DOCTORAL THESIS

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Structure and selforganization of aggregates of photosynthetic molecules

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Title: Structure and selforganization of agregates of photosynthetic molecules

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Abstract: In this work we demonstrate how quantum chemistry (QC) methods and molecular dynamics (MD) simulations can be used in combination with Frenkel exciton model (FEM) to obtain optical and excitation energy transfer properties of complex molecular systems from the molecular structure. The combination of QC and MD methods with FEM provides a powerful tool to study and explain molecular level processes, which are out of reach of the standard FEM parametrization. We use these methods to study and explain molecular mechanism of excitation energy transfer in rylene dyads, especially to explain observed fast excitation energy transfer in dyad with orthogonal arrangement of transition dipoles, where standard approach predicts no excitation energy transfer. On a fundamental level, we relate FEM to configuration interaction method of QC and propose extension of FEM, which accounts for interaction between excitonic manifolds. We investigate effects of this interaction on the optical properties. Inspired by the core features of FEM, we propose new concept of artificial light harvesting antenna based on fluorographene, with design principles inspired by natural light harvesting complexes. We use structure based methods to investigate its excitation transfer properties. We also introduce a new general method for treating environmental effects on excited state properties of embedded systems, which can be used as an extension of widely used polarizable QM/MM approach.

Keywords: Quantum chemistry, Embedded systems, Spectroscopy, QM/MM, Fluorographene, First principles
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Introduction

Studying optical properties of organic pigments is nowadays of great importance for many fields. Organic pigments are crucial components of many biological systems. Chlorophylls, bacteriochlorophylls and carotenoids play major role in light harvesting and excitation energy transfer in natural photosynthetic complexes [1], photoinduced isomerization of rhodopsin molecule is crucial for our vision [2] and photochemical reactions are needed for production of vitamin D in our bodies. Organic pigments are also used in artificial systems as fluorescent probes [3, 4], laser dyes [5, 6] or in solar cells [7, 8, 9] and organic light emitting diodes [10]. In both natural and artificial systems, pigment molecules are usually surrounded by complex environment, e.g protein, solvent or neighboring pigment molecules, which greatly influences their properties. Relating the molecular structure with observed optical properties of biological systems is important for understanding of their function and for selective applications of naturally designed mechanisms into artificial systems.

Optical spectroscopy presents a powerful tool for studying processes in biological systems. However, information which it can provide about underlying molecular mechanisms is still limited. To understand the studied biological processes on molecular level, we need to relate structural information with optical properties. For small isolated systems, it is possible to obtain their optical properties by performing quantum chemistry (QC) calculations of photoinduced processes, and simulate quantum dynamics of resulting excited state, for example by nonadiabatic molecular dynamic simulations [11, 12, 13]. Unfortunately, due to the large size and complexity of biological systems (e.g. pigment protein complexes), it is not possible to use this procedure in biological context. Nevertheless, accurate description of optical properties can still be obtain within framework of theory of open quantum systems. Theory of open quantum systems attacks the problem of the large system size by separating few degrees of freedom of interest which are described explicitly, and which are called the system, from of the rest of the degrees of freedom, called bath, which are treated implicitly. In optical spectroscopy, the system is usually constituted by the electronic degrees of freedom whereas nuclear degrees of freedom are included in the bath. Evolution of the system in presence of the bath is then obtained with quantum master equation approach [14]. Within this approach, we can obtain optical and excitation energy transfer properties even for large molecular complexes with large number of pigments.

The usual strategy in simulating optical spectra and simulating transport properties is to use empirical parameters for the Frenkel exciton model (FEM) Hamiltonian, which are tuned to correspond the measured optical spectra. This way we loose all structural information and the interpretation of the studied phenomena is dependent on the empirical model. However, optical and excitation energy transfer properties are closely related to system structure. For example, in natural light harvesting systems photosynthetic pigments are spatially arranged to enable efficient excitation energy transfer for broad range of external conditions. Different protein environment of otherwise symmetric pigment structure leads to an asymmetric electron transfer in reaction center [15], and the change in
protein conformations leads to different excitation energy pathways, creating of traps or even quenching the excitation [16]. Using the system structural information to parametrize the FEM is therefore crucial for understanding the effects of the system structure on optical and excitation energy transfer properties. Methods for calculating parameters of FEM Hamiltonian from structural information are usually referred to as first principles approaches or structure based methods.

In order to obtain Hamiltonian of large complex system, for example pigment protein complex (PPC), we would need to include the whole system into quantum chemistry (QC) calculation. This is obviously often impossible due to its large size. However, in PPC only few molecules (pigments) are directly involved in interaction with incoming light and excitation energy transfer. The properties of a small subsystem surrounded by large system can be obtained within the framework of theory of embedded systems. The idea behind the embedding theory is similar to the theory of open quantum systems, i.e. to separate the whole complex into small subsystem of interest (pigments) and its environment (protein). The subsystem is then treated with precise QC methods, whereas the environmental effects are included in an approximate way.

In this thesis, we relate FEM parameters to the structure based methods such as QC and molecular dynamics (MD) simulation. The combination of FEM with structure based methods allowed us to explain experimentally observed phenomena, which are beyond the reach of standard phenomenology of the FEM. We proposed improvements of both Frenkel exciton model and structure based methods for calculation of excited state properties of embedded quantum systems. This thesis can be divided into two main parts. In the first part, we extend standard FEM to include the interaction between excitonic manifolds (I). We study effects of this interaction on optical properties of a model dimer and carotenoid aggregate. Then we use FEM with combined MD and QC methods to explain fast excitation energy transfer observed in perylene dyad with orthogonal arrangement of transition dipoles (II). According to the standard FEM, there should be no excitation energy transfer allowed in this system. In the second part, we propose disordered fluorographene (FG) as medium for artificial antenna (III). The design principles of this system are inspired by natural light harvesting systems. We show using quantum chemical calculations that isles of graphene in a FG sheet can act as quasi-molecules similar to natural pigments, from which structures similar in function to photosynthetic antennae can be built, and we discuss efficiency of excitation energy transfer in model FG based antennae. The last part of the thesis is devoted to introduction of new general approach, quantum polarizable atom model, for treating environmental effects on excited state properties of embedded quantum systems (IV). This method is based on quantum mechanical description of the environment, and it can be used as an extension of widely used polarizable QM/MM method [17]. We then show that the proposed method provides reliable and computationally very efficient alternative to full QC calculation of excited state properties of disordered FG systems.

The thesis is organized as follows: In the chapter immediately following this introduction, we introduce basic concepts of linear spectroscopy and discuss effects of system-bath interaction. In the Chapter 2 we present structure based approaches for calculation of FEM parameters from QC and MD and discuss environmental effects on excited state properties of embedded systems. The sub-
sequent chapters then introduce in detail the topics (I) to (IV) and present computation as well as analytical results. The corresponding research papers, including the ones currently in submission process, are included in the appendix.
1. Theory of Optical Spectroscopy and Open Quantum Systems

This chapter introduces the theory of linear spectroscopy [14, 18] and related concepts of open quantum systems theory. After introduction of basic concepts of light-matter interaction and linear spectroscopy techniques we discuss effects of interaction with a bath, and its consequences for the selection of the most suitable basis representation.

1.1 Light-matter interaction

Properties of molecular systems are usually investigated with spectroscopic methods. The simplest ways of accessing information about system excited state properties are the linear spectroscopies such as absorption, fluorescence and circular dichroism spectroscopies. These spectroscopic methods are based on measuring intensity changes in incident electric field after an interaction with the sample. Propagation of a transversal part of electric field $\vec{E} \perp (\vec{r}, t)$ in dielectric medium can be described by the wave equation

$$-\Delta \vec{E} \perp (\vec{r}, t) = -\frac{1}{c^2} \frac{\partial^2}{\partial t^2} \left( \vec{E} \perp (\vec{r}, t) + \frac{1}{\varepsilon_0} \vec{P}(\vec{r}, t) \right),$$

where $\vec{P}(\vec{r}, t)$ corresponds to the polarization induced in the medium by the electric field. By inducing transition dipoles in the sample, electric field loses its energy and these loses are dependent on system properties. Polarization induced in the sample can be also represented as a response of the system to the incoming electric field as

$$\vec{P}(\vec{r}, t) = n_{mol} \int d^3 r \int_0^t d\tau \ S(\vec{r} - \vec{r}', t - \tau) E(\vec{r}', \tau),$$

where $S(\vec{r}, t)$ is the so-called linear response function. It describes how the system respond to an external electric field. The quantity $n_{mol}$ represents the density of molecules interacting with the incident light in the sample. For the small molecular systems, smaller than wavelength of external electric field, position dependence of response function can be neglected i.e. $S(\vec{r}, t) = \delta(\vec{r}) S(t)$. Fourier transform of the response function $S(\omega)$ is related to energy absorption in the sample.

$$\alpha(\omega) = \frac{\omega n_{mol}}{\varepsilon_0 n(\omega) c} \Im \{S(\omega)\}.$$  

Absorption of incident electric field intensity in the sample is described by the Lambert-Beer law, $I(\vec{r}, t) = I_0 e^{-\alpha(\omega) z}$, with absorption coefficient $\alpha(\omega)$ which is directly probed in spectroscopy experiments. Connection between microscopic properties of the sample and macroscopic signal is inherent in the response function.
1.2 Microscopic definition of response function

The light-matter interaction is generally described in a semi-classical approximation. Semi-classical approximation is based on treating the sample quantum mechanically to correctly describe its discrete energy levels and keeping light classical, because in vast majority of cases, quantum effects of light are not important in linear spectroscopy measurements. Total Hamiltonian is therefore separated into the sample part and the interaction terms (corresponding to the interaction with the external electric and magnetic fields)

\[ \hat{H}(t) = \hat{H}_{\text{sample}} - \hat{\mu} \cdot \vec{E}(t) - \hat{\mathbf{m}} \cdot \vec{B}(t). \]  

(1.4)

The electric dipole operator \( \hat{\mu} = -e \sum_i \hat{\mathbf{r}}_i \) and the magnetic dipole operator \( \hat{\mathbf{m}} = \frac{e^2}{2mc} \sum_i \hat{\mathbf{r}}_i \times (i\hbar \nabla_i) \) represent the interaction between the quantum systems and classical light. The evolution of the sample interacting with light is described by Liouville-von Neumann equation

\[ \frac{\partial \hat{\rho}(t)}{\partial t} = -\frac{i}{\hbar} \left[ \hat{H}(t), \hat{\rho}(t) \right]. \]  

(1.5)

Solution of the Liouville-von Neumann equation for sample interacting with external field described by Hamiltonian (1.4) can be obtained using perturbation expansion in orders of light-matter interaction. In the linear spectroscopy we assume weak external field and therefore the system evolution can be represented only by the linear term. For this case, the sample evolution can be described by time dependent density operator \( \hat{\rho}(t) \) in the form

\[ \hat{\rho}(t) = \hat{\rho}_{\text{eq}} + \frac{i}{\hbar} \int_{t_0}^{t} dt_1 \left[ \hat{\mu}^I(t - t_1), \hat{\rho}_{\text{eq}} \right] \vec{E}(t_1) + \frac{i}{\hbar} \int_{t_0}^{t} dt_1 \left[ \hat{\mathbf{m}}^I(t - t_1), \hat{\rho}_{\text{eq}} \right] \vec{B}(t_1), \]  

(1.6)

where \( \mu^I(t) \) is the dipole operator in the interaction picture with respect to the sample Hamiltonian, \( \mu^I,\text{sample}(t) = e^{iH_{\text{sample}}t} \mu e^{-iH_{\text{sample}}t} \). Connection between macroscopic signal and microscopic system evolution is established through the induced polarization in the system, which is equal to an expectation value of the sample dipole moment

\[ \vec{P}(t) = tr \left\{ \hat{\mathbf{P}} \right\} = \int_{t_0}^{t} dt_1 \frac{i}{\hbar} \langle \left[ \hat{\mu}^I(t - t_1), \hat{\mu} \right] \rangle_{\text{eq}} \vec{E}(t_1) + \int_{t_0}^{t} dt_1 \frac{i}{\hbar} \langle \left[ \hat{\mathbf{m}}^I(t - t_1), \hat{\mathbf{m}} \right] \rangle_{\text{eq}} \vec{B}(t_1). \]  

