operators. Here, they should be written

\[ c \rightarrow \tilde{c} = \exp(-\lambda (a^\dagger - a))c, \]  
\[ c^\dagger \rightarrow \tilde{c}^\dagger = \exp(+\lambda (a^\dagger - a))c^\dagger. \]  

(2.29)

We now utilize these modified excitation operators in the definition of the dipole operator,

\[ \vec{M} = \vec{\mu}(\tilde{c}^\dagger + \tilde{c}). \]  

(2.30)

The normalized zero-temperature absorption spectrum for the monomer coupled to a single oscillator can then be expressed as follows.

\[ A(\omega) = \sum_{M=0}^{\infty} \left| \langle M | \exp(\lambda (a^\dagger - a)) | 0 \rangle \right|^2 \delta(\epsilon_0 + \omega_0 (M - 0) - \omega) = \exp(-\lambda^2) \sum_{M=0}^{\infty} \frac{\lambda^{2M}}{M!} \delta(\epsilon_0 + \omega_0 M - \omega). \]  

(2.31)

The sum runs over the possible states after excitation. These are the combination of the electronically excited state, \(|e\rangle\), and vibrational states with a number of quanta denoted by \(M\). Due to the temperature being zero, the initial state is taken to be the electronic ground state accompanied by zero vibrational quanta, \(|g\rangle|N\rangle = |g\rangle|0\rangle\). The expression for the vibrational overlap integrals, \(\langle M | \exp(\lambda (a^\dagger - a)) | 0 \rangle\), is evaluated in Appendix B.3.

We see that the oscillator strength of the single molecule, that originally was located in one peak at energy \(\omega = \epsilon_0\), is now distributed over several peaks having a Poisson distribution of parameter \(\lambda^2\). This distribution of oscillator strength is called vibrational progression and is shown in Figure 2.8 for several values of \(\lambda\). This simple system, without electronic coupling, serves as an example as to what happens when exciton-phonon coupling is introduced: vibrational structure is added to the absorption spectrum.
2.5 Linear absorption spectra revisited

Figure 2.8: Calculated absorption spectra for the monomer for several values of the Huang-Rhys factor. For clarity, the spectral peaks have been broadened by Gaussian line shapes of standard deviation $\sigma = 0.28$. The area under each spectrum, representing the total oscillator strength of the system, is unity.

Although other methods like direct numerical diagonalization exist, essentially we applied a polaron transformation to the single-molecule Hamiltonian above to diagonalize it (the details of this transformation are explained in the next chapter). For the monomer this transformation exactly led us to the limit in which shifted oscillator states could be introduced and no perturbation theory was necessary to find the absorption spectrum. This serves as motivation to use a polaron transformation approach to find the optical response of larger systems involving exciton-phonon coupling as well, and we will start to do so in the next chapter.
Chapter 3

The adapted polaron transformation approach

In the current chapter a new method is proposed for the calculation of the optical response of aggregate systems described by the Holstein Hamiltonian. This method utilizes a modified form of the polaron transformation or Lang-Firsov transformation [32]. The polaron transformation is a canonical transformation that shifts the harmonic oscillator potential wells that are associated with the electronically excited states of the molecules comprising an aggregate, as we already saw for the case of a single molecule. It thus serves as a translation operator (in momentum space), altering the coupling between each exciton and the single vibrational mode it is coupled to.

It should be noted that for aggregates, in which electronic coupling does play a role, the polaron transformation does not provide us with an exactly diagonalized Hamiltonian, as was the case for the monomer. Therefore, to be able to go beyond the usual perturbative approaches, a more general form of the polaron transformation is applied. It allows for variable shifts, ranging from performing no shift at all to performing a full displacement of the excited state oscillators. Such a transformation is usually referred to as the partial polaron or variational polaron transformation.

In what follows, a variational polaron transformation will be applied to the Holstein Hamiltonian. The variational character of it allows us to minimize the magnitude of the perturbation term that results when utilizing a mean field approach. This optimization is performed through a minimization of the free energy of the system with respect to the variational parameter of the transformation. It is the aim of this chapter to outline the details of this method, with which we aim to study the optical response of an aggregate within the Holstein model and reproduce the well-known perturbative limits, but, more importantly, be able to probe the intermediate regime of couplings. Note that results for a more general exciton-phonon coupling are given in Appendix C.

3.1 Transforming the Hamiltonian

The model Hamiltonian for an \( N \)-molecule aggregate in which each molecule is coupled to a local vibration was introduced in the previous chapter in Equation (2.22) and it will be used as the starting point here, assuming equal vibrational frequencies (\( \omega_n = \omega_0 \)) and equal Huang-Rhys factors (\( \lambda_n = \lambda \)),

\[
H = \sum_{n=1}^{N} (\epsilon_n + \omega_0 \lambda^2) c_n^{\dagger} c_n + \sum_{n \neq m} J_{nm} c_n^{\dagger} c_m + \omega_0 \sum_{n=1}^{N} (a_n^{\dagger} a_n + \frac{1}{2}) + \omega_0 \lambda \sum_{n=1}^{N} (a_n^{\dagger} + a_n) c_n^{\dagger} c_n.
\]  

(3.1)

As a first step in the transformation of the Hamiltonian we exploit a symmetry of it: we rewrite the vibrational modes in a different basis, turning them into collective modes. We do this in such
a way that one of the modes can be written as the *totally symmetric* combination of the original modes. The reason for doing this will become clear soon; it turns out that such a totally symmetric mode can be treated in an exact fashion using a full polaron transformation. Rewriting the modes is done via an orthogonal transformation,

\[ a_q = \sum_n \psi_q(n)a_n. \]  

(3.2)

The coefficients of this transformation, the \( \psi_q(n) \)'s, are taken to have the following properties:

1. The \( \psi_q(n) \) should be real.
2. The \( \psi_q(n) \) should obey the orthonormality condition \( \sum_n \psi_q(n)\psi_q'(n) = \delta_{q,q'} \).
3. For one particular mode, say \( q = 0 \), the coefficients should be equal: \( \psi_0(n) = \psi_0(n') \).

These conditions are taken, because (1) allows us to keep the real form of the Hamiltonian we have now, not complicating its notation or transformation with complex numbers; (2) makes sure we apply an orthogonal transformation, helping us in the calculation of certain properties later on; condition (3) creates a totally symmetric mode.

A particular choice for the coefficients \( \psi_q(n) \) that suits our purpose is given by a real representation of the Bloch wavefunction coefficients of Equation (2.12). Using \( q \) to label the new modes (instead of \( k \) to label the excitons), we have

\[ \psi_q(n) = \begin{cases} 
\frac{1}{\sqrt{N}} & \text{if } q = 0 \\
\frac{1}{\sqrt{2}} \cos\left(\frac{2\pi qn}{N}\right) & \text{if } q > 0 \\
\frac{1}{\sqrt{2}} \sin\left(-\frac{2\pi qn}{N}\right) & \text{if } q < 0
\end{cases} \]  

(3.3)

when \( N \) is odd. For the case that \( N \) is even an additional rule holds:

\[ \psi_q(n) = \frac{1}{\sqrt{N}}(-1)^{n+1} \text{ if } q = \frac{N}{2}. \]  

(3.4)

The new set of modes described by these coefficients, \( \psi_q(n) \), allows us to cast the Holstein Hamiltonian in the following form. Note that the orthonormality condition, condition (2) in the above list, is used in the transformation.

\[
H = \sum_n (\epsilon_n + \omega_0 \lambda^2) c_n^\dagger c_n + \sum_{n \neq m} J_{nm} c_n^\dagger c_m + \omega_0 \lambda \sum_q (a_q^\dagger a_q + \frac{1}{2}) \\
+ \omega_0 \lambda (a_0^\dagger + a_0) \sum_n \frac{1}{\sqrt{N}} c_n^\dagger c_n + \omega_0 \lambda \sum_{q \neq 0} (a_q^\dagger + a_q) \sum_n \psi_q(n) c_n^\dagger c_n
\]  

(3.5)

Here, the \( q \)'s label the newly-chosen collective modes according to \( q = 0, \pm 1, \pm 2, \ldots \). For clarity, the term describing the coupling between excitons and the mode \( q = 0 \) has been split off.

Note that due to the symmetrization of modes, effectively we have introduced exciton-phonon coupling between each molecular excitation and collective mode. The strength of this interaction, between an excitation at molecule \( n \) and collective mode \( q \) say, is given by \( \omega_0 \lambda \psi_q(n) \).

### 3.1.1 Polaron transforming the Hamiltonian

We now perform a *full* polaron transformation of the Hamiltonian,

\[
\tilde{H} = e^{G} He^{-G} = H + [G,H] + \frac{1}{2!} [G,[G,H]] + \ldots
\]  

(3.6)
The significance of the basic operators for the annihilation and creation of vibrational quanta on the collective modes we performed is exact: the molecular interaction is not affected by the transformation, that is, the application of the transformation has the following effect on the electronic excitation operators.

Transformation of the ladder operators for the annihilation and creation of vibrational quanta on collective mode \( q \) gives

\[
\tilde{a}_q = a_q - \delta_{q0} \frac{\lambda}{\sqrt{N}} \sum_n c_n^\dagger c_n, \quad \tilde{c}_q^\dagger = c_q^\dagger - \delta_{q0} \frac{\lambda}{\sqrt{N}} \sum_n c_n^\dagger c_n.
\]

These results can be derived using Appendix B and they allow us to write the transformed Hamiltonian, again expressed in the original excitation and vibration creation and annihilation operators, in the following way.

\[
\tilde{H} = \sum_n (\epsilon_n + \omega_0 \lambda^2 (1 - \frac{1}{N})) c_n^\dagger c_n + \sum_{n \neq m} J_{nm} c_n^\dagger c_m + \omega_0 \sum_q (a_q^\dagger a_q + \frac{1}{2})
\]

\[
+ \omega_0 \lambda \sum_{q \neq 0} (a_q^\dagger + a_q) \sum_n \psi_q(n) c_n^\dagger c_n.
\]

First of all, we note that the exciton-phonon coupling term associated with the totally symmetric mode, \( q = 0 \), has vanished. This is expected because each electronic excitation couples to this mode in the same way. Secondly, and more importantly, we note that the particular transformation we performed is exact: the molecular interaction is not affected by the transformation, that is, the excitons are not dressed with the phonon of mode \( q = 0 \). This is also due to the nature of the totally symmetric mode, which is shifted by the same amount with respect to each electronically excited state. Furthermore, the terms involving other modes than the totally symmetric one are not affected. These other modes are now treated using a partial polaron transformation that is defined by the generator

\[
G = \rho \sum_{q \neq 0} (a_q^\dagger - a_q) \sum_n \psi_q(n) c_n^\dagger c_n.
\]

This transformation has the following effect on the electronic excitation operators.

\[
\tilde{c}_n = c_n \exp(-\rho \sum_{q \neq 0} \psi_q(n) (a_q^\dagger - a_q)), \quad \tilde{c}_n^\dagger = c_n^\dagger \exp(+\rho \sum_{q \neq 0} \psi_q(n) (a_q^\dagger - a_q)).
\]

The basic operators for the annihilation and creation of vibrational quanta on the collective modes transform due to it as

\[
\tilde{a}_q = a_q - (1 - \delta_{q0}) \rho \sum_n \psi_q(n) c_n^\dagger c_n, \quad \tilde{a}_q^\dagger = a_q^\dagger - (1 - \delta_{q0}) \rho \sum_n \psi_q(n) c_n^\dagger c_n.
\]

For all modes (other than the totally symmetric one) the same variational parameter, \( \rho \), has been used. It is restricted to lie in the interval

\[
0 \leq \rho \leq \lambda.
\]

The significance of \( \rho \) for the variational transformation is such, that a value of \( \rho = 0 \) corresponds to the case in which no transformation is applied. For \( \rho = \lambda \) the combined effect of the above generators is equivalent to that for a full polaron transformation of all the modes.
In what follows, \( \rho \) is seen as an optimization parameter, that allows us to select a system with a certain shift of the common modes associated with the electronically excited state oscillator potential wells. In principle, one can pick a different optimization parameter for each coupling term between an electronic excitation and a mode. The algebra for that case is worked out in Appendix C. Here, however, the actual optimization is only done for a single parameter, as outlined below. This is done for simplicity, but also to show the power of the current method, which will be referred to as the adapted polaron transformation approach (or APTA, for short), which is able to produce accurate results using just a single parameter.