(1.7)

Here, \( \langle \ldots \rangle_{\text{eq}} \) corresponds to a trace over equilibrium density operator. Relating the microscopic definition of the polarization (1.7) with the macroscopic one (1.2) yields microscopic definition of the single chromophore response function

\[ S(t) = \frac{i}{\hbar} \theta(t) \langle \left[ \hat{\mu}^I(t), \hat{\mu} \right] \rangle_{\text{eq}} + \frac{i}{\hbar} \theta(t) \langle \left[ \hat{\mathbf{m}}^I(t), \hat{\mathbf{m}} \right] \rangle_{\text{eq}}. \]  

(1.8)

The first term, dipole autocorrelation function, corresponds to the absorption or fluorescence spectra when the initial density operator is taken as the ground and the excited state equilibrium density operator, respectively. The second part represents circular dichroism which is more sensitive to system secondary structure, mutual orientations of individual chromophores in the sample and chirality of the chromophores due to the different selection rules.
1.3 Absorption and Fluorescence spectroscopy

Because of the complexity of biological systems, it would not be feasible to fully describe the evolution and dynamics of the system together with its environment quantum mechanically. Instead, we treat the chromophores as open quantum systems. The sample Hamiltonian is traditionally separated into

$$\hat{H}_{\text{sample}} = \hat{H}_S + \hat{H}_{SB} + \hat{H}_B,$$

where $\hat{H}_S$ is the system part containing the chromophores and the most important degrees of freedom, and $\hat{H}_B$ is the bath Hamiltonian containing everything else which is not included in the system (protein, membrane, solvent, ...). $\hat{H}_{SB}$ describes the mutual interaction between the bath and the system, and it is generally assumed to be bi-linear in the bath and system degrees of freedom (DOF). The bath contains all DOF which are not directly involved in the interaction with light. In the Frenkel exciton model, the bath is usually described as a set of harmonic oscillators coupled to the system DOF through which they alter energy of system states. The sample Hamiltonian can be then expressed in (so far) arbitrary basis of system states $|N\rangle$ as (Attachment A.1)

$$\hat{H}_S = \left[ \sum_N \varepsilon_N |N\rangle \langle N| + \frac{1}{2} \sum_{N\neq M} J_{NM} (|N\rangle \langle M| + |M\rangle \langle N|) \right] \otimes 1_B,$$

$$\hat{H}_{SB} = \frac{1}{2} \sum_{M,N} \hbar \omega_{\xi} g_{\xi} (M,N) \hat{Q}_{\xi} (|N\rangle \langle M| + |M\rangle \langle N|),$$

$$\hat{H}_B = \sum_{\xi} \frac{\hbar \omega_{\xi}}{4} \left( \hat{Q}_{\xi}^2 + \hat{P}_{\xi}^2 \right) \otimes 1_S,$$

where $\hat{Q}_{\xi}$ and $\hat{P}_{\xi}$ are dimensionless position and momentum of uncoupled harmonic oscillators, respectively, $\hbar \omega_{\xi}$ is the energy of vibrational quanta in the mode $\xi$, $g_{\xi} (M,N)$ is a dimensionless system-bath coupling strength, $\varepsilon_N$ is the energy of the system state $|N\rangle$ and $J_{MN}$ correspond to an interaction between state $M$ and $N$. Dimensionless coordinate and momentum are related to creation and annihilation operators $\hat{a}_{\xi}^\dagger$ and $\hat{a}_{\xi}$, respectively, of vibrational quanta by $\hat{Q}_{\xi} = \hat{a}_{\xi}^\dagger + \hat{a}_{\xi}$ and $\hat{P}_{\xi} = i \left( \hat{a}_{\xi}^\dagger - \hat{a}_{\xi} \right)$. Using the separated Hamiltonian, Eq. 1.10, the evolution of the whole sample can be decomposed into the evolution of the isolated system ($e^{-\frac{i}{\hbar}\hat{H}_S t}$), bath ($e^{-\frac{i}{\hbar}\hat{H}_B t}$) and their mutual interaction

$$\hat{U}(t) = e^{-\frac{i}{\hbar}\hat{H}_{\text{sample}} t} = e^{-\frac{i}{\hbar}\hat{H}_S t} e^{-\frac{i}{\hbar}\hat{H}_B t} \exp \left[ -\frac{i}{\hbar} \int_{t_0}^t d\tau \left( \hat{H}_{S-B} + \hat{H}_{S}^{\text{off-diag}} \right) I_{B+S} (\tau) \right].$$

Effects of the diagonal part of the system-bath interaction Hamiltonian can be included analytically through cumulant expansion, whereas the off-diagonal part has to be included perturbatively. Cumulant expansion is exact for harmonic bath and for a diagonal Hamiltonian. Therefore the proper basis for treatment of the sample evolution is the one, which minimize the off-diagonal elements of the sample Hamiltonian (Eq. 1.10) in electronic states.

In the absorption experiments, molecules are initially in the ground states and they are excited by interaction with incoming electric field. The initial equilibrium
density operator for absorption then corresponds to the system in the ground state
and the bath in a thermal equilibrium, defined as

$$\hat{\rho}_{eq} = |G\rangle \langle G| \frac{\exp \left[ -\beta \hat{H}_B \right]}{tr_B \left( \exp \left[ -\beta \hat{H}_B \right] \right)}, \quad (1.12)$$

where $\beta = (k_B T)^{-1}$ is inverse temperature and $tr_B \{\ldots\}$ represents trace over the
bath states. Absorption response function for the diagonal part of the system-
bath interaction can then be obtained using separation of evolution operator
(1.11) in Eq. (1.8) with the initial ground state equilibrium density operator
(1.12) in the form of

$$S^{(abs)}_{(t)} = i \frac{\theta}{\hbar} (t) \sum_N |\tilde{\mu}_{GN}|^2 e^{-i(\varepsilon_N - \varepsilon_G)t} e^{-\left( \int_0^t dt_1 \int_0^{t_1} dt_2 C_{NN(t_1-t_2)} \right)} + h.c., \quad (1.13)$$

$$C_{NN}(t) = \sum_\xi (\omega_\xi g_\xi (N,N))^2 \langle \tilde{Q}^I_{\xi\xi}(t) \tilde{Q}_{\xi\xi} \rangle_{B,eq}, \quad (1.14)$$

where $h.c.$ denotes hermitian conjugate, and $C_{NN}(t)$ is the bath correlation function
for the state $N$.

In the fluorescence experiments, the molecules are initially equilibrated in the
lowest excited state. The equilibrium density operator then correspond to the system in the lowest excited state $M$ and the bath equilibrated in the excited state

$$\hat{\rho}_{eq} = |M\rangle \langle M| \frac{\exp \left[ -\beta \hat{H}_B \right]}{tr_B \left( \exp \left[ -\beta \hat{H}_B \right] \right)}, \quad (1.15)$$

Here, $\tilde{B}$ denotes the bath in the excited state. The excited state potential surfaces
for the bath are shifted with respect to the ground state, which results in a
different equilibrium density operator. Following the same derivation as for the
absorption spectra, the response function for the fluorescence from the excited
state $M$ is obtained in the following form

$$S^{(fluor)}_{M}(t) = i \frac{\theta}{\hbar} (t) \sum_N |\tilde{\mu}_{GN}|^2 e^{\left( \varepsilon_M - \varepsilon_G - 2E^{(M)}_\lambda/\hbar \right)t} e^{-\left( \int_0^t dt_1 \int_0^{t_1} dt_2 C_{NN(t_1-t_2)} \right)} + h.c. \quad (1.16)$$

where $E^{(M)}_\lambda$ is the reorganization energy of the excited state $M$. The concepts of
reorganization energy will be discussed in more detail in the following section.

1.4 Bath correlation function

Bath correlation function describes how the bath fluctuations alter the energies of
the individual system states. The bath correlation function is usually treated in
Fourier domain in which the contribution is separated into the Fourier transform
of the real and the imaginary part as

$$C(\omega) = \int_{-\infty}^{\infty} dt \ C(t) e^{i\omega t} = C'(\omega) + C''(\omega)$$

$$C'(\omega) = \int_{-\infty}^{\infty} dt \ \Re \{C(t)\} e^{i\omega t}$$
\[ C^{\prime \prime} (\omega) = i \int_{-\infty}^{\infty} dt \Im \{ C(t) \} e^{i\omega t}. \] (1.17)

The Fourier transform \( C^{\prime \prime} (\omega) \) of the imaginary part of the bath correlation function \( C(t) \) is called spectral density. Both \( C^{\prime} (\omega) \) and \( C^{\prime \prime} (\omega) \) are real due to the time symmetry of the correlation function \( C(-t) = C^{\ast}(t) \). They both possess a frequency symmetry: \( C^{\prime} (-\omega) = C^{\prime} (\omega) \) is even and \( C^{\prime \prime} (-\omega) = -C^{\prime \prime} (\omega) \) is odd.

The whole \( C(\omega) \) also satisfies the detailed balance condition

\[ C (-\omega) = \exp (-\beta \hbar \omega) C (\omega), \] (1.18)

where \( \beta = (k_B T)^{-1} \) is the inverse temperature. Fluctuation dissipation theorem relates the imaginary and the real parts of the correlation function

\[ C^{\prime} (\omega) = \coth \left( \frac{\beta \hbar \omega}{2} \right) C^{\prime \prime} (\omega). \] (1.19)

Using this relation, the Fourier transform of the whole bath correlation function can be obtained from the spectral density \( C^{\prime \prime} (\omega) \) only as

\[ C (\omega) = \left( 1 + \coth \left( \frac{\beta \hbar \omega}{2} \right) \right) C^{\prime \prime} (\omega). \] (1.20)

These properties are general for any bath correlation function, and they are independent on the bath model.