Successively applying the full polaron transformation of the symmetric mode and the variational polaron transformation of the other modes, provides us with the following transformed Hamiltonian.

\[
\tilde{H} = \sum_n \tilde{\varepsilon}_n c_n^\dagger c_n + \sum_{n \neq m} \tilde{J}_{nm} c_n^\dagger c_m + \omega_0 \sum_q (a_q^\dagger a_q + \frac{1}{2}) \\
+ \omega_0 (\lambda - \rho) \sum_{q \neq 0} (a_q^\dagger + a_q) \sum_{n} \psi_q(n) c_n^\dagger c_n.
\]  

(3.15)

Here, the shifted molecular transition energies and the environment-dressed electronic couplings are given by

\[
\tilde{\varepsilon}_n = \varepsilon_n + \omega_0 (\lambda - \rho)^2 (1 - \frac{1}{N}), \\
\tilde{J}_{nm} = J_{nm} \exp(\rho \sum_{q \neq 0} (\psi_q(n) - \psi_q(m))(a_q^\dagger - a_q)).
\]  

(3.16)

3.1.2 Mean field approach

We would like to find the eigenstates of the Holstein Hamiltonian, and thereby the optical response of the system it describes. So far, we have obtained the above transformed form of that Hamiltonian. Due to the presence of the environment-dressed electronic coupling term and the term describing the (reduced) coupling between electronic excitations and vibrational modes other than the totally symmetric one, the eigenstates of this Hamiltonian still are of mixed (electronic-vibrational) origin. Therefore, we will look at it in a mean field approach, only taking into account the average effect of the dynamical degrees of freedom have on the aggregate we study. Assuming the bath is in thermal equilibrium, this is done by performing an average (a trace) over the bath coordinates. The details of this procedure can be found in Appendix C.1.2 and they lead to effective or renormalized electronic interactions that are given by

\[
\langle \tilde{J}_{nm} \rangle = J_{nm} \exp(-\rho^2 \coth(\frac{\omega_0}{2kT})).
\]  

(3.17)

It should be noted that even in the zero-temperature limit, for which \( \coth(\frac{\omega_0}{2kT}) \approx 1 \), the presence of vibrations reduces the original electronic coupling.

We now split the Hamiltonian in a zeroth-order (mean field) term and a perturbation term, \( \bar{H} = \bar{H}^0 + V \). The zeroth-order Hamiltonian, which we will consider for the calculation of the optical response, is given by

\[
\bar{H}^0 = \sum_n \tilde{\varepsilon}_n c_n^\dagger c_n + \sum_{n \neq m} \langle \tilde{J}_{nm} \rangle c_n^\dagger c_m + \omega_0 \sum_q (a_q^\dagger a_q + \frac{1}{2}).
\]  

(3.18)

This leaves us with the perturbation term that describes the fluctuations of the molecular interactions due to the presence of the bath and the remaining coupling between excitons and phonons,

\[
V = \sum_{n \neq m} [\tilde{J}_{nm} - \langle \tilde{J}_{nm} \rangle] c_n^\dagger c_m + \omega_0 (\lambda - \rho) \sum_{q \neq 0} (a_q^\dagger + a_q) \sum_{n} \psi_q(n) c_n^\dagger c_n.
\]  

(3.19)

In the following section, we will look into a method to minimize the magnitude of this perturbation term, having to do with optimization of the variational parameter, \( \rho \). Note that this magnitude...
is not made quantitative in the current project. It would be interesting however to look into, for instance, the mean square average of the chosen perturbation term (averaging over the bath coordinates, that is), to get an estimate of its magnitude. Cf. [42] for the results and analysis of such a calculation.

The virtue of the current choice of a zeroth-order Hamiltonian is that electronic excitations and phonons are no longer coupled. Therefore, the eigenstates of this Hamiltonian can be written as product states of electronic and vibrational wavefunctions. Remembering the eigenfunctions for a simple aggregate as given in Equation (2.6) and the wavefunctions that serve as a basis for the Holstein Hamiltonian in Equation (2.24), we have a new set of such product-type eigenstates that are given by

$$|k\rangle \prod_q |N_q\rangle = \sum_n \phi_k(n)|n\rangle \prod_q \frac{1}{\sqrt{N_q}}(a_q^\dagger)^{N_q}|0_q\rangle = \sum_n \phi_k(n)c_n^\dagger|g\rangle \prod_q \frac{1}{\sqrt{N_q}}(a_q^\dagger)^{N_q}|0_q\rangle. \quad (3.20)$$

Here, the coefficients used to diagonalize the electronic states, \(\phi_k(n)\), are not to be confused with the \(\psi_q(n)\) that were used to transform the vibrational modes. Also it is noted that the product ranges over the collective modes, labeled by \(q\).

### 3.2 Minimization of the free energy

One of the methods to fix the transformation parameter, \(\rho\), is to perform a minimization of the Helmholtz free energy of the system involved. Such a variational approach, in which the Bogoliubov upper bound of the free energy is minimized, is outlined in Reference [33], from which the essentials for our method are outlined in Appendix C.2.

The bound to the free energy of the aggregate described by the zeroth-order Hamiltonian given above involves the trace over its basis states,

$$A \leq A_B = -kT \ln \text{Tr}\{\exp(-\beta \tilde{H}_0)\}. \quad (3.21)$$

Picking the orthonormal set of eigenstates given in Equation (3.20) and using their product nature, the bound to the free energy can be expressed as the sum of two contributions, one due to the part of the Hamiltonian describing the electronic system and the other due to the bath.

$$A_B = -kT \ln \text{Tr}\{\exp(-\beta \tilde{H}_0)\} - kT \ln \text{Tr}\{\exp(-\beta H_b)\} \equiv A_{B,e} + A_{B,b} \quad (3.22)$$

Diagonalizing the electronic part of the Hamiltonian so as to obtain the electronic eigenstates described in Equation (2.6) and using the cyclic property of the trace, the contribution to the free energy due to the aggregate can be computed to be

$$A_{B,e} = -kT \ln \sum_k \exp(-\beta E_k), \quad (3.23)$$

where the \(E_k\) are the energies of the exciton eigenstates. Note that these energies implicitly depend on the variational parameter, \(\rho\), via its appearance in the single-molecule transition energies and the renormalized electronic couplings of Equation (3.16).

The trace over the bath Hamiltonian is the well-known partition function of a set of \(N\) quantum harmonic oscillators (one for each of the \(N\) molecules of the aggregate) with variable particle number,

$$\text{Tr}\{\exp(-\beta H_b)\} = \left(\frac{\exp(-\beta \omega_0)}{1 - \exp(-\beta \omega_0)}\right)^N. \quad (3.24)$$

Having obtained an expression for the upper bound of the free energy of the system we consider, we would like to minimize it with respect to the variational parameter, thereby also reducing
Chapter 3. The adapted polaron transformation approach

the free energy itself, according to the left-hand part of Equation (3.21). This minimization, or optimization, lies solely in the minimization of the electronic contribution to the free energy bound, \( A_{B,e} \), as the vibrational contribution, \( A_{B,b} \), has no \( \rho \)-dependence. We thus acquire the following operational method to fix the variational parameter.

\[
\frac{dA_{B,e}}{d\rho} = 0, \tag{3.25}
\]

where one should take care in selecting a minimum.

It should be mentioned here that even for the simple system of the dimer, this equation leads to a self-consistency equation for the parameter \( \rho \) due to the intricate way in which the molecular transition energies and the renormalized interactions of Equation (3.16) depend on it. We will discuss this specific example now by first inspecting the eigenstates and energies of the Hamiltonian in Equation (3.18) for the case of the dimer. In analogy with the results of Equation (2.8), the electronic energy levels of this dimer are given by

\[
E_k = \epsilon_1 + \epsilon_2 + \omega_0 (\lambda - \rho)^2 \pm \eta. \tag{3.26}
\]

Using these eigenstate energies, we can perform the optimization procedure for the following expression of the free energy, that derives from Equation (3.23).

\[
A_{B,e} = \epsilon_1 + \epsilon_2 + \omega_0 (\lambda - \rho)^2 - kT \ln(2 \cosh(\beta \eta)). \tag{3.27}
\]

Minimizing this expression with respect to the partial polaron transformation parameter, we obtain an equation for it that must be solved for self-consistently,

\[
\rho = \lambda \left[ 1 + \frac{2(J)^2}{\omega_0} \tanh(\frac{\eta}{kT}) \coth(\frac{\omega_0}{2kT}) \right]^{-1}. \tag{3.28}
\]

Note that this expression nicely uncovers the important (unitless) parameters of the system, being \( J/\omega_0, \lambda, kT/\omega_0 \) and \( \Delta/|J| = |\epsilon_2 - \epsilon_1|/|J| \).

3.3 Linear absorption spectra

To predict the optical response of the system described using the Hamiltonian from the adapted polaron transformation approach given in Equation (3.18), we (again) use the general expression for the linear absorption spectrum of Equation (2.14) as a starting point. For the initial and final states we take product wavefunctions of the form

\[
|i\rangle = |g\rangle \prod_q |N_q\rangle, \quad |f\rangle = |k\rangle \prod_q |M_q\rangle. \tag{3.29}
\]

Analogous to the case without vibrations, the dipole operator of the system under consideration that mediates the transitions between these initial and final states is taken to be the sum of single-molecule dipole operators. Here, however, a key point is to use the transformed single-molecule dipole operators following from Equations (3.8) and (3.12), in analogy to what was done for the monomer dipole operator in Section 2.5.1. We thus take as total dipole operator

\[
\tilde{M} = \sum_n \tilde{\mu}_n (\tilde{c}_n^\dagger + \tilde{c}_n^\prime)
\]

\[
= \sum_n \tilde{\mu}_n (c_n^\dagger \exp(+\sqrt{\frac{\lambda}{N}}(a_0^\dagger - a_0)) \exp(+\rho \sum_{q\neq 0} \psi_q(n)(a_q^\dagger - a_q))
\]

\[
+ c_n \exp(-\sqrt{\frac{\lambda}{N}}(a_0^\dagger - a_0)) \exp(-\rho \sum_{q\neq 0} \psi_q(n)(a_q^\dagger - a_q))). \tag{3.30}
\]
The normalized absorption spectrum corresponding to the $N$-molecule Holstein Hamiltonian from the adapted polaron transformation approach can now be expressed as

$$A(\omega) = \frac{1}{N} \sum_k \sum_{\{M\}} \sum_{\{N\}} P_{\{N\}} \cdots$$

$$\cdots \sum_n \phi_k(n) \langle M_0 | \exp(\frac{\omega k}{\sqrt{N}} (a_0^+ - a_0)) | N_0 \rangle \prod_{q \neq 0} \langle M_q | \exp(\rho \phi_q(n)(a_q^+ - a_q)) | N_q \rangle \cdots$$

$$\cdots \delta(E_k + \omega_0 \sum_q (M_q - N_q) - \omega).$$

(3.31)

The sums in the upper line run over the final electronically excited states ($k$) and the final ($\{M_q\}$) and initial ($\{N_q\}$) configurations of oscillators, i.e. all the possible ways in which to distribute a variable number of vibrational quanta over the harmonic oscillators.

The $P_{\{N\}}$ represents the temperature-dependent Boltzmann factor for any particular initial vibrational state, expressed in full as

$$P_{\{N\}} = \frac{\exp(-\beta \omega_0 \sum_q N_q)}{\sum_{\{N\}} \exp(-\beta \omega_0 \sum_q N_q)}.$$  \hspace{1cm} (3.32)

The transition dipole contains factors involving the electronic eigenstates of Equation (3.18) (this information is in the diagonalization coefficients $\phi_k(n)$), and vibrational overlap integrals of the form $\langle M | \exp(\lambda (a^+ - a)) | N \rangle$, as are calculated in Section B.3.

When zero-temperature absorption is considered, the Boltzmann factor dictates that the initial number of vibrational quanta on each common mode is set to zero, $N_q = 0$. Then, due to the fact that each oscillator has the same frequency, many transitions occur at the same energy and the above formula for the absorption spectrum can be greatly simplified. This is done by rewriting the sum over the final vibrational configurations, $\{M_q\}$,

$$\sum_{\{M\}} = \sum_{M=0}^{\infty} \sum_{\sum M_q = M} \cdots.$$

(3.33)

The restriction for the second sum indicates that it runs over a smaller set of permutations, namely, the possibilities to distribute a fixed number of $M$ quanta over the $N$ collective vibrational modes. Explicitly performing this sum using a trick outlined in Appendix C.1.2, we obtain the zero-temperature absorption spectrum as the following sum of intensities.

$$A(\omega)_{T=0} = \sum_k \sum_{M=0}^{\infty} I^k_{0-M} \delta(E_k + M \omega_0 - \omega).$$

(3.34)

The intensities $I^k_{0-M}$ give the oscillator strength for electronic excitation to exciton state $|k\rangle$ accompanied by what is called a $0-M$ transition of the harmonic oscillators. This $0-M$ transition signifies that the electronic ground state harmonic oscillators contain no vibrational quanta, whereas $M$ vibrational quanta are distributed over the electronically excited state oscillators. These intensities are given by

$$I^k_{0-M} = \frac{1}{N} \exp(-\frac{\lambda^2 + (N-1)\rho^2}{N}) \frac{1}{M!} \left[ \frac{\lambda^2 + (N-1)\rho^2}{N} \right]^M + \frac{\lambda^2 \rho^2}{N} \sum_{n \neq n'} \phi_k^*(n) \phi_k(n').$$

(3.35)

Both the wavefunction coefficients from the diagonalization of the electronic states, the $\phi_k(n)$, and the variational parameter, $\rho$, have a clear influence on the distribution of oscillator strength over the different peaks.

The above formulas for the absorption spectrum of a Holstein system at finite and zero temperature constitute the final result of this chapter. Several specific cases of it will be analyzed in the next, focusing on the model system of the dimer.
Chapter 4

Results and discussion

Now that in the previous chapter a new method has been proposed to calculate absorption spectra, let us turn to the particular results it predicts. A detailed analysis is presented of the influence of several parameters on these spectra. These parameters are the nearest-neighbor electronic coupling between monomers in the aggregate, $J$; the Huang-Rhys factor, that characterizes the coupling between electronic excitations and vibrations, $\lambda^2$; the amount of disorder that is present in the aggregate system, $\Delta$; and temperature, $T$. First, in the next section the structure of absorption spectra at zero temperature is studied, as the expression we obtained for it is particularly transparent. Section 4.2 provides the results for absorption at finite temperatures, leading to interesting observations of its influence on the optical properties of an aggregate.

Note that in what follows, we will express energies ($J$, $kT$ and $\Delta$) in terms of the vibrational frequency $\omega_0$, obtaining four unitless characteristics of the system when the Huang-Rhys factor is also included.

4.1 Zero-temperature absorption

The starting point of this section is the expression for the zero-temperature absorption spectrum that was derived using APTA, for a molecular aggregate coupled to local vibrations. It is given in Equations (3.34) and (3.35). Below, we will look at specific systems (sets of parameters) to see what kind of spectra the proposed method returns. These are compared to spectra that are produced using the two-particle approximation [27,28,38–40]. In the latter method, the basis set of the Holstein Hamiltonian is approximated by allowing for so-called one- and two-particle states only. Each one-particle state consists of an electronic excitation at a certain molecule, accompanied by some vibrational quanta on the oscillator it is coupled to. A two-particle state is an extension of a one-particle state, allowing for one additional (ground state) oscillator to be vibrationally excited (this oscillator belongs to a different molecule than where the electronic excitation is located). Note that for the dimer the two-particle approximation is exact, up to a cut-off imposed on the number of vibrational quanta that are taken into account. It thus allows for a full numerical diagonalization of the dimer Holstein Hamiltonian.

Obtaining results for the dimer that agree remarkably well with the two-particle approximation, we compare results from APTA to other polaron transformation methods, to show that a careful choice of transformation parameters had to be made to get good results.

4.1.1 The dimer spectrum

For the dimer, the zero-temperature absorption spectrum formula from the previous chapter reduces to the following sum of intensities.

$$A(\omega) = \sum_k \sum_{M=0}^{\infty} I_k^M \delta(E_k + M\omega_0 - \omega). \quad (4.1)$$
Again the intensities are labeled by $k$ and $M$, and they give the oscillator strength for the transition from the vibrationless electronic ground state to exciton state $|k\rangle$ with $M$ vibrational quanta distributed over the aggregate’s collective modes. Their expression is

$$I^k_{0\rightarrow M} = \frac{1}{2} \exp\left(-\frac{\lambda^2 + \rho^2}{2}\right) \frac{1}{M^!} \left[\frac{\lambda^2}{2}\right]^M + 2 \phi_k(1) \phi_k(2) \left[\frac{\lambda^2}{2}\right]^M].$$ (4.2)

It is assumed that the wavefunctions coefficients from the diagonalization of the electronic states, the $\phi_k(n)$, are real, here. Note that the total oscillator strength of all transitions is unity.

A different, but equivalent expression that is more convenient to apply in the limit of large electronic coupling, can be obtained when it is noted that in the general formula for the absorption spectrum, given in Equation (3.31), the vibrational overlap integral for the totally symmetric mode can be taken out of the square. Substituting $N_+ = N_- = 0$, but leaving the sum over the number of quanta that are on both common modes after excitation, given by $M_+$ and $M_-$, we obtain

$$A(\omega) = \sum_k \sum_{M_+ = 0}^\infty \sum_{M_- = 0}^\infty I^k_{0\rightarrow M_+ M_-} \delta(E_k + \omega_0(M_+ + M_-) - \omega),$$ (4.3)

for intensities corresponding to an electronic transition to exciton state $|k\rangle$ and a $0 - M_+ (0 - M_-)$ transition of the symmetric (antisymmetric) collective mode,

$$I^k_{0\rightarrow M_+ M_-} = \frac{1}{2} \exp\left(-\frac{\lambda^2 + \rho^2}{2}\right) \frac{1}{M^!} \left[\frac{\lambda^2}{2}\right]^M_+ \frac{1}{M^!} \left[\frac{\lambda^2}{2}\right]^M_- + 2 \phi_k(1) \phi_k(2) \left[\frac{\lambda^2}{2}\right]^M].$$ (4.4)

### Limiting cases

In this small section we look at the behavior of the dimer spectrum in certain limits, namely the perturbative limits of the original Holstein Hamiltonian. For simplicity we will set the disorder $\Delta = |\epsilon_2 - \epsilon_1| = 0$. It is clear from the Holstein Hamiltonian that the nature of the eigenstates now is determined by a competition between the electronic coupling and the exciton-phonon coupling, of which the latter is characterized by an interaction strength $\lambda\omega_0$.

i) $|J| \gg |\lambda\omega_0|$. In the limit in which the electronic coupling is large with respect to the exciton-phonon coupling we make the following observation. Having weak-exciton phonon coupling, we expect that no large shifts of the oscillators have to be applied so that $\rho \approx 0$ (we will see that this is indeed the case when investigating the free energy minimization in this limit). For this value of $\rho$, it follows from Equation (4.4), that only the symmetric electronic state, for which $2 \phi_+(1) \phi_+(2) = 1$, has oscillator strength. Also, no excitation of the antisymmetric vibrational mode can occur ($M_- = 0$). We conclude that the antisymmetric electronic eigenstate and antisymmetric collective mode are not important for the absorption spectrum. The absorption spectrum can be derived to be

$$A(\omega) \approx \exp\left(-\frac{1}{2} \lambda^2\right) \sum_{M_+ = 0}^\infty \frac{1}{M^!} \left[\frac{\lambda^2}{2}\right]^M_+ \delta(E_+ + M_+ \omega_0 - \omega).$$ (4.5)

All oscillator strength is contained in transitions to the symmetric electronic eigenstate. The presence of vibrations causes this oscillator strength to be distributed over several peaks: vibrational progression is observed when the value of $\lambda^2$ is large enough. This vibrational progression shows exchange narrowing, the parameter of the Poisson distributions for the vibrational progression is reduced to $\lambda \to \lambda^* = \frac{\lambda^2}{2}$.

ii) $|\lambda\omega_0| \gg |J|$. The limit in which the exciton-phonon coupling supersedes the electronic coupling can be seen as the single-molecule limit, as can be derived from Equations (4.1) and (4.2). We expect the shifted oscillator states that we encountered before to hold in this regime. Therefore, we expect $\rho \approx \lambda$. In the limit currently investigated $E_+ \approx E_- \approx \epsilon_0$, and the peaks corresponding to either eigenstate (almost) overlap, causing a normalized spectrum that seemingly consists of two single-molecule contributions,

$$A(\omega) \approx \exp\left(-\lambda^2\right) \sum_{M = 0}^\infty \frac{1}{M^!} \lambda^{2M} \delta(\epsilon_0 + M\omega_0 - \omega).$$ (4.6)
4.1 Zero-temperature absorption

The homogeneous dimer

Having discussed the optical behavior of the dimer system in the ordinary perturbation limits of the Holstein Hamiltonian, let us explicitly go into calculating spectra for the homogeneous dimer for a larger range of parameters, including the intermediate coupling regime where electronic and exciton-phonon coupling are of the same order.

As the absorption spectra following from APTA depend on the value of the variational parameter, let us investigate the behavior of the free energy minimization for the homogeneous dimer at zero temperature. When any of the parameters describing the system are changed, the electronic coupling and the Huang-Rhys factor in this case, the free energy is effected. Due to this its dependence on the variational parameter changes, leading to a different position of the minimum. Figure 4.1 shows the typical way in which the Bogoliubov bound of the free energy depends on the variational parameter, \( \rho \), for several values of the electronic coupling in this system. The Huang-Rhys factor is set to \( \lambda^2 = 1.0 \).

Figure 4.1: Graphs of the Bogoliubov bound of the free energy for a homogeneous dimer at zero temperature, showing the typical dependence on the variational parameter, \( \rho \), when the electronic coupling is varied. The strength of the electronic coupling, \( J \), is chosen differently in each figure, where it is given in units of the vibrational energy quantum, \( \omega_0 \). The Huang-Rhys factor is taken \( \lambda^2 = 1.0 \).

Indeed this behavior can be seen when the free energy is investigated for a larger range of values of the electronic coupling. Figure 4.2a shows how the variational parameter that results from the minimization of the free energy depends on the electronic coupling strength for constant \( \lambda^2 = 1.0 \). The ratio of the renormalized and original interactions (i.e., the renormalization factor) that results from this optimization parameter changes is shown in Figure 4.2b. It can be seen that the effective electronic interaction is tending towards the original interaction when the latter increases. This is the exciton limit.

Having analyzed what values of \( \rho \) are to be taken for different values of the electronic coupling within the homogeneous dimer, let us turn to the spectra that can be obtained from Equations (4.1) and (4.2). Figure 4.3 shows such spectra for several values of the electronic coupling resulting from APTA, which are compared to those coming for a full numerical diagonalization of the Hamiltonian. The Huang-Rhys factor is taken to be unity in each spectrum, \( \lambda^2 = 1.0 \). The details of some of these spectra are shown in Figure 4.4.