One of the widely used models for the description of the bath correlation function, is the so-called Brownian oscillator model. Within this model, a single normal mode is subjected to a stochastic external force together with friction \( \gamma \xi \), representing the combined effects of all other DOF acting on the selected normal mode. Spectral density \( C^{\prime \prime}_{NN} (\omega) \) for the Brownian oscillator model reads as

\[ C^{\prime \prime}_{NN} (\omega) = \sum_{\xi} g_{\xi}^2 (N, N) \frac{2\omega_{\xi}^2 \gamma_{\xi} \omega}{(\omega_{\xi}^2 - \omega^2)^2 + \omega^2 \gamma_{\xi}^2}. \] (1.21)

The Brownian oscillator model provides us with a general description of a harmonic bath. Some other commonly used models can be recovered using different limits of Brownian oscillator model. When the friction is small, \( \gamma_{\xi} \to 0 \), the model corresponds to a discrete set of undamped harmonic oscillators. For this case the spectral density has the form of a sum of delta functions at normal mode frequencies

\[ C^{\prime \prime}_{NN} (\omega) = \pi \sum_{\xi} g_{\xi}^2 (N, N) \omega_{\xi}^2 [\delta (\omega - \omega_{\xi}) - \delta (\omega + \omega_{\xi})]. \] (1.22)

Another interesting limit is obtained for large friction \( \gamma_{\xi} \gg 2\omega_{\xi} \). Large friction results in an overdamped harmonic oscillator. Spectral density then has Ohmic form with Drude-Lorentz cutoff and it corresponds to a continuous distribution of harmonic oscillators

\[ C^{\prime \prime}_{NN} (\omega) = \sum_{\xi} \frac{2\lambda_{\xi} \Lambda_{\xi} \omega}{\Lambda_{\xi}^2 + \omega^2}. \] (1.23)

Here \( \lambda_{\xi} = g_{\xi}^2 (N, N) \omega_{\xi} \) and \( \Lambda_{\xi} = \omega_{\xi}^2 / \gamma_{\xi} \).
Excitation of the system from the ground to excited state occurs on fs timescale whereas the movement of the bath is much slower. Therefore, during the system excitation, bath remains in the same state as for the ground state. When the system is in the excited state, the bath starts adjusting to a new conditions and reorients around the molecule. The reorientation of the bath results in a different optimal geometry of the system in the excited state compared to the system in the ground state. The energy difference connected with the reorganization of the system in the excited state is called reorganization energy $E_{\lambda}^{(N)}$. For harmonic bath, the reorganization energy can be obtained from bath correlation function as

$$E_{\lambda}^{(N)} = \frac{\hbar}{2\pi} \int_{-\infty}^{+\infty} d\omega \frac{C_{NN}(\omega)}{\omega} = \frac{\hbar}{2\pi} \int_{-\infty}^{+\infty} d\omega \frac{C_{NN}'(\omega)}{\omega}.$$  \hspace{1cm} (1.24)

### 1.5 Preferred basis

Evaluation of the response function depends on the basis used for the description of the system. Finding the proper (preferred) basis for given general system is still an unresolved problem and heavily discussed topic. However, there are some limits when the preferred system basis is known. In the case of the weak resonance coupling between excited states of individual chromophores, as compared to the interaction with the bath, excitation tends to localize on individual chromophores. The preferred basis is therefore the site basis constructed as a simple product of eigenstates of individual chromophores

$$|N\rangle = |(m_1, n_2, o_3, \ldots)\rangle = |m_1\rangle|n_2\rangle|o_3\rangle\cdots,$$  \hspace{1cm} (1.25)

where $|n_i\rangle$ is nth state of chromophore $i$. The quantities $\varepsilon_N$ in the system Hamiltonian then represents a sum of energies of individual chromophores. In the site basis system-bath interaction operator is diagonal. The only non-diagonal part of the sample Hamiltonian corresponds to small coupling between individual chromophores $J_{MN}$. The effect of the off-diagonal part can be included as a small perturbation, which results in excitation energy transfer between individual chromophores. This parameter regime is well described by the Förster energy transfer theory [19].

In case of strong resonance coupling, excitation is delocalized over many chromophores. The preferred basis therefore corresponds to the delocalized, so-called exciton basis, in which the system Hamiltonian $\hat{H}_S$ is diagonal. States obtained by the diagonalization of $\hat{H}_S$ using unitary transformation are called excitons [20], and they are linear combinations of the site basis wavefunctions

$$|N\rangle = \sum_{n,m,o,\ldots} c_{(m,n,o,\ldots)}^{(N)} |(m_1, n_2, o_3, \ldots)\rangle.$$  \hspace{1cm} (1.26)

The resulting eigenvalues $\varepsilon_N$ of system Hamiltonian are called exciton energies. Off-diagonal part of the system bath interaction can be treated, like in the previous case, as a small perturbation, leading to the so-called Redfield theory [19]. Off-diagonal elements of the system-bath coupling are then responsible for the energy transfer between individual exciton states.
For many biologically relevant and interesting systems, system-bath interaction is comparable to the coupling between individual sites. They lie in an intermediate regime between the Redfield and the Förster theories. For these systems the preferred basis is unknown, however, good results were obtained using delocalized exciton basis with the so-called Modified Redfield theory [19]. In the intermediate regime, the two limiting approaches described above can be combined together. The system can be divided into strong interacting clusters which are diagonalized separately. Energy transfer within these clusters can be described by the (Modified) Redfield theory, while the small interaction between individual building blocks and resulting energy transfer can be described by Förster theory (see e.g. [21]).

1.6 Energy gap correlation function

Evolution of the system subjected to an interaction with a bath can be described more generally without using the harmonic bath assumption of Section 1.3. In the site basis the Hamiltonian of the whole system interacting with an environment, can be described using a general bath as

\[
\hat{H}_S = \left[ \sum_n \varepsilon_n^0 |n\rangle \langle n| + \frac{1}{2} \sum_{N \neq M} J_{nm} (|n\rangle \langle m| + |m\rangle \langle n|) \right] \otimes 1_B,
\]

\[
\hat{H}_{SB} = \sum_n \left( \hat{V}_n \langle \{Q\} \rangle - \hat{V}_g \langle \{Q\} \rangle \right) |n\rangle \langle n|,
\]

\[
\hat{H}_B = \left( \hat{T} + \hat{V}_g \langle \{Q\} \rangle \right) \otimes 1_S,
\]

where \( \varepsilon_n^0 \) corresponds to the energy of an electronic system in the state \( n \) in the minimum of the potential surface \( V_n \langle \{Q\} \rangle \). The response function for this general system is derived using the same procedure as for the harmonic bath in Section 1.3

For the cumulant expansion it is desirable to have zero expectation value of the system-bath interaction operator. This is achieved by reorganizing the system Hamiltonian and system-bath operator into

\[
\hat{H}_S = \left[ \sum_n \varepsilon_n |n\rangle \langle n| + \frac{1}{2} \sum_{N \neq M} J_{nm} (|n\rangle \langle m| + |m\rangle \langle n|) \right] \otimes 1_B,
\]

\[
\hat{H}_{SB} = \frac{1}{2} \sum_n \left( V_n \langle \{Q\} \rangle - V_g \langle \{Q\} \rangle - \langle V_n \langle \{Q\} \rangle - V_g \langle \{Q\} \rangle \rangle_{eq} \right) |n\rangle \langle n|,
\]

where \( \varepsilon_n = \varepsilon_n^0 + \langle V_n \langle \{Q\} \rangle - V_g \langle \{Q\} \rangle \rangle_{eq} \) corresponds to the excited state energy of the chromophores in the ground state geometry (vertical transition energy). The sign \( \langle \ldots \rangle_{eq} \) represents a trace over the equilibrium density matrix. We further assume that the bath has the Gaussian property, i.e. that the higher-order correlation functions can be expressed in terms of the second-order correlation.
functions through the Wick’s theorem. For this type of the bath, the second order cumulant expansion is exact. We can then follow the same procedure as for the harmonic bath, which results in the same expression for the response function as for the harmonic bath, namely Eqs. (1.13) and (1.16), only with a general form of the correlation function

\[ C_{mn}(t) = \sum_{ij} C_{n_i n_j}(t), \]

\[ C_{n_i n_j}(t) = \frac{1}{\hbar^2} \langle \Delta V_{n_i}^{1B}(t) \Delta V_{n_j} \rangle_{eq}. \]  

(1.29)

Here \( \Delta V_{n_i} = V_{n_i} (\{Q\}) - V_{g_i} (\{Q\}) - \langle V_{n_i} (\{Q\}) \rangle - V_{g_i} (\{\langle Q \rangle \}) \) describes a change of the transition energy between the ground state and the exited state \( n_i \) of the chromophore \( i \) with the bath coordinates \( Q \). \( C_{n_i n_j}(t) \) is called energy gap correlation function. Energy gap correlation function describes, how the transition energies on the same chromophore \((i = j)\) or between two different chromophores \((i \neq j)\) are correlated, when the system is subjected to thermal fluctuations in its ground state \( g \).

The previous results for the harmonic bath, Eq. (1.14), can be recovered using the following definition

\[ \hat{T} = \sum_{\xi} \hat{p}_\xi^2 \frac{\hbar^2}{2m_\xi} \hat{p}_\xi^2; \]

\[ \hat{V}_g (\{Q\}) = \sum_{\xi} \frac{1}{2} \hbar \omega_\xi q_\xi^2 = \sum_{\xi} \frac{\hbar \omega_\xi}{4} \hat{Q}_\xi^2; \]

\[ \hat{V}_m (\{Q\}) = \sum_{\xi} \frac{\hbar \omega_\xi}{4} \left( \hat{Q}_\xi + 2g_\xi (\{m, m\})^2 \right), \]  

(1.30)

where \( \hat{q}_\xi \) and \( \hat{p}_\xi \) are the harmonic oscillator coordinate and momentum, respectively, and \( m_\xi \) is the mass of the harmonic oscillator. Here, we have also used the dimensionless coordinate \( \hat{Q}_\xi = \sqrt{\frac{2m_\xi \omega_\xi}{\hbar}} \hat{q}_\xi \) and momentum \( \hat{p}_\xi = \sqrt{\frac{2}{\hbar m_\xi \omega_\xi}} \hat{p}_\xi \) introduced earlier in Section 1.3. For the harmonic bath, excited state potential \( \hat{V}_m (\{Q\}) \) corresponds to a shifted ground state harmonic potential. The dimensionless coupling constants \( g_\xi (\{m, m\}) \), which correspond to the potential surface shifts, and the energy gap correlation functions \( C_{mn}(t) \) are obtained for the site basis. These quantities can be transformed into an arbitrary basis, as used for the harmonic bath in Section 1.3, by a basis transformation \( |M\rangle = \sum_m c_{m}^{(M)} |m\rangle \) resulting in

\[ g_\xi (M, N) = \sum_{m,n} c_{n}^{(M)} c_{n}^{(N)} g_\xi (m, n), \]

\[ C_{NN}(t) = \sum_{m,n} c_{m}^{(N)} c_{n}^{(N)} C_{mn}(t). \]
2. Structure Based Methods for Optical Spectroscopy

In the previous chapter we discussed the basic principles of optical spectroscopy and introduced Hamiltonian operator (in the standard form) of a system coupled to vibrational bath, which is used for description of system optical properties. In this chapter we introduce methods for calculation of parameters of this Hamiltonian from structural information.

2.1 Introduction

In order to calculate optical properties of a molecular system by the methods described in the previous chapter, Hamiltonian elements and transition dipoles have to be supplied. Usually, empirical models are used for construction of system and system-bath interaction Hamiltonian operators. Some parameters of these simplified models are obtained directly from spectroscopy measurements on simplified systems, whereas others from fitting the experimental spectra. With an increasing number of different experiments, these parameters can become more and more refined, and the models are adjusted to explain new results. Although this procedure often leads to reliable and generally accepted models, molecular mechanisms of studied processes remain hidden. As a consequence, there might be more competing interpretations of observed phenomena. For some cases, decision between different interpretations is not in reach of today’s experimental methods. In order to correctly and reliably describe molecular mechanisms of processes such as excitation energy transfer in pigment protein complexes, non-photochemical quenching etc., the structure based methods are required.

In the structure based methods, the known molecular structure of the system is used to obtain the initial parameters for calculation of optical spectra or excitation energy transfer. This approach is called the first-principles or ab initio calculation. The structure of the system is usually obtained from crystallographic experiments or from molecular dynamics (MD) simulations. The systems with only few pigments, usually dyads or triads, form a special group of systems, which were chemically synthesized to study specific phenomena and whose structure is known, or very limited number of conformations is allowed.

Basically, we need to obtain four properties of the system, namely, transition energies and corresponding transition dipoles of individual chromophores, interaction energies between the chromophores and spectral density of the bath which describes how the bath DOF influence system transition and interaction energies. Because of the complexity and size of the studied biological systems, the whole system has to be separated into chromophore system and the environment. The chromophore system consists of those parts of the whole system, which interact directly the light or are involved in the excitation energy transfer. The chromophore system can be described within quantum chemistry (QC) methods or combined QC and molecular dynamic (QM/MM) methods. The resulting eigenstates and energies are the ones used for calculation of the optical properties of the system. The environment contains the remaining part of the system (protein,
solvent, membrane,...). Because of the size of the environment, its effects on
the chromophore system are included using approximate methods. Although the
environment does not directly interact with the light, correct description of its
interaction with the chromophore system is necessary for simulating properties of
whole coupled system. For example, small changes in pH or in conformation of
the protein might lead to different excitation energy transfer path or they might
even quench the excitation [22].