The two spectra for the smallest values of \( J \) in Figures 4.3a and 4.3b clearly show the single-molecule limit that was discussed before. This is verified by the spectrum in Figure 4.4a that shows that each eigenstate contributes exactly the same to the total spectrum. The spectra in Figures 4.3g, h and i show the exciton limit. Only the symmetric electronic eigenstate contains oscillator strength there, as can be seen in the spectrum of Figure 4.4c. This oscillator strength is distributed over a vibrational progression of peaks with an effective Huang-Rhys factor of \( \frac{\lambda^2}{2} \).
Figure 4.2: Graphs showing the result of the minimization of the Bogoliubov bound of the free energy for a homogeneous dimer at zero temperature when the electronic coupling strength is increased. The Huang-Rhys factor is taken $\lambda^2 = 1.0$. Figure (a) shows the resulting value of the optimization parameter, $\rho$, in terms of its maximal value, $\lambda$. Figure (b) shows the resulting value of the renormalization factor, being the ratio of the renormalized (effective) electronic interaction, $\langle \tilde{J} \rangle$, and the original interaction strength, $J$.

The spectrum where the deviation of both methods seems to be largest, Figure 4.3c, is investigated further in the spectrum of Figure 4.4b, where the contribution from both eigenstates within APTA are plotted. We observe that the peak at lowest energy, that originates from the transition from the vibrationless electronic ground state to the symmetric eigenstate without vibrations, is positioned very accurately, and also its height matches the result coming from the full numerical diagonalization. The other peaks contributing to this eigenstate’s spectrum, coming from transitions involving a change in the number of vibrational quanta, seem to be too low. We conclude that the antisymmetric electronic eigenstate borrows too much of the oscillator strength of the symmetric electronic eigenstate. Also the former state’s peak positions are predicted to be at too low energies.

Apart from these discrepancies the results of both methods match remarkably well. Most of the peak positions and heights are predicted accurately by APTA, also in the intermediate regime of couplings where $|J| \approx |\lambda|\omega_0$ (Figures 4.3d to f).

When the Huang-Rhys factor is varied, the behavior of the free energy minimization is altered. Figure 4.5 shows the dependence of the variational parameter and the renormalization factor on the value of $\lambda$ for several values of the electronic coupling. It can be seen that upon increase of $\lambda$, at a certain point the electronic interaction is reduced heavily by the presence of vibrations. This is the limit in which the exciton-phonon coupling determines the eigenstates of the system: the shifted oscillator states.

Absorption spectra coming from APTA and a full numerical diagonalization of the Hamiltonian are shown for several values of $\lambda^2$ and $J$ in Figure 4.6. The three spectra at the top show the single-molecule spectra, resulting when $J = 0$ is taken, and they can be compared to the monomer spectra in Figure 2.8. The opposite limit, that of strong electronic coupling, is shown in the fourth row. The motional narrowing of vibrational structure can be clearly observed there, as follows from a comparison of Figures 4.6a and k, and b and l. Again, although some discrepancies can be found, the spectra of both methods match pretty well. This is also the case for different combinations of $J$ and $\lambda^2$ than those shown.
Figure 4.3: Calculated zero-temperature absorption spectra for the homogeneous dimer following from the adapted polaron transformation approach (APTA, in blue) and the two-particle approximation (TPA, in black). The strength of the electronic coupling, $J$, is varied and it is given in units of $\omega_0$ in each spectrum. The Huang-Rhys factor is taken $\lambda^2 = 1.0$. For clarity, the spectral peaks have been broadened by Gaussian line shapes of standard deviation $\sigma = 0.28\omega_0$. The area under each spectrum, representing the total oscillator strength of the system per contributing molecule, is unity.

Figure 4.4: Details of some of the calculated zero-temperature absorption spectra of Figure 4.3. The absorption of each of the eigenstates following from APTA is shown (in red and green), and so is the total spectrum from the two-particle approximation (TPA, in black). In Figure (a) the green and red curves overlap. In Figure (c) the red and black curves overlap.
Figure 4.5: Graphs showing the result of the minimization of the Bogoliubov bound of the free energy for a homogeneous dimer at zero temperature when the exciton-phonon coupling (of strength $\lambda \omega_0$) is increased. The strength of the electronic interaction is taken $J = -0.5$ (dotted), $J = -1.0$ (dashed), $J = -2.0$ (solid line) in units of $\omega_0$. Figure (a) shows the resulting value of the optimization parameter, $\rho$, in terms of its maximal value, $\lambda$. Figure (b) shows the resulting value of the renormalization factor, being the ratio of the renormalized (effective) electronic interaction, $\langle \tilde{J} \rangle$, and the original interaction strength, $J$. 
Figure 4.6: Calculated zero-temperature absorption spectra for the homogeneous dimer following from the adapted polaron transformation approach (APTA, in blue) and the two-particle approximation (TPA, in black). The Huang-Rhys factor, $\lambda^2$, that is characteristic for the strength of the exciton-phonon coupling, is chosen differently for each column of spectra as indicated. The electronic coupling, $J$, is varied per row and it is given in units of $\omega_0$ in each spectrum. For clarity, the spectral peaks have been broadened by Gaussian line shapes of standard deviation $\sigma = 0.28\omega_0$. The area under each spectrum, representing the total oscillator strength of the system per contributing molecule, is unity.
The heterogeneous dimer

The introduction of disorder in the electronic transition energies allows for the modeling of small (environmental) differences as was mentioned in Section 2.1. One can distinguish two limits for the disordered, or heterogeneous, dimer. The one, in which the disorder, or detuning, \( \Delta = |\epsilon_2 - \epsilon_1| \), is much smaller than the electronic coupling, is essentially captured by the behavior of the homogeneous dimer. When, however, \( \Delta / 2 \gg |J| \), the disorder is expected to overcome the tendency of the electronic coupling to delocalize the eigenstates.

In the current scheme, increasing the disorder leads to an additional effect due to which exciton delocalization is suppressed. The minimum of the free energy shifts to higher values of \( \rho \), causing a larger reduction of the original electronic interaction. This behavior is shown in Figure 4.7. It can be seen that for a disorder \( \Delta > 5|J| \) the electronic interaction is reduced to about 40% of its original value.

![Figure 4.7](image)

Figure 4.7: Graphs showing the result of the minimization of the Bogoliubov bound of the free energy for a heterodimer dimer at zero temperature, when the detuning between both transition energies, \( \Delta = |\epsilon_2 - \epsilon_1| \), is increased. The electronic interaction is set to \( J = -\omega_0 \), so that essentially the ratio of disorder and the electronic coupling strength is shown on the horizontal axis, \( \Delta / \omega_0 = \Delta / |J| \). The Huang-Rhys is taken \( \lambda^2 = 1.0 \). Figure (a) shows the resulting value of the optimization parameter, \( \rho \), in terms of its maximal value, \( \lambda \). Figure (b) shows the resulting value of the renormalization factor, being the ratio of the renormalized (effective) electronic interaction, \( \langle J \rangle \), and the original interaction strength, \( J \).

The influence of the value of \( \Delta \) on the absorption spectra of the heterodimer is shown in Figure 4.8, where spectra from APTA and the two-particle approximation are shown. The strength of the electronic coupling and the Huang-Rhys factor are kept fixed: \( J = -\omega_0 \) and \( \lambda^2 = 1.0 \), respectively.

The spectra that result from APTA in Figures 4.8a to e represent the behavior of the heterogeneous dimer in the limit of small disorder. For \( \Delta = 0.25\omega_0 \) this is motivated in Figure 4.9a, where it is shown that the optical response of the symmetric electronic eigenstate (as computed using APTA) follows the result from the full numerical diagonalization. Having exciton states for values of the disorder \( \Delta \leq 1.5\omega_0 \) seems to make sense as there still \( \langle |\langle J \rangle| > \Delta / 2 \), even though the two-particle approximation starts to exhibit different behavior already. In the other limit, that of large disorder, it is expected that the absorption spectrum consists of two separate single-molecule contributions. That this is indeed the case is shown in Figures 4.8h and i and 4.9c and it can be seen that the APTA and two-particle approximation results match very well there. Seemingly, APTA is somewhat faster in going to this single-molecule limit, perhaps due to the reduction of the electronic interaction due to the disorder.

In the intermediate regime of disorder, notably in Figure 4.8f and its details in Figure 4.9b, the methods that are compared deviate quite much. The position of the low-energy absorption peak of
the eigenstate that used to be the symmetric eigenstate for smaller disorder is estimated a bit less precise than for other parameters, but still it seems pretty well. Also the total oscillator strength in the low-energy part of the spectrum seems to match, although it is distributed differently.

The position of the other eigenstate’s absorption peaks seems to be incorrect, however, just like the oscillator strength contained in it. These effects we observed before, when discussing the intermediate regime of couplings in which electronic and exciton-phonon coupling are similar in Figure 4.4b. Some new effect is visible in the spectra predicted by the two-particle approximation for the regime in which disorder and electronic coupling have similar magnitude, however. The spacing between different vibrational peaks in the absorption spectrum deviates from the usual spacing, which is the energy of the vibrational quantum, $\omega_0$.

The introduction of disorder clearly shows us some deficits of the adapted polaron transformation approach when calculating spectra, manifested in the intermediate regime. The limits of small and large disorder (with respect to the electronic coupling) are reproduced accurately.

![Figure 4.8](image)

**Figure 4.8:** Calculated zero-temperature absorption spectra for the heterodimer following from the adapted polaron transformation approach (APTA, in blue) and the two-particle approximation (TPA, in black). The detuning, $\Delta = |\epsilon_2 - \epsilon_1|$, that is characteristic for the disorder is varied and it is given in units of $\omega_0$ in each spectrum. The detuning should be compared with the electronic coupling, that is taken $J = -\omega_0$. The Huang-Rhys factor is set to $\lambda^2 = 1.0$. For clarity, the spectral peaks have been broadened by Gaussian line shapes of standard deviation $\sigma = 0.14\omega_0$. The area under each spectrum, representing the total oscillator strength of the system per contributing molecule, is unity.

Usually when static disorder is considered, spectra are calculated that correspond to an average over an ensemble of systems, all having a different realization of the disorder (sometimes seen as uncorrelated, drawn from a Gaussian distribution). We will not go into such an analysis here, but
it can be expected that within such spectra the clear structure of vibrational peaks that is visible in the previous results is blurred, especially when the disorder is of the order of or is larger than the exciton-phonon coupling. The influence of vibrations then reduces to an extra broadening of absorption peaks (on top of the broadening due to disorder). Having less features in the absorption spectrum in that situation, we expect results from ATPA to agree better with results from the two-particle approximation.

**Comparison with other polaron transformation methods**

In the polaron transformation literature, mostly when energy transport properties of molecular aggregates are considered, generally other polaron transformation methods than the one proposed in this thesis are used [33, 41–43]. We will look into some of these other methods to calculate absorption spectra for the dimer here, but the results hold for an aggregate of arbitrary size.

Consider applying a full polaron transformation of the Holstein Hamiltonian, first. For the monomer this treatment is exact and gave the desired result, as we saw in Section 2.5.1. For the dimer and larger systems, it is necessary to apply perturbation theory, as polaron transformation methods mix electronic and vibrational wavefunctions.

After the application of a full polaron transformation, we can follow a similar mean field approach as that used in Chapter 3 to come up with the following formula for the normalized zero-temperature absorption spectrum. Note that it is not necessary to change basis to collective modes, because each molecular vibrational mode is treated using the same polaron transformation parameter, $\lambda$.

$$A(\omega) = \frac{1}{2} \exp(-\lambda^2) \sum_k \left((1 + 2\phi_k(1)\phi_k(2)) \delta(E_k - \omega) + \sum_{M=1}^{\infty} \frac{\lambda^{2M}}{M!} \delta(E_k + M\omega_0 - \omega)\right).$$  \hspace{1cm} (4.7)

In fact, this result follows straight away upon substitution of $\rho = \lambda$ in the Equations (4.1) and (4.2). We observe that diagonalization of the electronic states, that depends on the interplay between electronic coupling, exciton-phonon coupling and disorder, only influences the distribution of oscillator strength over the 0-0 transitions of each eigenstate. Thus, for the homogeneous dimer, the 0 → 0 transition of the symmetric electronic eigenstate contains oscillator strength $\exp(-\lambda^2)$, whereas the same transition of the antisymmetric eigenstate is dark.

The oscillator strength of transitions that involve a change in the number of vibrational quanta only depend on the exciton-phonon coupling parameter, $\lambda$ and the same vibrational band structure holds for all the electronic eigenstates. For the homogeneous dimer this is a quite unexpected
result. Of course some vibrational borrowing can occur, transferring oscillator strength from the symmetric eigenstates to the originally dark antisymmetric eigenstate, but 50% is too much, as was seen before when analyzing results from the two-particle approximation.

The application of a partial polaron transformation using the same parameter $\rho$ for each mode results in an absorption spectrum of similar structure as that for a full polaron transformation, as can be obtained by direct substitution of $\rho = \lambda$ in Equations (4.1) and (4.2).

$$A(\omega) = \frac{1}{2} \exp(-\rho^2) \sum_k \left[ (1 + 2\phi_k(1)\phi_k(2)) \delta(E_k - \omega) + \sum_{M=1}^{\infty} \frac{\rho^{2M}}{M!} \delta(E_k + M\omega_0 - \omega) \right]$$

Due to $\rho \leq \lambda$ from the free energy minimization that has to be applied (for a free energy bound that is slightly different than that for APTA), there is less oscillator strength contained in transitions where vibrational quanta are involved. The structure of the corresponding peaks in the absorption spectrum still is the same for each electronic eigenstate, however.

Having presented the above analysis of different polaron transformation methods than the one employed in the current work, let us compare the spectra these methods produce for different values of the electronic coupling, $J$. Such a comparison is presented in Figure 4.10. Remember that the results from APTA agreed remarkably well with those from a full numerical diagonalization (Figure 4.3), so it can be seen as the desired result to which the other methods can be compared.

Looking at the curves for the full polaron transformation method (in red) first, especially in Figure 4.10e it can be seen that the vibrational structure of both electronic eigenstates (the exciton states in this limit) is the same and that too much oscillator strength is granted to the antisymmetric eigenstate. In the other figures a similar situation holds, although there the electronic eigenstates are less separated and their optical response thus overlaps. It can be seen that this method places peaks at too high energies.

Similar behavior can be distinguished for the variational polaron transformation method (in green). Figures 4.10c and d show the problem with the vibrational structure within the antisymmetric electronic eigenstate most clearly.

In the strong electronic coupling limit, having some exciton-phonon coupling as well, the two methods deviate the most from APTA, as is shown in Figures 4.10d and e. In this limit the variational method produces a result that is not expected to represent the behavior of the dimer system correctly: no vibrational structure can be seen at all.

In the limit of weak electronic coupling, the single-molecule limit, all methods are expected to yield the same result, for there $\rho \approx \lambda$ for each of them. This is indeed seen in Figure 4.10a. Also when exciton-phonon coupling hardly plays a role, not in comparison to the electronic coupling, but having $|\lambda| \ll 1$, the methods should give about the same results as then $\rho \approx \lambda \approx 0$ (cf. Figure 4.10f). Apart from these limiting cases, the results from the full polaron transformation method and the method in which each mode is treated according to the same variational polaron transformation deviate quite much from APTA, and thus from the results obtained from full numerical diagonalization. It can be concluded that the exact way in which the coupling with each mode is treated using a polaron transformation approach should be chosen with care, and a good choice was made by treating the totally symmetric collective mode exactly using a full polaron transformation and the antisymmetric collective mode using a variational one.
Figure 4.10: Calculated zero-temperature absorption spectra for the homogeneous dimer following from different polaron transformation approaches, namely, those involving a full polaron transformation (FPT, in red), a variational polaron transformation in which each vibrational mode is treated on the same footing (VPT, in green) and the adapted polaron transformation (APTA, in blue). The strength of the electronic coupling, $J$, is varied in Figures (a) to (e) and it is given in units of the vibrational energy quantum, $\omega_0$, there. The Huang-Rhys factor is taken $\lambda^2 = 1.0$. In Figure (a) the blue and green curves overlap. Figure (f) shows a spectrum for large electronic coupling and a small Huang-Rhys factor. For clarity, the spectral peaks have been broadened by Gaussian line shapes of standard deviation $\sigma = 0.28 \omega_0$. The area under each spectrum, representing the total oscillator strength of the system per contributing molecule, is unity.

4.1.2 Spectra of larger aggregates

In the current section, we will look at the zero-temperature optical response of larger homogeneous aggregate systems. For simplicity and easy interpretation of the spectra we will assume nearest-neighbor interactions of strength $J$ only, and apply periodic boundary conditions to eliminate finite-size effects regarding the distribution of oscillator strength over the 0-0 transitions of the electronic eigenstates.

Figure 4.11 shows absorption spectra following from APTA for different aggregate sizes. The nearest-neighbor coupling is set to $J = -\omega_0$ for each aggregate. Effects of disorder are not taken into account. As the aggregate size increases more oscillator strength goes to the 0-0 transition of the totally symmetric electronic eigenstate. For $N = 64$ the percentage of the oscillator strength that is contained in this transition has converged to about 87%, meaning that it contains around 7 times more oscillator strength than all the other transitions. This number is comparable to the ratio of 5 to 1 that Spano mentions for the areas of 0-0 and 0-1 peaks in absorption spectra of similar aggregates in this region of electronic coupling. [28]

In our method, however, the oscillator strength that is not within the first main peak is distributed over a long tail that resembles the density of states. This originates from the fact that we treat all other modes than the totally symmetric one using the same variational parameter. This means, just like we saw when applying the variational polaron transformation approach to the dimer, that all electronic eigenstates have the same vibrational structure for $M > 0$. It can be expected that this leads to too much vibrational borrowing from the peaks of the symmetric electronic eigenstate. This clearly is a deficit of the current method.

Let us look at its comparison with results from the two-particle approximation, nonetheless.
Figure 4.11: Calculated zero-temperature absorption spectra for homogeneous aggregates following from the adapted polaron transformation approach (APTA). The number of molecules the aggregate consists of, $N$, is varied and it is given in each spectrum. Only nearest-neighbor interactions of strength $J = -\omega_0$ were taken into account and periodic boundary conditions were assumed. The Huang-Rhys factor is taken $\lambda^2 = 1.0$. For clarity, the spectral peaks have been broadened by Gaussian line shapes of standard deviation $\sigma = 0.14\omega_0$. The area under each spectrum, representing the total oscillator strength of the system per contributing molecule, is unity.

Figure 4.12 provides spectra resulting from both methods for the homogeneous octomer, assuming periodic boundary conditions, for several values of the nearest-neighbor coupling. The Huang-Rhys factor is taken to be unity in each spectrum, $\lambda^2 = 1.0$. The single-molecule spectrum that is expected for $J = 0$ is shown in Figure 4.12a. Increasing the coupling introduces deviations between both methods fast. The 0-1 peak to which all exciton states contribute evenly, within APTA, but at slightly different energies, differs most. It shows a broader peak with a small plateau, whereas the two-particle approximation predicts a sharp peak. Also the oscillator strength of the first peak seems to be overestimated. Probably APTA is failing here, as it treats too many modes using the same variational parameter. Increasing the electronic coupling to the exciton regime leads to results that match very well again. There it is the symmetric eigenstate that dominates the optical response. Note that in this regime of the electronic coupling the ratio between the 0-0 (the first) peak and the 0-1 (the second) peak is expected to go to $N/\lambda^2$ [28], which indeed seems to be the case.

Results for a slightly larger aggregate, the 32-mer, are shown in Figure 4.13. There, Figure 4.13b, for $J = -0.25\omega_0$, shows a result similar to that for the octomer, for which APTA deviates quite strongly from the two-particle approximation result. Increasing the coupling somewhat again leads to a regime in which the oscillator strength in the first peak seems to be overestimated by APTA. In the strong electronic coupling limit the deviations seems to become smaller and the ratio between the 0-0 and 0-1 goes to $N/\lambda^2$. It is a matter of question, however, which method gives the best results for $|J|/\omega_0 \geq 1 = |\lambda|$, because in that regime the assumption that states in which more than two oscillators are excited can be excluded (the two-particle approximation) may no longer hold.

Having discussed the quantitative details of absorption spectra for larger aggregates coming from our adapted polaron transformation approach and their comparison to two-particle approximation results, let us briefly go into the computational cost of the calculations involved. In a numerical
implementation of Equation (3.31) in which one scans through all the possible distributions of a certain number of quanta (up to a phonon number cut-off chosen such that at least a certain percentage of the oscillator strength is contained in the transitions that are taken into account) spectra for the octomer can be calculated in less than a minute on a normal desktop computer.

Due to the factorial scaling of these vibrational configurations with the number of oscillators, soon it is starting to take minutes to run through all the possible transitions. However, when zero-temperature absorption is considered, one only needs to numerically implement Equations (3.34) and (3.35), of which calculation takes less than ten seconds, including the free energy minimization process.

These figures should be compared to 40-minute and over 3-hour calculation times within the two-particle approximation for the octomer and 32-mer, respectively.
4.2 Thermal effects

Within the current model it is possible to take into account temperature effects. This is done by summing over a Boltzmann distribution of initial (vibrational) states in the formula for the absorption spectrum, Equation (3.31).

4.2.1 The monomer and dimer spectra

We will investigate the influence of temperature on the optical properties of aggregates by looking at monomer and dimer spectra, but before we do so, we will try to understand the behavior of the free energy minimization at finite temperatures. Figure 4.14 shows the bound to the Helmholtz free energy as a function of the optimization parameter for several values of the temperature. The electronic coupling and Huang-Rhys factor are taken $J = -\omega_0$ and $\lambda^2 = 1.0$, respectively. For this specific set of parameters one can see that an increase in temperature leads to the occurrence of a second local minimum in the free energy, which is located at some distance of the first local minimum. At a certain point, when the temperature increases enough, the second local minimum becomes
the global minimum. This leads to a sudden jump in the value of the optimization parameter. This effect is detailed further in Figure 4.15. There explicitly the temperature dependence of the variational parameter and the renormalized interaction are shown for several values of the electronic coupling. The Huang-Rhys factor is again fixed to $\lambda^2 = 1.0$. The dotted graph in both panels, corresponding to $J = -0.5\omega_0$, shows a continuous increase (decrease) of the variational parameter (renormalized interaction). Increasing the electronic interaction to $J = -\omega_0$ (dashed curve) leads to a jump discontinuity in both panels. When the temperature is increased enough it joins the dotted curve. The third graph (solid line) represents the temperature dependence of the variational parameter and the renormalization factor for $J = -2\omega_0$. It seemingly shows a small increase in the effective interaction with temperature. Out of the domain of the current graph however, at higher temperatures, it shows a similar jump discontinuity as that observed for $J = -\omega_0$. It is clear that the discontinuities we observe here arise from the structure of the free energy, that has two well-separated minima for certain input parameters. It seems unlikely, however, that the transition that occurs when temperature increases – almost like a phase transition – will occur in nature. We regard it as a deficit of the free energy minimization method, that occurs in some regions of the parameter space (not necessarily at finite temperatures), whereas in others it shows a smooth behavior. We do stress, however, that the general behavior of the free energy minimization when temperature is increased makes sense: there is a clear low-temperature regime in which the electronic interaction is reduced only slightly due to the presence of phonons, and there is a high-temperature regime in which the effective electronic interaction is very small.