Even the chromophore system is often too large to be treated by QC methods
as a whole. For example, in light the harvesting complex II (LHCII) in higher
plants, the chromophore system is composed of 14 chlorophyll and 4 carotenoid
molecules, which is too big for most of the QC methods, especially for excited
state calculations. Therefore, pigments in the system are divided into individual
groups between which there is no molecular orbital overlap. The pigments with
large molecular orbital overlap, such as for example the so-called special pair in
the photosynthetic reaction center, must be treated as a single supermolecule. QC
methods are then used to obtain properties of each molecule (group) separately,
without taking into account the interaction with the other molecules (groups).
Starting from this system of noninteracting chromophores, the eigenstates of the
full system can be obtained using perturbation or variation approach.

Natural basis for both perturbation expansion in intermolecular interaction
and the variational approach is the site basis (1.25). Site basis provides the
easiest way for calculation of the interaction energies, and also a simple physical
interpretation of the individual interaction terms.

2.2 Approximate approaches in quantum chemistry

In this section, we describe standard approximate approaches which are used
in quantum chemistry for obtaining properties of complex systems. Biologically
relevant systems are generally too complicated to be treated by precise quantum
mechanic (QM) methods. However, even much smaller systems, such as molecules
or even non-hydrogen atoms, are not in reach of precise QM methods. These
systems are generally treated the same way no matter the size of the system
(individual atoms or clusters of molecules). The whole system is separated into
two parts

\[ \hat{H} = \hat{H}_0 + \hat{V}, \]  

(2.1)

where \( \hat{H}_0 \) describes part of the system, with known solution or which can be
calculated by standard QM methods. The operator \( \hat{V} \) describes the complicated
part of the system, the perturbation. The effect of the perturbation is included
using approximate methods. The eigenstates \( |n\rangle \) of the system without the per-
turbation, where \( \varepsilon_n |n\rangle = \hat{H}_0 |n\rangle \), provide a basis set for the solution of the full
coupled system \( |N\rangle \), where \( E_N |N\rangle = \hat{H} |N\rangle \), in form of linear combination of
the basis functions \( |N\rangle = \sum_i c_{iN} |i\rangle \). In Quantum Theory, there are two basic
methods which can be used for an approximate solution of the full Hamiltonian,
the variational method and the perturbation approach.

The decision which method to use, is depends on the form of the perturbation
and also on the original unperturbed system. The perturbation approach pro-
vides faster convergence with the number of basis functions for systems, where energetic separation of eigenstate of interest from the rest of the eigenstates of the unperturbed system is large in comparison to the perturbation \( V \). However, when the eigenstates are energetically close and the perturbation is strong, variation method should be used. Systems where the original energy levels are close together, or even degenerate, but the perturbation is small, belongs to a special group. For this group of the systems, the terms \((\varepsilon_n - \varepsilon_l)^{-1}\) in the perturbation expansion (2.3) and (2.4) might diverge and therefore the so-called degenerate perturbation theory should be used.

### 2.2.1 Variational method

Variational method is based on minimization of the total energy with respect to the expansion coefficients \( c_iN \). In the variational method, expansion coefficients \( c_iN \) and corresponding energies \( E_N \) are obtained as a solution of the following eigenvalue problem

\[
\begin{pmatrix}
\varepsilon_0 + \langle 0 | \hat{V} | 0 \rangle & \langle 0 | \hat{V} | 1 \rangle & \langle 0 | \hat{V} | 2 \rangle & \cdots \\
\langle 1 | \hat{V} | 0 \rangle & \varepsilon_1 + \langle 1 | \hat{V} | 1 \rangle & \langle 1 | \hat{V} | 2 \rangle & \cdots \\
\langle 2 | \hat{V} | 0 \rangle & \langle 2 | \hat{V} | 1 \rangle & \varepsilon_2 + \langle 2 | \hat{V} | 2 \rangle & \cdots \\
\vdots & \vdots & \vdots & \ddots
\end{pmatrix}
\begin{pmatrix}
c_0N \\
c_1N \\
c_2N \\
\vdots
\end{pmatrix}
= E_N
\begin{pmatrix}
c_0N \\
c_1N \\
c_2N \\
\vdots
\end{pmatrix},
\]

where \( |0\rangle, |1\rangle, \ldots \) are basis functions of the system without the perturbation and \( \varepsilon_0, \varepsilon_1, \ldots \) are corresponding energies. The great advantage of the variational method is that the exact energy is approached from above. This means that the lower the energy of resulting wavefunction is, the better approximation to the exact wavefunction it provides. This might be used to extrapolate the exact energy using the set of variational energies for different basis sizes.

### 2.2.2 Perturbation expansion

The perturbation expansion is based on expansion of the wavefunction \( |N\rangle \) of the whole system in orders of the perturbation operator \( \hat{V} \). We assume that the perturbation is small and therefore the wavefunction of the whole system should be close to the wavefunction of the noninteracting one. The exact wavefunction of the full system is, within this approach, approximated as

\[
|N\rangle \approx |n\rangle + \sum_{k \neq n} \frac{\langle n | \hat{V} | k \rangle}{\varepsilon_n - \varepsilon_k} |k\rangle + \sum_{k \neq n \neq l \neq n} \frac{\langle n | \hat{V} | l \rangle \langle l | \hat{V} | k \rangle}{(\varepsilon_n - \varepsilon_l)(\varepsilon_n - \varepsilon_k)} |k\rangle
- \langle n | \hat{V} | n \rangle \sum_{k \neq n} \frac{\langle k | \hat{V} | k \rangle}{(\varepsilon_n - \varepsilon_k)^2} |k\rangle - \frac{1}{2} \sum_{k \neq n} \frac{\langle k | \hat{V} | k \rangle \langle k | \hat{V} | n \rangle}{(\varepsilon_n - \varepsilon_k)^2} |n\rangle + \ldots, \quad (2.3)
\]

and the corresponding energy reads as

\[
E_N \approx \varepsilon_n + \langle n | \hat{V} | n \rangle + \sum_{k \neq n} \frac{\langle n | \hat{V} | k \rangle^2}{\varepsilon_n - \varepsilon_k} + \sum_{k \neq n \neq l \neq n} \frac{\langle n | \hat{V} | l \rangle \langle l | \hat{V} | k \rangle \langle k | \hat{V} | n \rangle}{(\varepsilon_n - \varepsilon_l)(\varepsilon_n - \varepsilon_k)}
- \langle n | \hat{V} | n \rangle \sum_{k \neq n} \frac{\langle k | \hat{V} | k \rangle^2}{(\varepsilon_n - \varepsilon_k)^2} + \ldots, \quad (2.4)
\]
The perturbation expansion should provide fast convergence to the exact eigenstates of the full system when the perturbation is small compared to the energetic splitting of the unperturbed system eigenstates. Problems, however, arise for systems where individual eigenstates are energetically close and the terms \((\varepsilon_n - \varepsilon_k)^{-1}\) might diverge. Another disadvantage of this approach is that the exact solution can be approached from both sides, it can be overestimated, underestimated or it might even oscillate around the exact solution. For some cases it might be therefore hard to guess at which order one should cut the expansion.

2.2.3 Degenerate perturbation approach

The degenerate perturbation approach eliminates the largest problem of the perturbation approach, the diverging terms for close-to-degenerate systems. This approach is based on combined variation and perturbation treatment. First the matrix representation of the full Hamiltonian is separated into individual blocks where the states are energetically close. Then we transform the initial basis to have no interaction between states inside the block as

\[
C^\dagger = \begin{pmatrix}
\varepsilon_1 & V_{12} & V_{13} & V_{14} & V_{15} \\
V_{12} & \varepsilon_1 & V_{23} & V_{24} & V_{25} \\
V_{13} & V_{23} & \varepsilon_1 & V_{34} & V_{35} \\
V_{14} & V_{24} & V_{34} & \varepsilon_2 & V_{45} \\
V_{15} & V_{25} & V_{35} & V_{45} & \varepsilon_2
\end{pmatrix} = \begin{pmatrix}
\tilde{\varepsilon}_1 & 0 & 0 & \tilde{V}_{14} & \tilde{V}_{15} \\
0 & \tilde{\varepsilon}_2 & 0 & \tilde{V}_{24} & \tilde{V}_{25} \\
0 & 0 & \tilde{\varepsilon}_3 & \tilde{V}_{34} & \tilde{V}_{35} \\
\tilde{V}_{14} & \tilde{V}_{24} & \tilde{V}_{34} & \tilde{\varepsilon}_4 & 0 \\
\tilde{V}_{15} & \tilde{V}_{25} & \tilde{V}_{35} & 0 & \tilde{\varepsilon}_5
\end{pmatrix}, \tag{2.5}
\]

where elements with tilde correspond to the Hamiltonian elements in the new basis. \(C\) is the transformation matrix between the old and new basis which has a block diagonal form

\[
C = \begin{pmatrix}
c_{11} & c_{12} & c_{13} & 0 & 0 \\
c_{21} & c_{22} & c_{23} & 0 & 0 \\
c_{31} & c_{32} & c_{33} & 0 & 0 \\
0 & 0 & 0 & c_{44} & c_{45} \\
0 & 0 & 0 & c_{54} & c_{55}
\end{pmatrix}. \tag{2.6}
\]

In the columns of the matrix \(C\) there are expansion coefficients into the new basis \(|\tilde{n}\rangle = \sum c_{n\tilde{n}} |i\rangle\). The basis functions \(|\tilde{n}\rangle\) of the new basis have different energies, \(\tilde{\varepsilon}_n\), then the original ones, \(\varepsilon_n\). Due to the partial diagonalization, there is no interaction between states which are energetically close. However, by partial diagonalization we have included some parts of the interaction operator into the "unperturbed system". Therefore, the new basis is not the eigenbasis of \(H_0\) anymore, which violates the original assumptions for the perturbation expansion. This can be corrected by reorganization of the perturbation operator \(\hat{V}\) and the unperturbed Hamiltonian \(\hat{H}_0\). All elements of the perturbation operator which are included into the partial diagonalization of the full Hamiltonian, should be included into the "unperturbed system". For the presented example (Eq. 2.5) this will result in

\[
\hat{H} = \hat{H}_0 + \hat{V},
\]

\[
\hat{H}_0 = \hat{H}_0 + \sum_{i,j=1}^3 V_{ij} |i\rangle \langle j| + \sum_{i,j=4}^5 V_{ij} |i\rangle \langle j|,
\]

18
\[ \hat{V} = \hat{V} - \sum_{i,j=1}^{3} V_{ij} |i\rangle \langle j| - \sum_{i,j=4}^{5} V_{ij} |i\rangle \langle j|. \]  

(2.7)

The new basis \(|\tilde{n}\rangle\) is the eigenbasis of the Hamiltonian \(\hat{H}_0\) and \(\hat{V}\) is the new perturbation operator used for the perturbation expansion. This way we got rid of the diverging terms in the perturbation expansion (2.3) and (2.4), and it is therefore safe to use the perturbation approach with the new basis for including the effects of the remaining coupling \(\mathcal{V}\).