![Figure 4.14: Graphs of the Bogoliubov bound of the free energy for a homogeneous dimer, showing the typical dependence on the variational parameter, $\rho$, when temperature is varied. Temperature is given as $kT$ in units of $\omega_0$ in each figure. The strength of the electronic coupling is taken $J = -\omega_0$ and the Huang-Rhys factor is set to $\lambda^2 = 1.0$.](image)

In Figure 4.16 monomer and dimer spectra are shown for several values of the temperature ($kT$ in units of $\omega_0$). The electronic interaction is taken $J = -\omega_0$, the exciton-phonon coupling parameter $\lambda = 1.0$. Focusing on the monomer spectra first (in gray), we recognize the zero-temperature single-molecule spectrum with its characteristic vibrational progression in Figure 4.16a. The increase of temperature makes it more likely that initially the system resides in the electronic ground state that is accompanied by a non-zero number of vibrational quanta. This leads to a range of new possible transitions, mostly occurring at the lower energy side of the spectrum (resulting from a higher initial than final number of vibrational quanta). Overall, the spectrum is broadened, even up to the situation in which the original asymmetric absorption spectrum of Figure 4.16a becomes the symmetric spectrum of Figure 4.16i. A similar broadening of the spectra can be observed for the dimer (in blue) when temperature is increased. But an additional effect plays a role, there, as we discussed at length above. The electronic interaction between the two molecules is reduced by temperature, destroying the coherence between them. The first few figures show the delocalized exciton regime, that is, the exciton limit, where this effect plays no role yet and the dimer spectrum is clearly distinguishable from the monomer one. From $kT \gtrsim 1.2\omega_0$ onward, the electronic interaction is reduced so much that the
4.2 Thermal effects

Figure 4.15: Graphs showing the result of the minimization of the Bogoliubov bound of the free energy for a homogeneous dimer when temperature is increased. The strength of the electronic interaction is taken $J = -0.5$ (dotted), $J = -1.0$ (dashed), $J = -2.0$ (solid line) in units of $\omega_0$. Figure (a) shows the resulting value of the optimization parameter, $\rho$, in terms of its maximal value, $\lambda$. Figure (b) shows the resulting value of the renormalization factor, being the ratio of the renormalized (effective) electronic interaction, $\langle \tilde{J} \rangle$, and the original interaction strength, $J$.

dimer and monomer spectra match. This is the localized exciton regime and we conclude that temperature has a two-fold effect: it leads to broadening of the vibrational absorption band and it leads to a destruction of exciton coherence.
Figure 4.16: Calculated absorption spectra for the monomer (in gray) and homogeneous dimer (in blue) following from the adapted polaron transformation approach (APTA). The temperature is varied and it is given as $kT$ in units of $\omega_0$ in each spectrum. The strength of the electronic coupling is taken $J = -\omega_0$ and the Huang-Rhys factor is set to $\lambda^2 = 1.0$. In Figures (f) to (i) the blue and gray curves (almost) overlap. For clarity, the spectral peaks have been broadened by Gaussian line shapes of standard deviation $\sigma = 0.28\omega_0$. The area under each spectrum, representing the total oscillator strength of the system per contributing molecule, is unity.
Motivated by suggestions that exciton-phonon coupling plays an important role in determining electronic and optical properties of molecular aggregates, we have aimed at modeling such dynamical effects. Taking the Holstein Hamiltonian as a starting point, a new method is proposed to predict the optical response of molecular aggregates that reside in a dynamical environment. In the current work the focus lies on the calculation of linear absorption spectrum of small molecular aggregate systems.

Several perturbative limits exist in which these and other optical properties of Holstein-like systems can be described. Therefore, the behavior in the limits of small electronic coupling and small exciton-phonon coupling is relatively well-understood. They do not allow us to probe the optical response in the intermediate regime where these couplings are of similar magnitude, however.

Improving on these perturbative approaches, we propose a variational polaron transformation method (it is termed APTA, adapted polaron transformation approach) that holds over a large range of parameters, including the intermediate regime. This polaron method consists of an exact treatment of the totally symmetric collective vibrational mode using a full polaron transformation, whereas the other vibrational modes to which the molecular aggregate is coupled are treated using a variational polaron transformation. The value of the corresponding variational parameter is obtained from a minimization procedure of the Helmholtz free energy of the system. Analytic expressions for absorption spectra at finite and zero temperatures follow from this method.

In this thesis a detailed analysis of the behavior of this free energy minimization and the linear absorption spectra that follow from APTA is presented for different values of the parameters involved, namely the electronic coupling, the exciton-phonon coupling, disorder and temperature. Also the number of molecules of the aggregate is varied. Results are compared to absorption spectra that are predicted by a two-particle basis set approach of the Holstein Hamiltonian.

Much attention is devoted to studying the molecular dimer at zero temperature, for which the two-particle approximation amounts to a full numerical diagonalization of the Hamiltonian and, thus, is exact (up to a cut-off concerning the number of phonons taken into account).

Comparing results, we see that the currently proposed method is valid over a large range of coupling parameters. When the electronic coupling is small with respect to the exciton-phonon coupling the expected single-molecule limit is reproduced. In the opposite limit, in which the electronic coupling is large, the exciton limit is observed with absorption spectra showing peaks that clearly belong to delocalized electronically excited state, with (exchange narrowed) vibrational structure imposed on them. In both these regimes and also when the electronic and exciton-phonon coupling are of comparable magnitude, the results from APTA very closely follow the spectra as obtained from full numerical diagonalization apart from some small discrepancies.

When diagonal disorder is introduced, the homogeneous (small disorder) and inhomogeneous (large disorder) limits are nicely reproduced by APTA, comparing very well to the two-particle result. When the disorder and the electronic coupling are of similar magnitude, the two methods slightly deviate from each other, so that seemingly some intermediate regime of parameters can be found in which APTA produces results that are a bit less accurate. An interesting effect that occurs when an aggregate is disordered is that it causes an extra reduction of the original electronic
interaction (just like the presence of phonons does).

For the dimer, next to a comparison with two-particle approximation results, also a comparison of APTA is made with two other polaron transformation methods. The one method utilizes a full polaron transformation, the other a variational, but both treat all vibrational modes in the same fashion. These methods are shown to work only in the limits of small electronic coupling and small exciton-phonon coupling, just like the perturbative approaches that we wished to improve on. Their main problem is that the vibrational structure of each electronic eigenstate’s optical response is the same and that the antisymmetric electronic eigenstate borrows too much oscillator strength from the symmetric eigenstate.

When the number of molecules of an aggregate is increased, the peaks belonging to the symmetric electronic eigenstate are expected to contain more oscillator strength than is the case for smaller aggregates. Generally, this behavior is nicely reproduced. In the regime where the electronic coupling is of the order of $J = -\omega_0$, for instance, the 0-0 transition of the electronic eigenstate contains about five times more oscillator strength than 0-1 transitions. These latter transitions, however, occur in a tail in the APTA absorption spectra, making the comparison with the two-particle approximation less good. The reason for this is that the current method treats all vibrational modes other than the totally symmetric one using the same variational parameter, giving each electronic eigenstate other than the symmetric one the same vibrational structure in its optical response. This behavior disappears when the electronic coupling is increased, where the ratio of the oscillator strength within 0-0 and 0-1 more or less converges to a value of $N/\lambda^2$. APTA and TPA results resemble each other very well in this strong electronic coupling regime, with some slightly different behavior of the latter method.

Increasing the temperature leads to two interesting effects. Firstly, the vibrational band structure broadens, as can clearly be observed in monomer spectra, and is also seen for the dimer. Secondly, the presence of phonons effectively reduces the electronic coupling between molecules in an aggregate with increasing temperature, leading to thermal destruction of exciton coherence. Two temperature regimes are observed that can be identified as a localized exciton and a delocalized exciton regime. Sometimes a seemingly nonphysical jump occurs between them, which probably points at a deficit of the free energy minimization procedure.

Overall, the currently-proposed adapted polaron transformation approach for the calculation of linear absorption spectra of small Holstein-like systems is shown to be valid over a large range of parameters when it is compared to spectra from a two-particle basis set approach. Not only limiting behavior is produced, for which other perturbative approaches can be devised, but spectra from both methods in an intermediate regime of couplings also compare very well. Additionally, pronounced temperature effects are observed.

A clear advantage of APTA over the two-particle approach is that the current method leads to insightful analytic expressions for the linear absorption spectra, that are based on Born-Oppenheimer product wavefunctions of electronic and vibrational excitations. Furthermore, the computational costs of numerical implementation of these spectra are low, as zero-temperature spectra can be calculated within seconds, whereas the two-particle method may take up to hours for larger aggregates.

### 5.1 Outlook

The method proposed in this thesis forms a nice starting point in understanding and calculating the optical response of molecular aggregates in which vibrational degrees of freedom play an important role. The focus lay on small model systems containing up to a few tens of molecules, where with each molecule one quantum harmonic oscillator, used to model the dynamical environment, was associated. An obvious extension of the current method, therefore, is to try to model the optical response of larger aggregate systems or perhaps include more vibrational modes or a spectral density of modes.

Concerning the first idea, we have the impression that perhaps one variational parameter is not enough to describe very large Holstein-like aggregates in which there are many (collective) modes,
for the other than symmetric electronic eigenstates are predicted to have the same vibrational structure in their optical response in that case. Introducing more variational parameters to transform the modes is possible, but it may prove to be challenging (numerically speaking) to determine their value by minimization of the Helmholtz free energy. Pursuing such a method can, however, serve as verification or validation of the approach proposed in the current work, in which one transformation parameter was fixed (the full polaron transformation parameter) and the other was determined variationally. Such verification may also lie in estimates of the mean square size of the perturbation term, as is sought for in, for instance, Reference [42].

It would also be very interesting to look at coupling aggregate systems, like the double-walled cylindrical aggregates mentioned before. The current work provides an indication that the dynamical environment causes a destruction of exciton coherence, but it must still be shown to work in the same way for (large) coupling systems, where it should somehow allow for the coupling between aggregates to be reduced, while still having coherent coupling within aggregates. Studying coupling aggregates in the first place may require a smarter treatment of the (collective) vibrational modes.

This brings us to different possible extensions of the current method. It may be desirable to allow electronic excitations to couple to more (intramolecular) vibrational modes, or to have several electronic excitations interact with one specific vibrational mode, a phonon in the aggregate or the solvent, for instance. Introducing more modes per molecule is easily done, but it does complicate the calculation of spectra, especially when it comes to the summing over all possible transitions. New numerical and/or analytic methods need to be created for that purpose. The treatment of solvent phonons perhaps requires a different physical approach than the one used for intramolecular vibrational modes used in this thesis. Such an approach may involve the introduction of a spectral density of modes, which in the literature is investigated already [37,41–45].

Other work can be aimed at refining the method, especially when it comes to the procedure of minimization of the free energy. There, sometimes discontinuous jumps of the optimization parameter were observed that are not regarded as physical. New methods have to be found to circumvent such behavior.

Hopefully the current work, in which it was aimed to understand the basic concepts of the optical response of molecular aggregates involving vibrations, and the above suggestions provide enough motivation for future research.
Acknowledgments

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I look back on a really enjoyable year and, for that matter, on a great five years of studying in Groningen during which I could count on the support of my father Frank, Margreet and my brother Wouter, who is also studying here. Many thanks to them and to all the others with whom I stayed in touch.

To you, reader, perhaps our paths cross once again. But first, buen camino!
Appendix A

Creation and annihilation operators of excitations and vibrations

A.1 Excitation creation and annihilation operators

The one-exciton states of molecular aggregates that are considered in this thesis, can be described using the Pauli operators for the creation ($c_n^\dagger$) and annihilation ($c_n$) of an excitation at a certain molecule (labeled by $n$). They are called Pauli operators, because of the equivalence between the two-level systems that are used to model the molecules and the electron spin system.