### 2.3 Molecular polarizability

In this section we relate classical definition of molecular polarizability, as the first order response to external electric field, with quantum mechanical properties of the molecule. The electric polarizability, \(\alpha\), of a molecule is a measure of its ability to respond to an external electric field \(\vec{E}\) and acquire an electric dipole moment, \(\vec{\mu}\). Interaction of the molecule with an external field is treated in semiclassical approximation and described by Hamiltonian \(\hat{H} = \hat{H}_0 - \vec{\mu} \cdot \vec{E}\), Eq. (1.4). The electric polarizability is defined as a linear response parameter of the molecule’s dipole moment on the electric field

\[ \langle \vec{\mu} \rangle = \langle \vec{\mu} \rangle_0 + \alpha \cdot \vec{E} + \sigma (\vec{E}^2), \]  

(2.8)

where \(\langle \vec{\mu} \rangle_0\) corresponds to a dipole moment of the molecule without an external electric field. The dipole moment of the molecule can be related through Hellmann–Feynman theorem to the energy derivative. With the semiclassical Hamiltonian, in form of Eq. (1.4), it reads as

\[ \frac{dE}{d\vec{E}} = \left\langle \frac{\partial E}{\partial \vec{E}} \right\rangle = -\langle \vec{\mu} \rangle. \]  

(2.9)

The total energy of the molecule in the presence of an external field can be written in form of a Taylor expansion as

\[ E(\mathcal{E}) = E_0 + \left( \frac{dE}{d\mathcal{E}} \right)_0 \mathcal{E} + \frac{1}{2} \left( \frac{d^2E}{d\mathcal{E}^2} \right)_0 \mathcal{E}^2 + \ldots, \]  

(2.10)

where the subscript 0 corresponds to \(\mathcal{E} = 0\). With the known energy derivative (Eq. (2.9)) together with definition of dipole (Eq. (2.8)) we can identify the individual terms in Taylor expansion as

\[ \left( \frac{dE}{d\mathcal{E}} \right)_0 = -\langle \vec{\mu} \rangle_0, \]  

\[ \left( \frac{d^2E}{d\mathcal{E}^2} \right)_0 = -\alpha_{ij}. \]  

Using these relations we can write the total energy of the system in the presence of an external electric field in the form of

\[ E(\mathcal{E}) = E_0 - \langle \vec{\mu} \rangle_0 \cdot \vec{E} - \frac{1}{2} \vec{E} \cdot \alpha \cdot \vec{E} + \ldots \]  

(2.11)
The total energy can be also obtained by means of perturbation expansion (2.4) with $-\hat{\mu} \cdot \vec{E}$ as an perturbation operator

$$E(\mathcal{E}) = E_0 - \langle \hat{\mu} \rangle_0 \cdot \vec{E} + \sum_n \left| \frac{\vec{E} \cdot \langle g | \hat{\mu} | n \rangle}{E_{0g} - E_{0n}} \right|^2 + \ldots ,$$

(2.12)

where $|g\rangle$ is the ground state with energy $E_{0g}$ of the molecule without an external electric field, and $n$ stands for the excited states. Comparing the two equivalent expressions for the energy (2.11) and (2.12), we obtain the quantum definition of the molecule’s static polarizability

$$\alpha_{ij} = 2 \sum_n \frac{\langle g | \hat{\mu}_i | n \rangle \langle g | \hat{\mu}_j | n \rangle}{E_{0n} - E_{0g}},$$

(2.13)

where $i,j \in \{x,y,z\}$ indicates cartesian coordinates. The static polarizability describes the response of the molecule to a static external electric field. However, in spectroscopic experiments we usually have time dependent electric fields. We can use similar approach as above combined with time dependent perturbation theory to derive dynamic polarizability \(\vec{\alpha}(\omega)\) of a molecule \(\text{[23]}\). The dynamic polarizability describes the response of the molecule to an external electric field at frequency $\omega$ as

$$\vec{\alpha}_{ij}(\omega) = 2 \sum_n \frac{(E_{0n} - E_{0g}) \langle \hat{\mu}_{gn} \rangle_i \langle \hat{\mu}_{gn} \rangle_j}{(E_{0n} - E_{0g})^2 - (\hbar \omega)^2},$$

(2.14)

where $\hat{\mu}_{gn} = \langle g | \hat{\mu} | n \rangle$ is a transition dipole between the ground and excited states.

When applying Eqs. (2.13) and (2.14) for QC calculation of molecular polarizabilities, it is important, at least for some cases, to include all excited states into the calculation. For example for hydrogen atom, including only bound states into the expansion results in $4/5$ of the experimental polarizability, whereas including also the continuum states yields the correct experimental value.

### 2.4 Resonance coupling without environment

In this section we introduce methods, which can be used for calculation of resonance coupling (interaction between excited states of different chromophores) for isolated systems without environment, e.g. pigments in vacuum. We show, how the resonance coupling is defined and present methods for its numerical calculation. In subsequent section (Section 2.5) these methods provide a starting point for inclusion of system-environment interaction into the calculation of excited state properties.

The off-diagonal terms in the system Hamiltonian, Eq. (1.9), correspond to interaction energy (resonance coupling) between individual molecules of the system. Within the Förster transfer theory, the off-diagonal Hamiltonian elements are responsible for excitation energy transfer. The transfer is therefore triggered by electrostatic interaction between transition densities of individual molecules. On the other hand within the Redfield transfer theory, the interaction between excited state results in delocalization of the excited states and formation of the
exciton states (Eq. [1.26] and Section 1.5). The electrostatic interaction between
transition densities is responsible for formation the exciton manifold on which
the excitation energy transfer occurs.

The procedure for calculation of the resonance coupling will be demonstrated
on a simple system, however, the results can be easily generalized to more complex
systems. Our system consist of two interacting molecules $A$ and $B$, each with a
ground and excited states. The system is then described by following Hamiltonian

$$
\hat{H} = \hat{H}_A + \hat{H}_B + \hat{V}_{AB},
$$

where the lower case letters correspond to electronic indexes, upper case letters
correspond to nuclear indexes and $Z$ represents the nuclear charge. The multidi
dimensional position $\vec{r} = (\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_{N+M})$ corresponds to the position of all electrons from both molecules. Further we assume no overlap between molecular orbitals from different molecules. In this approximation the basis function can be constructed as a simple Hartree product of eigenstates of individual molecules, the site basis (Eq. (1.25) and Section 1.5)

$$
\langle \vec{r} | \hat{V}_{AB} | \vec{r} \rangle = V_{AB} (\vec{r}) = \sum_{i \in A} \sum_{j \in B} \frac{1}{|\vec{r}_j - \vec{r}_i|} + \sum_{I \in A} \sum_{J \in B} \frac{Z_I Z_J}{|\vec{R}_J - \vec{R}_I|} - \sum_{i \in A} \sum_{j \in B} \frac{Z_J}{|\vec{R}_J - \vec{r}_i|} - \sum_{j \in B} \sum_{I \in A} \frac{Z_I}{|\vec{R}_I - \vec{r}_j|},
$$

(2.15)

The interaction energy between molecules in ground state $V_{gg,gg}$ is defined as a
matrix element of the interaction operator $\hat{V}_{AB}$

$$
V_{gg,gg} = \langle gg | \hat{V}_{AB} | gg \rangle = \int d^3r_1 \int d^3r_2 \rho_g^{(A)} (\vec{r}_1) V_{AB} (\vec{r}_1, \vec{r}_2) \rho_g^{(B)} (\vec{r}_2),
$$

(2.17)

where $\rho_g^{(A)} (\vec{r}_1)$ and $\rho_g^{(B)} (\vec{r}_1)$ are total ground state electron density of molecule $A$ and $B$, respectively. The total ground and excited state densities are defined as

$$
\rho_{g/e}^{(A)} (\vec{r}_1) = N \int d^3r_2 \cdots \int d^3r_N |\psi_{g/e}^{(A)} (\vec{r}_1, \ldots, \vec{r}_N)|^2.
$$

(2.18)

In exactly the same way, we can define the interaction energy between excited sates $V_{ge,eg}$ as a matrix element between two different excited states

$$
V_{ge,eg} = \langle ge | \hat{V}_{AB} | eg \rangle = \int d^3r_1 \int d^3r_2 \rho_{ge}^{(A)} (\vec{r}_1) \frac{1}{|\vec{r}_1 - \vec{r}_2|} \rho_{ge}^{(B)} (\vec{r}_2),
$$

(2.19)

where $\rho_{ge}^{(A)} (\vec{r}_1)$ and $\rho_{ge}^{(B)} (\vec{r}_1)$ are the transition electron densities of molecule $A$ and $B$, respectively, defined as

$$
\rho_{ge}^{(A)} (\vec{r}_1) = N \int d^3r_2 \cdots \int d^3r_N \psi_g^{*(A)} (\vec{r}_1, \ldots, \vec{r}_N) \psi_e^{(A)} (\vec{r}_1, \ldots, \vec{r}_N).
$$

(2.20)
The interaction $V_{ge,eg}$ between singly excited states $|ge⟩$ (molecule $A$ in the ground state and molecule $B$ in the excited state) and $|eg⟩$ (molecule $A$ in the excited state and molecule $B$ in the ground state) corresponds to the Coulomb interaction of transition densities of the individual molecules.

The matrix element $V_{gg,ee}$ of the interaction operator, corresponds to the interaction of the ground and doubly excited states. It has exactly the same value as the interaction between two singly excited states $V_{ge,eg}$:

$$V_{gg,ee} = \langle gg | \hat{V}_{AB} | ee \rangle = \sum_{i,j} \int d\vec{r}_A \int d\vec{r}_B \psi^*_e (\vec{r}_A) \psi^*_e (\vec{r}_B) \frac{1}{|\vec{r}_i - \vec{r}_j|} \psi_g (\vec{r}_A) \psi_g (\vec{r}_B), \quad (2.21)$$

where $\vec{r}_A = (\vec{r}_1, \vec{r}_2, \ldots \vec{r}_N)$ are positions off all electrons from the molecule $A$ and $\vec{r}_B$ from the molecule $B$.

In the standard Frenkel exciton model it is assumed that the diagonal interaction matrix elements and the elements between states with different number of excitations are zero, i.e.

$$V_{gg,gg} = V_{gg,eg} = V_{ee,gg} = V_{ee,ee} = \cdots = 0.$$  

The only non-zero elements accounted for in Frenkel excitaton model are couplings between the states of the same manifold i.e $V_{ge,eg}$. For the purpose of the verification of the above assumptions, let us assume that both molecules neutral are in the ground and excited states and they have no permanent dipole moment. These conditions are generally fulfilled for most of the photosynthetic pigments. We can use the multipole expansion of the interaction terms (2.22). For the neutral molecules without permanent dipole moment the lowest non-zero terms of the multipole expansion for diagonal interaction elements ($V_{gg,gg}, V_{eg,eg}, \ldots$) correspond to a quadrupole-quadrupole interaction. For the interaction elements between states which differ only in a single excitation ($V_{gg,eg}, V_{ee,eg}, \ldots$), the lowest non-zero multipole expansion element is transition dipole-quadrupole interaction. Both of these terms decay rapidly with the intermolecular distance and therefore they can be safely neglected for larger intramolecular distances. However, as it was shown before in (2.21) the interaction between states which differ by two excitations (ground and double excited state) are exactly the same as interaction between excited states from the same manifold (interaction between two singly excited states). The effect of the interaction between different excitation manifolds is, however, diminished by the energy difference between manifolds. The effects of the interaction between different excitation manifolds on excited state and optical properties are discussed later in Section 2.4.4 and Chapter 3.
2.4.1 Multipole expansion - point dipole approximation

By far the most popular method for evaluation of the interaction integrals between transition densities is the dipole approximation. The dipole approximation is based on multipole expansion of coulombic interaction term in intermolecular distances. In this approach, electron coordinate \( \vec{r}_i \) is expressed relative to center of corresponding molecule \( \vec{R}_A \) as \( \vec{r}_i = \vec{R}_A + \vec{r}_{Ai} \) where \( \vec{R}_A \) is the position of the center of the molecule. The coulombic interaction term can be then expressed as a Taylor series in intermolecular distances

\[
\frac{1}{|\vec{r}_1 - \vec{r}_2|} \approx \frac{1}{|\vec{R}_{AB}|} + \frac{(\vec{r}_{A1} - \vec{r}_{B2}) \cdot \vec{R}_{AB}}{|\vec{R}_{AB}|^3} + \frac{\vec{r}_{A1} \cdot \vec{r}_{B2}}{|\vec{R}_{AB}|^3} - 3 \frac{(\vec{r}_{A1} \cdot \vec{R}_{AB}) (\vec{r}_{B2} \cdot \vec{R}_{AB})}{|\vec{R}_{AB}|^5} \\
+ \frac{3 (\vec{r}_{A1} \cdot \vec{R}_{AB})^2}{|\vec{R}_{AB}|^5} + \frac{(\vec{r}_{B2} \cdot \vec{R}_{AB})^2}{|\vec{R}_{AB}|^5} + \frac{\vec{r}_{A1} \cdot \vec{r}_{B2}}{|\vec{R}_{AB}|^3} + \ldots \tag{2.22}
\]