Denoting the electronically excited state of molecule $n$ using the Dirac bra-ket notation as $|n\rangle$ and its ground state as $|g\rangle$, the two are related via the Pauli operators as follows,

\[ |n\rangle = c_n^\dagger |g\rangle, \quad c_n |n\rangle = |g\rangle. \]  

(A.1)

Only taking into account one-exciton states, double (de)excitations are forbidden, so that

\[ c_n^\dagger |n\rangle = 0, \quad c_n |g\rangle = 0. \]  

(A.2)

The Pauli operators pertaining to one molecule obey the Fermi commutation relation (an anticommutation relation, that is), being,

\[ \{c_n, c_n^\dagger\} = c_n c_n^\dagger + c_n^\dagger c_n = 1. \]  

(A.3)

Pauli operators pertaining to different molecules commute.

A.2 Vibrational creation and annihilation operators

The vibrational modes (the quantum harmonic oscillators) to which the electronic excitations of the molecular aggregate are coupled in the Holstein model, can be described using their momentum ($p_q$) and coordinate ($x_q$) operators, and their frequency ($\omega_q$). A more convenient description is provided by the ladder operators for the creation ($a_q^\dagger$) and annihilation ($a_q$) of vibrational quanta of a certain frequency $\omega_q$, however. Assuming a unit mass for the oscillators, these two descriptions are related via

\[ x_q = \sqrt{\frac{1}{2\omega_q}} (a_q + a_q^\dagger), \]

\[ p_q = -i \sqrt{\frac{\omega_q}{2}} (a_q - a_q^\dagger). \]  

(A.4)
Denoting the state in which oscillator $q$ contains $N$ vibrational quanta using $|N\rangle$ (in the thesis it is denoted $|N_q\rangle$), the vibration creation operators behave as follows.

\[ a_q^\dagger|N\rangle = \sqrt{N+1}|N+1\rangle, \]
\[ (a_q^\dagger)^k|N\rangle = \sqrt{(N+k)\cdots(N+2)}|N+k\rangle = \frac{\sqrt{(N+k)!}}{N!}|N+k\rangle. \]  

(A.5)

For the annihilation operator we have

\[ a_q|N\rangle = \sqrt{N-1}|N-1\rangle, \]
\[ (a_q)^k|N\rangle = \sqrt{N(N-1)\cdots(N-k+1)}|N-k\rangle = \frac{\sqrt{N!}}{(N-k)!}|N-k\rangle. \]  

(A.6)

with the additional rule that this operator annihilates the vibrational ground state, that is,

\[ a_q|0\rangle = 0. \]  

(A.7)

The vibrational (or phonon) excitation and creation operators for a certain mode are bosonic in nature and, thus, obey the Bose commutation relation. Operators for different modes commute.

\[ [a_q, a_q^\dagger] = a_qa_q^\dagger - a_q^\dagger a_q = \delta_{q,q'} \]  

(A.8)
The partial polaron transformation

B.1 Workings

The polaron or Lang-Firsov transformation is a canonical transformation utilized to (approximately) diagonalize the Holstein Hamiltonian in the regime in which exciton-phonon coupling plays a more important role than electronic coupling. It serves as a translation operator in momentum space, it shifts the harmonic oscillator potential well associated with each electronically excited state of molecular aggregate so that it is aligned with the ground state oscillator again. The partial or variational polaron transformation forms an extension of the polaron (full polaron) transformation in the sense that it allows for variable shifts of the excited state harmonic oscillators. It thus is able to describe the application of a full polaron transformation, no polaron transformation, and anything in between. In what follows we will focus on this type of a transformation, taking into account a further extension on which we will elaborate in Appendix C: we will allow for coupling between any molecular excitation and mode and, therefore, also allow for shifts of any oscillator with respect to any molecular excitation. In this way, the results derived in this Appendix and the next can be reduced to any desired situation: that of a full polaron transformation, a variational polaron transformation, the adapted polaron transformation approach outlined in this thesis, no polaron transformation, etc.

Any operator $O$ can be transformed according to a transformation generator $G$ as follows,

$$\tilde{O} = e^G O e^{-G} = O + [G, O] + \frac{1}{2!} [G, [G, O]] + \ldots \tag{B.1}$$

Here, $[A,B]$ denotes the commutator of any two operators $A$ and $B$, being

$$[A,B] = AB - BA. \tag{B.2}$$

The expression for the transformed operator using commutators follows from the Taylor expansion of the transformation generator exponential. Note that the transform of a product of operators is just the product of transforms,

$$e^G A e^{-G} = e^G A e^{-G} e^G B e^{-G} = \tilde{A} \tilde{B}. \tag{B.3}$$

The generator of the partial polaron transformation that we consider here is given by

$$G = \sum_{n=1}^{N} \sum_{q} \rho_{nq} (a_{q}^{\dagger} - a_{q}) c_{n}^{\dagger} c_{n}. \tag{B.4}$$

The first sum ranges over the $N$ molecules of the aggregate, the second over the modes of which the number or nature is not specified here. The values of the variational parameters $\rho_{nq}$ lie in the
interval
\[ 0 \leq \rho_{nq} \leq \lambda_{nq}, \quad (B.5) \]
where \( \lambda_{nq} \) characterizes the coupling between the electronic excitation at molecule \( n \) and the vibrational mode labeled by \( q \).

### B.2 Transforming the basic operators

In this section the partial polaron transformation is applied to the creation and annihilation operators of electronic excitations and vibrations. Starting with the excitation annihilation operator,
\[
\tilde{c}_n = e^G c_n e^{-G} = c_n + [G, c_n] + \frac{1}{2!} [G, [G, c_n]] + \ldots \quad (B.6)
\]
Working out the first-order term leads to
\[
[G, c_n] = -\sum_{m} \sum_{q} \rho_{nq}(a_q^\dagger - a_q) [c_n, c_m^\dagger c_m] = -c_n \sum_{q} \rho_{nq}(a_q^\dagger - a_q) \quad (B.7)
\]
from which subsequent terms are easily determined. This gives
\[
\tilde{c}_n = c_n - c_n \sum_{q} \rho_{nq}(a_q^\dagger - a_q) + c_n \left( \sum_{q} \rho_{nq}(a_q^\dagger - a_q) \right)^2 - \ldots \quad \text{\( (B.8) \)}
\]
Transformation of the excitation creation operator leads to a similar result,
\[
\tilde{c}_n^\dagger = c_n^\dagger \exp(\sum_{q} \rho_{nq}(a_q^\dagger - a_q)) = c_n^\dagger \Theta^\dagger_n \quad \text{\( (B.9) \)}
\]
Note that from combining the above two transforms it follows that \( \tilde{c}_n^\dagger \tilde{c}_n = c_n^\dagger c_n \) is invariant under the partial polaron transformation.

In turning our attention to the transformation of the phonon creation and annihilation operators, we note that
\[
[G, a_q] = \sum_{n} \sum_{q'} \rho_{nq'}[a_{q'}^\dagger - a_{q'}, a_q] c_n^\dagger c_n = -\sum_{n} \rho_{nq} c_n^\dagger c_n \quad (B.10)
\]
in which the phonon operators have disappeared. Therefore, all higher-order terms in the transformation vanish and we obtain
\[
\tilde{a}_q = a_q - \sum_{n} \rho_{nq} c_n^\dagger c_n \quad \text{\( (B.11) \)}
\]
The phonon creation operator undergoes the same shift. Its transform is
\[
\tilde{a}_q^\dagger = a_q^\dagger - \sum_{n} \rho_{nq} c_n^\dagger c_n \quad \text{\( (B.12) \)}
\]
Summarizing the operator transforms,
\[
\tilde{c}_n = c_n \exp(-\sum_{q} \rho_{nq}(a_q^\dagger - a_q)), \quad \tilde{c}_n^\dagger = c_n^\dagger \exp(+\sum_{q} \rho_{nq}(a_q^\dagger - a_q)), \quad \tilde{a}_q = a_q - \sum_{n} \rho_{nq} c_n^\dagger c_n, \quad \tilde{a}_q^\dagger = a_q^\dagger - \sum_{n} \rho_{nq} c_n^\dagger c_n \quad \text{\( (B.13) \)}
\]
B.3 Partial polaron transformation matrix elements

It turns out to be useful to calculate the matrix elements of the operator $\Theta_n$ defined in Equation (B.8). We focus on the calculation of the matrix element for one mode, in which, for simplicity we drop all subscripts and leave out the minus sign in the exponential,

$$
\langle M | \exp(-\rho_n (a_0^\dagger - a_0)) | N \rangle = \langle M | \exp(\rho (a_0^\dagger - a_0)) | N \rangle \equiv \langle M | \Theta | N \rangle.
$$

We will apply the Baker-Campbell-Hausdorff formula,

$$
\exp(A+B) = \exp(A) \exp(B) \exp\left(-\frac{1}{2} [A,B]\right),
$$

and the commutation relation of the phonon operators of Equation (A.8) to split the exponential of operators

$$
\exp(\rho (a_0^\dagger - a_0)) = \exp(\rho a_0^\dagger) \exp(-\rho a_0) \exp\left(-\frac{1}{2} \rho^2\right).
$$

Expanding the exponentials of the phonon operators gives

$$
\langle M | \Theta | N \rangle = \exp\left(-\frac{1}{2} \rho^2\right) \sum_{k=0}^{\infty} \frac{\rho^k}{k!} \sum_{l=0}^{\infty} \frac{(-\rho)^l}{l!} \langle M | (a_0^\dagger)^k (a_0)^l | N \rangle.
$$

The properties of the vibration creation and annihilation operators of Equations (A.5) and (A.6) allow us to obtain

$$
\langle M | \Theta | N \rangle = \exp\left(-\frac{1}{2} \rho^2\right) \sum_{k=0}^{\infty} \frac{\rho^k}{k!} \sum_{l=0}^{\infty} \frac{(-\rho)^l}{l!} \frac{(N-l+k)!}{(N-l)!} \frac{\sqrt{N!}}{\sqrt{(N-l)!}} |N-l+k\rangle.
$$

Expanding the exponentials of the phonon operators gives

$$
\langle M | \Theta | N \rangle = \begin{cases} 
\exp\left(-\frac{1}{2} \rho^2\right) \sum_{l=0}^{N} \frac{(-\rho)^l}{l!} \frac{(N-l+k)!}{(N-l)!} \sqrt{M!N!} & \text{if } M \geq N \\
(-1)^{M-N} \langle N | \Theta | M \rangle & \text{if } M < N
\end{cases},
$$

For the case that $M = N$ the diagonal matrix element follows, being

$$
\langle N | \Theta | N \rangle = \exp\left(-\frac{1}{2} \rho^2\right) \sum_{l=0}^{N} \frac{(-1)^l \rho^l}{l!} \frac{N!}{(N-l)!} = \exp\left(-\frac{1}{2} \rho^2\right) \sum_{l=0}^{N} \frac{(-1)^l \rho^l}{l!} \left(\frac{N!}{(N-l)!}\right).
$$

This result happens to contain a particular form of a so-called Laguerre polynomial [47, p. 1000],

$$
L_N^0(x) = \sum_{l=0}^{N} \frac{(-1)^l x^l}{l!} \frac{(N + \alpha)}{(N - l)},
$$

as we can see by comparing the expressions above. We have

$$
\langle N | \Theta | N \rangle = \exp\left(-\frac{1}{2} \rho^2\right) L_N^0(\rho^2).
$$

This result is used in Appendix C.1.2.
C.1 The exciton-phonon Hamiltonian

Extending the Holstein Hamiltonian by allowing electronic excitations to couple to any vibrational mode, we can formulate the following exciton-phonon Hamiltonian for an $N$-molecule aggregate that is coupled to a set of quantum harmonic oscillators.

\[
H = \sum_{n=1}^{N} (\epsilon_n + \sum_q \omega_q \lambda_n^2 \lambda_n^q c_n^\dagger c_n + \sum_{n \neq m} J_{nm} c_n^\dagger c_m + \sum_q \omega_q (a_q^a a_q + \frac{1}{2})) + \sum_{n=1}^{N} \sum_q \omega_q \lambda_n (a_q^a + a_q) c_n^\dagger c_n
\]  
(C.1)

Just like in the Holstein model, we assume the exciton-phonon coupling to be linear in the bath coordinates, and we assume it to be diagonal in the electronic states. The coupling strength between an electronic excitation at molecule $n$ and the vibrational mode labeled by $q$ is given by $\omega_q \lambda_n^q$. The above Hamiltonian can be reduced to the Holstein Hamiltonian by taking $\lambda_n^q = \lambda_n \delta_{nq}$. The Hamiltonian with collective modes of Equation (3.5) is obtained from it by taking the exciton-phonon coupling strength $\omega_q \lambda_n = \omega_0 \lambda \psi_q (n)$, with the collective modes defined according to Equation (3.2).