Here, \( \vec{R}_{AB} = \vec{R}_B - \vec{R}_A \) is the intermolecular distance. From the definition of the transition density (2.20) and from the orthogonality of the ground and excited states (\( \int d^3r \rho^{ge}_{ge}(\vec{r}) = 0 \)) we can see that first nonzero term in the multipole expansion for the interaction between excited states, is the dipole-dipole interaction between point transition dipoles on different molecules. The interaction energy (resonance coupling) reads as

\[
J_{AB} = V_{ge,eg} \approx \frac{\vec{\mu}^{(A)}_{eg} \cdot \vec{\mu}^{(B)}_{eg}}{|\vec{R}_{AB}|^3} - 3 \frac{(\vec{\mu}^{(A)}_{eg} \cdot \vec{R}_{AB}) (\vec{\mu}^{(B)}_{eg} \cdot \vec{R}_{AB})}{|\vec{R}_{AB}|^5}, \tag{2.23}
\]

where transition dipole is defined in atomic units as \( \mu^{(A)}_{eg} = - \int d^3r \vec{r} \rho^{(A)}_{ge}(\vec{r}) \).

The transition dipoles of individual molecules can be obtained from experimental measurements and this method therefore provides a very simple and useful approximation of the resonance coupling. However, point dipole approximation is valid only for the large intermolecular distances. When molecules are close \( \vec{r}_{A1} \sim \vec{R}_{AB} \), their structure has to be taken into account and dipole approximation breaks down. This could be corrected by including higher multipoles in the interaction energy expansion, however, these are not directly experimentally accessible and usually the method would require including a large number of higher multipoles.

2.4.2 Transition density cube method

Another approach how to evaluate the interaction integrals (2.17) and (2.19) is called the transition density cube method (TDC) [24]. This method is based on discretization of transition densities on three dimensional grid around each molecule. The transition density is integrated within the elementary grid cube into point charge located at each grid point. The interaction energy is then simply calculated as Coulomb interaction between the point grid charges from different molecules. When the grid is dense enough, it is reasonable to assume uniform electron density within the elementary grid cube and integration of the electron

23
density over the cube can be replaced by the density value at the grid point multiplied by the volume of the grid cube. Interaction energy is then obtained as

\[ J_{AB} = V_{ge,eg} \approx \Delta V^{(A)} \Delta V^{(B)} \sum_{(i,j,k)} \sum_{(a,b,c)} \frac{\rho_{ge}^{(A)}(\vec{r}_{ijk}) \rho_{ge}^{(B)}(\vec{r}_{abc})}{|\vec{r}_{ijk} - \vec{r}_{abc}|}, \]  

(2.24)

where \((i, j, k)\) and \((a, b, c)\) are grid point indexes corresponding to equidistant grids around molecules \(A\) and \(B\), respectively, \(\vec{r}_{abc}\) is position of the grid point, \(\rho_{ge}^{(A)}(\vec{r}_{ijk})\) is the value of electron transition density at specified grid point, and \(\Delta V\) is volume of the elementary grid cube. This method provides very reliable approximation to the exact interaction energy even for small intermolecular distances. Although this method is very simple and easy to implement, the major drawback is computational cost. Reliable representation of an electron density require around \(10^5 - 10^6\) grid points which results in \(10^10 - 10^{12}\) mutual interaction terms which need to be evaluated.

### 2.4.3 TrEsp method

An alternative approach to the interaction energy calculation is used in TrEsp (transition charges from electrostatic potential) method [25]. The electrostatic potential \(\Phi_{aa'}(r)\) generated by the electron density \(\rho_{aa'}(\vec{r})\) is approximated by electrostatic potential of point charges as

\[ \Phi_{aa'}(r) = \int d^3r \frac{1}{|\vec{r} - \vec{r}_1|} \rho_{aa'}(\vec{r}) \approx \sum J q_J(\vec{R}_J), \]  

(2.25)

where \(\vec{R}_J\) is the position of a point charge \(q_J(a, a')\). In this expansion, the positions of the point charges could be arbitrary, but fixed, and the value of the charge is obtained by fitting of the electrostatic potential generated by electron density, in the area outside the molecule (RESP procedure [26]). The electrostatic potential used for the charge fitting is obtained from QC calculation. The position of the charge is usually chosen to be the coordinate of the nuclei. The resulting charges are then called atomic charges. The advantage of using the atomic charges, is the possibility to use them in molecular dynamic (MD) simulations, where the position of the charge is moving together with the nuclear coordinate without the need to calculate the charges for every conformation of the molecule. The \(q_J(g, g)\) corresponds to the ground state atomic charges which are used in the standard MD simulations, where atomic charge is considered a sum of the electronic atomic charge and the charge of the corresponding nucleus. Within the TrEsp method, the interaction energy between two excited states is obtained as a Coulomb interaction between point transition charges \(q_J(g, e)\) from different molecules

\[ J_{AB} = V_{ge,eg} \approx \sum_{I \in A} \sum_{J \in B} q_J^{(A)}(g, e) q_J^{(B)}(g, e) \frac{1}{|\vec{R}_I - \vec{R}_J|}. \]  

(2.26)

The TrEsp method provides the same accuracy for interaction energy calculation as TDC method with a much lower computational cost. For the usual photosynthetic molecules, the TrEsp interaction energy calculation requires evaluation of only around \(10^3\) pair interaction terms.
2.4.4 Strongly interacting homodimer

On a simple example of strongly interacting homodimer in the vacuum, we present how the interaction energy between two molecules can be extracted from the results of standard QC methods. The QC calculation with fixed nuclei of the chromophores corresponds to a chromophore system in vacuum at zero temperature, therefore without any interaction with a heat bath or environment. For such case the interaction between monomers always lead to delocalization of the excited states no matter how strong the interaction between them is.

Within Frenkel exciton model, the delocalized, exciton (1.26), eigenstates of the system can be obtained from variational principle (Section 2.2.1) as a linear combination of the site basis (1.25)

\[
\begin{pmatrix}
0 & 0 & 0 & V_{gg,ee} \\
0 & \varepsilon_{eg} & V_{ge,eg} & 0 \\
0 & V_{eg,ge} & \varepsilon_{eg} & 0 \\
V_{ee,gg} & 0 & 0 & 2\varepsilon_{eg}
\end{pmatrix}
\begin{pmatrix}
c^{(i)}_{gg} \\
c^{(i)}_{ge} \\
c^{(i)}_{eg} \\
c^{(i)}_{ee}
\end{pmatrix} = E_i
\begin{pmatrix}
c^{(i)}_{gg} \\
c^{(i)}_{ge} \\
c^{(i)}_{eg} \\
c^{(i)}_{ee}
\end{pmatrix},
\] (2.27)

where the energy of the ground state was set to zero. This results in replacing the excitation energies by transition ones, \(\varepsilon_{eg} = \varepsilon_e - \varepsilon_g\). The \(c^{(i)}_j\) is an expansion coefficient of the eigenstate \(i\) in the site basis element \(j\). To construct the Hamiltonian, we assumed neutral molecules without permanent dipoles separated by sufficient distance to yield zero interaction between transition density and the ground state, as described in Section 2.4. These conditions are generally fulfilled for natural pigment protein complexes and they are required by the standard Frenkel exciton model of the excitation transfer. These assumptions about the system lead to a block separated Hamiltonian with no interaction between the blocks. First block corresponds to the interaction between singly excited states

\[
\begin{pmatrix}
\varepsilon_{eg} & V_{ge,eg} \\
V_{eg,ge} & \varepsilon_{eg}
\end{pmatrix}
\begin{pmatrix}
c^{(i)}_{ge} \\
c^{(i)}_{eg}
\end{pmatrix} = E_i
\begin{pmatrix}
c^{(i)}_{ge} \\
c^{(i)}_{eg}
\end{pmatrix},
\] (2.28)

and it results in splitting of the excited state levels. The resulting excited states for interacting system are

\[
|E_1\rangle = \frac{1}{\sqrt{2}} (|ge\rangle + |eg\rangle) \quad E_{E_1} = \varepsilon_{eg} + V_{ge,eg},
\]

\[
|E_2\rangle = \frac{1}{\sqrt{2}} (|ge\rangle - |eg\rangle) \quad E_{E_2} = \varepsilon_{eg} - V_{ge,eg}.
\] (2.29)

The interaction energy \(V_{ge,eg}\) between two singly excited states can be then simply obtained from exiton energies \((E_{E_1} \text{ and } E_{E_2})\) of the resulting eigenstates as

\[
J_{AB} = V^{(\text{homodimer})}_{ge,eg} = \frac{1}{2} (E_{E_2} - E_{E_1}).
\] (2.30)

When the exciton energies are substituted by the excitation energies obtained from QC calculation of the dimer, this simple relation can be used for QC evaluation of the homodimer excited state interaction energy.

The second Hamiltonian block corresponds to the interaction between the ground and the doubly excited states, where we used the equality \((V_{gg,ee} = V_{eg,ge})\) (2.21) yielding

\[
\begin{pmatrix}
0 & V_{ge,eg} \\
V_{eg,ge} & 2\varepsilon_{eg}
\end{pmatrix}
\begin{pmatrix}
c^{(i)}_{gg} \\
2c^{(i)}_{ge}
\end{pmatrix} = E_i
\begin{pmatrix}
c^{(i)}_{gg} \\
2c^{(i)}_{ge}
\end{pmatrix}.
\] (2.31)
The interaction between the ground and the doubly excited states results in energy shift and redistribution of the transition dipole moment. The resulting ground $|G\rangle$ and excited $|F\rangle$ state of the interacting system together with the corresponding energies are

$$|G\rangle \approx |gg\rangle - \frac{V_{ge,eg}}{2\varepsilon_{eg}} |ee\rangle, \quad E_G \approx -\frac{V_{ge,eg}^2}{2\varepsilon_{eg}},$$

$$|G\rangle \approx |ee\rangle + \frac{V_{ge,eg}}{2\varepsilon_{eg}} |gg\rangle, \quad E_F \approx 2\varepsilon_{eg} + \frac{V_{ge,eg}^2}{2\varepsilon_{eg}}. \quad (2.32)$$

The energy shift of the ground and the doubly excited state is by the factor of $V_{ge,eg}/2\varepsilon_{eg}$ smaller than the energy shift of the singly excited states $(2.29)$, however, for strongly interacting molecules or large aggregate it might result in a measurable transition energy shift.

The interaction between the ground and the double excited states also results in a transition dipole redistribution. The transition dipoles between the ground and the singly excited states have the following form

$$\vec{\mu}_{GE_1} = -\sum_i \langle G| \vec{r}_i |E_1\rangle \approx \sqrt{2} \left(1 - \frac{V_{ge,eg}}{2\varepsilon_{eg}}\right) \vec{\mu}_{ge},$$

$$\vec{\mu}_{GE_2} = -\sum_i \langle G| \vec{r}_i |E_1\rangle = 0, \quad (2.33)$$

For the standard Frenkel exciton model, the interaction between the ground state and the doubly excited state is neglected. Resulting oscillator strength $f \propto \sum_i |\vec{\mu}_i|^2$ is then independent of the interaction energy and equal to the oscillator strength of the separated non-interacting molecules. However, when the interaction between the ground and the doubly excited state is taken into account, the total oscillator strength is changed (it can be both lowered or enhanced, depending on sign of the resonance coupling $V_{ge,eg}$). The change of the oscillator strength can be observed in absorption spectroscopy, where the surface under the absorption spectra (curve) is proportional to the total oscillator strength of the studied system.