C.1.1 Transforming the Hamiltonian

Applying a partial polaron transformation to the above Hamiltonian according to the generator

\[
G = \sum_n \sum_q \rho_{nq} (a_q^a - a_q^,) c_n^\dagger c_n,
\]  
(C.2)

the results of Appendix B help us to acquire

\[
\tilde{H} = \sum_n \tilde{\epsilon}_n c_n^\dagger c_n + \sum_{n \neq m} \tilde{J}_{nm} c_n^\dagger c_m + \sum_q \omega_q (a_q^a a_q + \frac{1}{2}) + \sum_n \sum_q \omega_q (\lambda_{nq} - \rho_{nq}) (a_q^a + a_q) c_n^\dagger c_n
\]  
(C.3)

where the shifted molecular transition energies and the environment-dressed electronic couplings are given by

\[
\tilde{\epsilon}_n = \epsilon_n + \sum_q \omega_q (\lambda_{nq} - \rho_{nq})^2,
\]

\[
\tilde{J}_{nm} = J_{nm} \exp\left(\sum_q (\rho_{nq} - \rho_{mq}) (a_q^a - a_q)\right) \equiv J_{nm} \Theta_n^a \Theta_m.
\]  
(C.4)
Note that when performing a full polaron transformation, corresponding to \( \rho_{nq} = \lambda_{nq} \), the exciton-phonon coupling term in the above Hamiltonian disappears. Relating the above outcome to the particular result from APTA after applying a full and a variational polaron transformation in Equations (3.15) and (3.16), there we have specified the partial polaron transformation parameters according to

\[
\rho_{nq} = \lambda \psi_q(n) \delta_{q0} + \rho \psi_q(n)(1 - \delta_{q0}).
\]  

(C.5)

All the results that follow from APTA can be obtained by substituting this particular choice of the variational parameters in the general formulas mentioned below.

### C.1.2 Mean field approach

The transformed Hamiltonian of Equation (C.3) is split into two contributions, \( \tilde{H} = \tilde{H}^0 + V \). We define the zeroth-order Hamiltonian as

\[
\tilde{H}^0 = \sum_n \tilde{\epsilon}_n c_n^\dagger c_n + \sum_{n \neq m} \langle \tilde{J}_{nm} \rangle c_n^\dagger c_m + \sum_q \omega_q (a_q^\dagger a_q + \frac{1}{2})
\]  

(C.6)

and the perturbation term as

\[
V = \sum_{n \neq m} [\tilde{J}_{nm} - \langle \tilde{J}_{nm} \rangle] c_n^\dagger c_m + \sum_n \sum q \omega_q (\lambda_{nq} - \rho_{nq})(a_q^\dagger + a_q) c_n^\dagger c_n.
\]

(C.7)

Both terms involve the trace of the transformed molecular interaction over the bath coordinates, \( \langle \tilde{J}_{nm} \rangle = J_{nm} \langle \Theta_n^\dagger \Theta_m \rangle \), an averaged or effective interaction so to say.

The average of any operator \( O \) over the bath coordinates is given by

\[
\langle O \rangle = \frac{\text{Tr}\{ O \exp(-\beta H_b) \}}{\text{Tr}\{ \exp(-\beta H_b) \}},
\]

(C.8)

where the trace runs over the eigenstates of the bath Hamiltonian that is defined by

\[
H_b = \sum q \omega_q (a_q^\dagger a_q + \frac{1}{2}).
\]

(C.9)

Focusing on the grand partition function of the bath first,

\[
Z \equiv \text{Tr}\{ \exp(-\beta H_b) \} = \sum_{N=0}^\infty \langle N | \exp(-\beta H_b) | N \rangle = \sum_{N=0}^\infty \sum_{\{N_q\}} \prod q \exp(-\beta \omega_q (N_q + \frac{1}{2})).
\]

(C.10)

It is to be noted that the summation over the set \( \{N_q\} \) indicates that we should sum over all possible configurations of the bath for which the particle number \( \sum_q N_q = N \). We will resort to a trick used in [48, p. 186] to arrive at the following result.

\[
Z = \prod_q \sum_{N_q=0}^\infty \exp(-\beta \omega_q (N_q + \frac{1}{2})) = \prod_q \exp(-\beta \omega_q (N_q + \frac{1}{2}))
\]

(C.11)

\[
= \prod_q \exp(-\beta \omega_q (N_q + \frac{1}{2})) \frac{1}{1 - \exp(-\beta \omega_q)},
\]

which is a product partition functions of single vibrational modes.

Using this same method, the trace of the phonon-dressed molecular interactions can be written

\[
\text{Tr}\{ \Theta_n^\dagger \Theta_m \exp(-\beta H_b) \} = \prod_q \sum_{N_q=0}^\infty \langle N_q | \exp((\rho_{nq} - \rho_{mq})(a_q^\dagger - a_q)) | N_q \rangle \exp(-\beta \omega_q (N_q + \frac{1}{2})).
\]

(C.12)
Here, the matrix elements are of the same form as those calculated in Section B.3. Substituting their outcome and using the fact that the specific sum above then involves Laguerre polynomials and exponentials it can be performed explicitly according to [47, p. 1002] so as to lead to
\[ \langle \tilde{J}_{nm} \rangle = J_{nm} \exp(-\frac{1}{2} \sum_q (\rho_{nq} - \rho_{mq})^2 \coth(\frac{\omega q}{2kT})). \] (C.13)

C.2 Minimization of the free energy

Here, some general considerations pertaining to the minimization of the free energy from Reference [33] are outlined.

The Helmholtz free energy \( A \) of a system defined by a Hamiltonian \( H \) operating on a separable Hilbert space spanned by the orthonormal set \( |i\rangle \) at temperature \( T \) and volume \( V \) is given by
\[ A = -kT \ln \sum_i \langle i | \exp(-\beta H) | i \rangle \equiv -kT \ln \text{Tr}\{\exp(-\beta H)\}. \] (C.14)

Now, several upper bounds exist for the free energy, of which we will employ the Feynman-Bogoliubov upper bound. Given a Hamiltonian \( H \) that can be written in the form \( H = H^0 + V \), satisfying the conditions
1. \( \text{Tr}\{\exp(-\beta H)\} \) is finite for \( kT < \infty \),
2. \( \text{Tr}\{\exp(-\beta H^0)\} \) is finite for \( kT < \infty \),
the free energy is bounded by
\[ A \leq A_B = -kT \ln \text{Tr}\{\exp(-\beta H^0)\} + \langle V \rangle_{H^0}. \] (C.15)

Here, the term on the right represents the average of the perturbation Hamiltonian over the zeroth-order Hamiltonian,
\[ \langle V \rangle_{H^0} = \frac{\text{Tr}\{V \exp(-\beta H^0)\}}{\text{Tr}\{\exp(-\beta H^0)\}}. \] (C.16)

The trace runs over the eigenstates of Hamiltonian \( H^0 \).

C.2.1 Application to the exciton-phonon Hamiltonian

We consider the transformed exciton-phonon Hamiltonian, \( \tilde{H} \), and its partition into a zeroth-order and perturbation term. We can thus express the free energy of this system as
\[ A \leq A_B = -kT \ln \text{Tr}\{\exp(-\beta \tilde{H}^0)\} + \langle V \rangle_{\tilde{H}^0}, \] assuming condition (1) in the above list is specified. By construction, the second term on the right-hand side of this equation vanishes [33,37].

As we saw in Section 3.2, the free energy can be split into two contributions, the one being
\[ A_{B,e} = -kT \ln \sum_k \exp(-\beta E_k) \] (C.18)
for eigenenergies \( E_k \) of the electronic part of the Hamiltonian in Equation (C.6). The other contribution comes from the bath and it can be expressed using the partition function of Equation (C.11),
\[ A_{B,e} = -kT \ln Z. \] (C.19)

For the general exciton-phonon coupling chosen here, the free energy should be minimized with respect to each variational parameter \( \rho_{nq} \).
C.3 Linear absorption spectra

For the system at hand we take the following dipole operator that is expressed in transformed single-molecule dipole operators,

\[
\tilde{M} = \sum_n \tilde{\mu}_n (\tilde{c}_n^\dagger + \tilde{c}_n) = \sum_n \tilde{\mu}_n (\mathfrak{c}_n^\dagger \exp\left(\sum_q \rho_{nq} (a_q^\dagger - a_q)\right) + \mathfrak{c}_n \exp\left(-\sum_q \rho_{nq} (a_q^\dagger - a_q)\right)).
\]

(C.20)

Using this transformed dipole operator and transitions between the Born-Oppenheimer product wavefunctions of the form given in Equation (3.29), the absorption spectrum for the \(N\)-molecule exciton-phonon coupling Hamiltonian we started with can be expressed as

\[
A(\omega) = \sum_k \sum_{\{M_q\}} \sum_{\{N_q\}} P_{\{N_q\}} \cdots \left| \sum_n \phi_k(n)(\tilde{\mu}_n \cdot \tilde{e}) \prod_q \langle M_q | \exp(\rho_{nq} (a_q^\dagger - a_q)) | N_q \rangle \right|^2 \cdots \delta(E_k - E_g + \sum_q \omega_q (M_q - N_q) - \omega).
\]

(C.21)

Here, \(P_{\{N_q\}}\) represents the Boltzmann factor for the particular initial vibrational state and \(\phi_k(n)\) represent coefficients from the diagonalization of the eigenstates of the electronic part of the Hamiltonian in Equation (C.6).

When turning to zero-temperature absorption, only the vibrationless electronic ground state of the aggregate can serve as the initial state, leading to the following expression for the absorption spectrum.

\[
A(\omega) |_{T=0} = \sum_k \sum_{\{M_q\}} \cdots \left| \sum_n \phi_k(n)(\tilde{\mu}_n \cdot \tilde{e}) \prod_q \exp(-\frac{\rho_{nq}^2}{2}) \frac{M_q}{\sqrt{M_q!}} \right|^2 \cdots \delta(E_k - E_g + \sum_q \omega_q M_q - \omega).
\]

(C.22)

Here we have used Equation (B.19) to evaluate the vibrational overlap integrals.

It is again emphasized that the absorption spectra as acquired from APTA, given in Section 3.3, follow from the general results given here by taking

\[
\omega_q \lambda_n = \omega_0 \lambda \psi_q(n), \quad \rho_{nq} = \lambda \psi_q(n) \delta_{q0} + \rho \psi_q(n) (1 - \delta_{q0}).
\]

(C.23)

Also other methods are covered by the above results, consider the full and variational polaron transformation approaches of Equations (4.7) and (4.8), for instance. They are obtained from the above results by taking

\[
\omega_q \lambda_n = \omega_0 \lambda \delta_{nq}, \quad \rho_{nq} = \lambda \delta_{nq}
\]

(C.24)

and

\[
\omega_q \lambda_n = \omega_0 \lambda \delta_{nq}, \quad \rho_{nq} = \rho \delta_{nq}
\]

(C.25)

respectively.
Bibliography