Similar procedure can be also applied to systems, where individual chromophores have different excitation energies. For these systems, energies of the eigenstates read as

$$E_{E_1} = \frac{\varepsilon^{(A)}_{eg} + \varepsilon^{(B)}_{eg}}{2} - \sqrt{\left(V_{ge,eg}(AB)\right)^2 + \left(\frac{\varepsilon^{(B)}_{eg} - \varepsilon^{(A)}_{eg}}{2}\right)^2},$$

$$E_{E_2} = \frac{\varepsilon^{(A)}_{eg} + \varepsilon^{(B)}_{eg}}{2} + \sqrt{\left(V_{ge,eg}(AB)\right)^2 + \left(\frac{\varepsilon^{(B)}_{eg} - \varepsilon^{(A)}_{eg}}{2}\right)^2}.$$ 

The resonance coupling can be then extracted from the eigenstates of the coupled system as

$$|J_{AB}| = |V_{ge,eg}(AB)| = \frac{1}{2} \sqrt{(E_{E_2} - E_{E_1})^2 - \left(\varepsilon^{(B)}_{eg} - \varepsilon^{(A)}_{eg}\right)^2}. \quad (2.34)$$
The Eq. (2.34), provides a general formula for calculation of interaction energies between two chromophores. The eigenstates of the coupled system can be calculated for example by QC methods. From comparison of transition energies of coupled system with transition energies of individual chromophores, we could in principle obtain the resonance coupling. However, for chromophores with large gap between the transition energies, the shift of the excited states induced by the interaction is smaller than the numerical error of QC methods for calculation of eigenstates. Therefore, the formula (2.34) can be used for QC calculation of resonance coupling only for homodimers or chromophores with similar transition energies.

Figure 2.1: Graphical representation of the methods for resonance coupling calculation. a) System structure. b) Direct evaluation of resonance coupling from Coulomb interaction of transition densities c) Interaction between two transition dipoles (point transition dipole approximation) d) Transition density cube method e) TrEsp method. The QC electrostatic potential (solid contour lines) is approximated by potential of point atomic charges (dashed contour lines). Balls represent the individual atoms and the color represents the TrEsp charge. f) Calculation of the resonance coupling from the splitting of electronic eigenstates. For homodimer the interaction energy is a half of the excited state energy splitting.
2.5 Chromophores embedded in environment

In biological systems, pigments are embedded in a protein or dissolved in a solution. This environment is constantly interacting with the pigment system, changing its structure, shifting the energy of its states and also screening the interactions between individual pigment molecules. Due to this interaction we cannot simply use the site energies and interaction energies obtained for pigments in vacuum by QC calculation as input parameters for the simulation of the optical and excitation energy transfer properties, but the environment effects must be also included. The environment is usually very large and contains a large number of DOF, we cannot therefore include it into the full QC calculation of the system parameters. In the past years substantial effort was devoted to the development and improvement of models that account for the environment in the excited state quantum chemical calculations. These methods can be divided into quantum subsystem approaches (QM/QM), combined quantum mechanical and molecular mechanical methods (QM/MM) and polarizable continuum models (PCM). In this section, we will present examples of methods from each of these groups and discuss mutual similarities between these approaches.

The properties which are affected by the environment can be separated into two groups. In the first group there are static properties such as excitation energies and corresponding transition dipoles or interaction energies between individual pigments. These properties are related only to the optimal structure of the system. For some very simple systems, usually systems with only a single pigment, all of these quantities are directly accessible by spectroscopy methods. The transition energies correspond to the peak positions in the absorption and fluorescence spectra, whereas the peak intensities correspond to the transition dipoles. In the other group, there are dynamical properties which are related to the time evolution of the whole system or to its conformation energy landscape. An example of such a quantity is the spectral density. The spectral density describes how the change in environment DOF is reflected on system properties. Spectral density is also accessible experimentally for systems containing only a single pigment, e.g. from fluorescence line narrowing experiments at low temperatures [27].

In this section we will discuss the environmental effects on the static properties of the system and some approximate methods for including these effects into calculations. The dynamic properties are discussed in Section 2.6.

2.5.1 System definition

The simplest system for presenting methods for including environmental effects is a two chromophore system interacting with its environment. This coupled system is described by the following Hamiltonian

\[
\hat{H} = \hat{H}_A + \hat{H}_B + \hat{H}_E + \hat{V},
\]

\[
\hat{V} = \hat{V}_{AB} + \hat{V}_{AE} + \hat{V}_{BE} + \hat{V}_{EE},
\]

(2.35)

where \(\hat{H}_A\) is Hamiltonian of the isolated chromophore \(A\) in vacuum (without the environment) with eigenstates \(|m^{(A)}\rangle\) and corresponding energies \(\varepsilon_m^{(A)}\). Exactly the same way, we define the Hamiltonian and the corresponding eigenstates
for the chromophore $B$. $\hat{H}_E = \sum_n \hat{H}_E^{(n)}$ is the environment Hamiltonian which is composed of noninteracting parts $\hat{H}_E^{(n)}$ (atoms, molecules, clusters, ...) with eigenstates $|\eta^{(n)}\rangle$ and energies $E_{\eta}^{(n)} = \langle \eta^{(n)} | \hat{H}_E^{(n)} | \eta^{(n)} \rangle$. $\hat{V}_{SE}$ is the coupling between the environment and the system, and $\hat{V}_{EE} = \frac{1}{2} \sum_{n,n'} V_{nn'}$ is the coupling between individual environment molecules. The coupling term between the system and the environment corresponds to the Coulomb interaction between individual electrons and cores. We further assume no overlap between chromophores $A$ and $B$, between chromophores and the environment, and also between individual environment molecules. For such system, the basis functions can be constructed as a simple Hartree product of the eigenfunctions of individual parts $|m^{(A)}\rangle |k^{(B)}\rangle \prod_n |\eta^{(n)}\rangle$. For simplifying the description of the environment states we introduce multi-index $\eta = (\eta_1, \eta_2, \ldots, \eta_n, \ldots)$ to abbreviate the notation for the electronic states of the environment. The basis functions can be then written in a shorter notation as
\begin{equation}
|m, k, \eta\rangle = |m^{(A)}\rangle |k^{(B)}\rangle \prod_n |\eta^{(n)}\rangle.
\end{equation}

### 2.5.2 Resonance coupling definition

The interaction energy between two chromophores in vacuum is defined as a Coulomb interaction between two transition densities of different molecules (2.19). However, the interaction between two molecules embedded in the environment has a more complicated form. The prescription for the interaction energy calculation depends on a purpose for which the resulting value is used. In the Frenkel exciton model used for the description of the system optical and energy transfer properties, the interaction energy corresponds to the interaction between states of individual pigments in which the interaction with the environment is already included. The interaction of the individual chromophores with the environment induces shifts in their transition energies. The shifted states form the site basis manifold and correspond to the diagonal elements of the system Hamiltonian (1.10). The interaction energies between individual pigments correspond to the off-diagonal elements of the system Hamiltonian (1.10). The interaction between pigments triggers the energy transfer between individual pigments and leads to a formation of the delocalized exciton basis, depending on whether the interaction is weak or strong. The correctly defined interaction energy should therefore lead to the formation of the same eigenstates, starting from the shifted site basis, as the ones obtained from the full QC treatment of the system including the environment.

Let's assume that we only have a two chromophore system with the environment. We further assume that we know the transition energies of individual chromophores where the environmental effects are already included ($\tilde{\varepsilon}_A$ and $\tilde{\varepsilon}_B$). According to the exciton model, when the interaction between two chromophores $J_{AB}$ is introduced, it will result in delocalized states and in a splitting of the original energies. The new excitonic energies of the resulting states are obtained from variation principle (2.2) in the form
\begin{equation}
E_1 = \left( \frac{\tilde{\varepsilon}_A + \tilde{\varepsilon}_B}{2} \right) + \sqrt{\left( \frac{\tilde{\varepsilon}_A - \tilde{\varepsilon}_B}{2} \right)^2 + J_{AB}^2}.
\end{equation}
When the eigenstates $E_1$ and $E_2$ are known from QC calculation of the whole system including the environment or some approximate approach, we can use them to extract the absolute value of the interaction energy between individual states as

$$|J_{AB}| = \frac{1}{2} \sqrt{(E_2 - E_1)^2 - (\tilde{\epsilon}_B - \tilde{\epsilon}_A)^2}.$$  (2.37)

The sign of the interaction energy is then taken the same as the sign of the interaction energy between two chromophores without the environment. In the case of a symmetric homodimer ($\tilde{\epsilon}_B = \tilde{\epsilon}_A$), symmetric in a sense of the interaction with the environment, the interaction energy is equal to the half of the excited state splitting. This is exactly the same prescription as for the calculation of the interaction energy for homodimer without the environment (2.30) and follows from the symmetry considerations of the individual interaction terms.

### 2.5.3 Alternative resonance coupling definition

Another possible and straightforward definition of the resonance coupling, is to use the eigenstates of the individual chromophores including the environment $|\tilde{n}\rangle$ and obtain the interaction energy as an element of interaction operator in these states as

$$J_{AB} = \langle \tilde{\epsilon}^{(A)} | \langle \tilde{g}^{(B)} | \hat{V} | \tilde{g}^{(A)} \rangle | \tilde{\epsilon}^{(B)} \rangle.$$  (2.38)

Although this approach is used in the literature, it does not lead to the correct value of the interaction energy in the context of Frenkel exciton model.

In order to gain some insight into the different approaches for calculation of the interaction energy and to better understand the reason, why the simple and intuitive approach characterized by Eq. (2.38) fails, the individual methods will be demonstrated on a simple model system shown in figure (2.2). The system is composed of two identical chromophores with only one excited state each and a single environment molecule also with only one excited state. For the environment molecule we use general assumption that its transition energy $F_{ge}$ is much larger then the transition energy of the chromophore ($F_{ge} \gg \varepsilon_{ge}$). We further assume no interaction between singly excited states and the ground state, which results in a block separation of the total Hamiltonian, where only the singly exited block is important for the formation of excited eigenstates (as shown in subsection
This system is the simplest system in which the environment effect on the interaction energy can be investigated. The system described here is characterized by the Hamiltonian (2.35), and the site basis in form of

\[
|A\rangle = |e^{(A)}\rangle \big| g^{(B)}\rangle \big| \eta_g \rangle ,
\]

\[
|B\rangle = |g^{(A)}\rangle \big| e^{(B)}\rangle \big| \eta_g \rangle ,
\]

\[
|E\rangle = |g^{(A)}\rangle \big| g^{(B)}\rangle \big| \eta_e \rangle .
\] (2.39)

### 2.5.3.1 Variation method

First, the system will be treated within the variation approach to obtain the new eigenstates from which the interaction energy can be obtained from Eq. (2.37). The variation method provides the exact eigenstates within the Hilbert space defined by this limited basis, and it will be therefore used as a benchmark for the other approaches. The variation method results in an eigenvalue problem

\[
\begin{pmatrix}
\varepsilon_{ge} & V_{AB} & V \\
V_{AB} & \varepsilon_{ge} & V \\
V & V & F_{ge}
\end{pmatrix}
\begin{pmatrix}
c_{AN} \\
c_{BN} \\
c_{EN}
\end{pmatrix}
= E \begin{pmatrix}
c_{AN} \\
c_{BN} \\
c_{EN}
\end{pmatrix},
\]

where \( V_{AB} \) is the interaction energy between chromophores without the environment, and \( V \) is an interaction between chromophore and the environment molecule which is, due to the symmetry of the system, the same for both chromophores. The two lowest excited state energies of the coupled system are obtained in form of

\[
E_1 = \varepsilon_{ge} - V_{AB},
\]

\[
E_2 = \frac{\varepsilon_{ge} + F_{ge} + V_{AB}}{2} - \frac{1}{2}\sqrt{(\varepsilon_{ge} - F_{ge} - V_{AB})^2 + 8V^2},
\]

(2.41)

When the interaction energy between the two chromophores is much smaller then the energy difference between the excited states of the chromophore and the environment molecule \( V_{AB} \ll F_{ge} - \varepsilon_{ge} \), the eigenstates and the corresponding interaction energies obtained from (2.37) read as

\[
E_1 = \varepsilon_{ge} - V_{AB},
\]

\[
E_2 = \varepsilon_{ge} + V_{AB} - 2\frac{V^2}{F_{ge} - \varepsilon_{ge}} + \sigma \left( \frac{V}{F_{ge} - \varepsilon_{ge}} \right)^2,
\]

\[
J_{AB} = V_{AB} - \frac{V^2}{F_{ge} - \varepsilon_{ge}} + \sigma \left( \frac{V}{F_{ge} - \varepsilon_{ge}} \right)^2.
\] (2.42)

### 2.5.3.2 Degenerate perturbation approach

When the degenerate perturbation approach (described in section 2.2.3) is used, the first eigenstates of the interacting chromophores without the environment are formed. This results in a new basis functions \(|1\rangle = \frac{1}{\sqrt{2}} \left( |A\rangle - |B\rangle \right)\) with energy \( \varepsilon_{ge}^{(1)} = \varepsilon_{ge} - V_{AB} \) and \(|2\rangle = \frac{1}{\sqrt{2}} \left( |A\rangle + |B\rangle \right)\) with energy \( \varepsilon_{ge}^{(1)} = \varepsilon_{ge} + V_{AB} \) whereas the last basis function \(|E\rangle\) remains unchanged. Applying the perturbation expansion
on the top of the new basis, we obtain energies of the whole chromophore system including the interaction with the environment

\[ E_1 = \varepsilon_{eg} - V_{AB}, \]

\[ E_2 = \varepsilon_{eg} + V_{AB} - 2 \frac{V^2}{F_{ge} - \varepsilon_{ge}} + \sigma \left( \left[ \frac{V}{F_{ge} - \varepsilon_{ge}} \right]^2 \right), \]

\[ J_{AB} = V_{AB} - \frac{V^2}{F_{ge} - \varepsilon_{ge}} + \sigma \left( \left[ \frac{V}{F_{ge} - \varepsilon_{ge}} \right]^2 \right), \]

(2.43)

where, as in variation method, we have used the assumption \( V_{AB} \ll F_{ge} - \varepsilon_{ge} \).

The excited state energies and the interaction energy obtained from the degenerate perturbation approach are, within the used approximation and order of the expansion in \( V/(F_{ge} - \varepsilon_{ge}) \), the same as for the variation method (2.42).

### 2.5.3.3 Element of interaction operator

Now we present a method based on a direct evaluation of the interaction element (2.38) from the initial wavefunctions in which the interaction with the environment is already included. The eigenstates of the chromophore interacting with its environment can be obtained by different approaches. One possibility is to include the environment into the QC calculation of the chromophore eigenstates classically as an electrostatic field interacting with the chromophore electrons. Another way, which is used in the presented example, is to include its effect by the perturbation approach (Eq. (2.3)). Within the perturbation approach the initial eigenstates are obtained as

\[ |\tilde{e}(A)\rangle = |e(0)\rangle + |e(1)\rangle + \ldots = |e(0)\rangle - \frac{V}{F_{ge} - \varepsilon_{ge}} |E(0)\rangle + \ldots, \]

\[ |\tilde{g}(B)\rangle = |g(0)\rangle + |g(1)\rangle + \ldots = |g(0)\rangle - \frac{V}{F_{ge} - \varepsilon_{ge}} |E(0)\rangle + \ldots. \]

(2.44)

The first problem of these functions is the non-orthogonality. However, if we forget about this problem for now, and calculate the interaction energy by the direct evaluation of the interaction operator (2.38), we obtain

\[ J_{AB} = \langle \tilde{e}(A) | \hat{V} | \tilde{g}(B) \rangle = V_{AB} - 2 \frac{V}{F_{ge} - \varepsilon_{ge}} + \sigma \left( \left[ \frac{V}{F_{ge} - \varepsilon_{ge}} \right]^2 \right). \]

(2.45)

The direct evaluation of the resonance coupling as the element of the interaction operator \( \hat{V} \) in the basis of individual chromophores with environment, Eq. (2.38), therefore yields an incorrect resonance coupling for embedded systems. When we compare this resonance coupling, Eq. (2.45) with the results from the previous methods, we can see that this method overestimates the the effect of the environment by the factor of two. The reason for this factor is that we included the environment interaction twice. First as an interaction of unperturbed excited state of the chromophore \( A \) with the excited state of the chromophore \( B \) perturbed by the environment as \( \langle A(0) | \hat{V} | B(1) \rangle \), and for the second time as an interaction of
the unperturbed exited state of the chromophore $B$ with the perturbed excited state of the chromophore $A$ as $\langle A^{(1)} | \hat{V} | B^{(0)} \rangle$.

The correct approach should include only single contribution of this type. Better approximation of the interaction energy is therefore obtained when the environment is included only into a single chromophore, whereas the other is treated as the isolated chromophore without the environment. The resulting interaction energy can then be interpreted as the transition density of the isolated chromophore in the potential generated by the transition density of the other chromophore including the environment as

$$J_{AB} = \langle \tilde{e}^{(A)} | \langle g^{(B)} | \hat{V} | \tilde{g}^{(A)} \rangle | e^{(B)} \rangle = \int d^3r_1 \int d^3r_2 d^3r \rho^{(A)} (\vec{r}_1) \frac{V}{|\vec{r}_1 - \vec{r}_2|} \rho^{(B)} (\vec{r}_2) \rho^{(E)} (\vec{r}_1) \rho^{(E)} (\vec{r}_2)$$

$$= \int d^3r_2 \Phi^{(A+E)}_{ge} (\vec{r}_2) \rho^{(B)} (\vec{r}_2) = V_{AB} - \frac{V}{\varepsilon_{ge} - F_{ge}} + \sigma \left( \left( \frac{V}{\varepsilon_{ge} - F_{ge}} \right)^2 \right).$$

Here $|\tilde{e}^{(A)} \rangle$ is the ground and $|\tilde{e}^{(A)} \rangle$ excited state of the chromophore $A$ including the interaction with the environment and $|g^{(B)} \rangle$ is the ground and $|e^{(B)} \rangle$ excited state of the isolated chromophore $B$ in vacuum. The quantity $\Phi^{(A+E)}_{ge} (\vec{r})$ corresponds to the potential generated by the total transition density of the chromophore $A$ with the environment.

Physical interpretation of the Eq. 2.46 is the interaction of the chromophore $B$ in vacuum cavity with the transition density of the rest of the system (chromophore $A$ and the environment). Because the environment excitation energy is much higher that the excitation energy of the chromophore, the transition density should be mostly localized on the chromophore with only small part in the environment. This physical picture is very similar to the Poisson Boltzmann method (2.5.5), where the whole system is represented as individual chromophores in vacuum cavities surrounded by a classical polarizable dielectric continuum, representing the environment.

### 2.5.4 Perturbation expansion

The usual pigment environment in biological systems consists of the protein which is composed of the individual amino-acids. The individual amino-acids are small molecules with optical transition in the middle ultraviolet region. Therefore, we can safely assume that the transition energies of the environment molecules are larger than the lowest transitions of pigments, which are in the visible region. The interaction of the pigment with its environment can then be treated as a small perturbation, leading to an energy shift of the pigment electronic ground and excited states.

#### 2.5.4.1 Energy shift

The energy of the $k$-th electronic state of the chromophore interacting with the environment can be obtained in the form of the perturbation expansion, Eq. (2.4).
\[ E_k = \varepsilon_k + \langle k | 0 \rangle \hat{V} | k, 0 \rangle + \sum_{m,\eta} \frac{\langle k, 0 \rangle \hat{V} | m, \eta \rangle | k, 0 \rangle^2}{F_0 - F_\eta + \varepsilon_k - \varepsilon_m} \]
\[ + \sum_{m,\eta,\nu} \frac{\langle k, 0 \rangle \hat{V} | m, \eta \rangle \langle \nu | l, \nu \rangle \langle l, \nu | \hat{V} | k, 0 \rangle}{(F_0 - F_\eta + \varepsilon_k - \varepsilon_m)(F_0 - F_\nu + \varepsilon_k - \varepsilon_l)} \]
\[ - \langle k, 0 \rangle \hat{V} | k, 0 \rangle \sum_{m,\eta} \frac{\langle k, 0 \rangle \hat{V} | m, \eta \rangle^2}{|F_0 - F_\eta + \varepsilon_k - \varepsilon_m|^2} + \ldots, \quad (2.47) \]

where \( 0 \) represents all environment molecules in the ground state, and \( F_\eta \) represents the sum of energies of the environment molecules. When we use the definition of the interaction operator, Eq. (2.35), the energy of the \( k \)-th electronic state of the chromophore embedded in the environment reads as

\[ E_k = \varepsilon_k + \sum_n \langle k | \langle 0^{(n)} | \hat{V}_{SE} | 0^{(n)} \rangle | k \rangle + \frac{1}{2} \sum_{n,n'} \langle 0^{(n)} | \hat{V}_{\eta\eta'} \langle 0^{(n')} | 0^{(n')} \rangle \langle 0^{(n')} | \hat{V}_{\eta\eta'} \langle 0^{(n)} | 0^{(n)} \rangle \]
\[ + \sum_n \frac{\langle k | \langle 0^{(n)} | \hat{V}_{SE} + \hat{V}_{EE} | \eta^{(n)} \rangle | k \rangle^2}{F_0^{(n)} - F_\eta^{(n)}} \]
\[ + \sum_{m} \sum_{n,\eta} \frac{\langle k | \langle 0^{(n)} | \hat{V}_{SE} | \eta^{(n)} \rangle | m \rangle^2}{F_0^{(n)} - F_\eta^{(n)} + \varepsilon_k - \varepsilon_m} + \ldots. \quad (2.48) \]

For the most of the pigment protein complexes only the few lowest excited states are important for their optical and excitation energy transfer properties. It is therefore safe to treat the pigments as two or three level molecules, described by the ground state and one or two excited states. For the calculation of the transition energy shifts, we restrict ourselves to the two level system, however the procedure can be easily generalized to include more excited states. The transition energy shift \( \Delta E_{g\rightarrow e} = (E_e - E_g) - (\varepsilon_e - \varepsilon_g) \) of the two level chromophore induced by the interaction with its environment reads as

\[ \Delta E_{g\rightarrow e} = \sum_n \left[ \langle e | \langle 0^{(n)} | \hat{V}_{SE} | 0^{(n)} \rangle | e \rangle - \langle g | \langle 0^{(n)} | \hat{V}_{SE} | 0^{(n)} \rangle | g \rangle \right] \]
\[ + \sum_{n,\eta} \left[ \frac{|\langle g | \langle 0^{(n)} | \hat{V}_{SE} | \eta^{(n)} \rangle | g \rangle|^2}{F_\eta^{(n)} - F_0^{(n)}} - \frac{|\langle e | \langle 0^{(n)} | \hat{V}_{SE} | \eta^{(n)} \rangle | e \rangle|^2}{F_\eta^{(n)} - F_0^{(n)}} \right] \]
\[ + \sum_{n,\eta} \frac{|\langle g | \langle 0^{(n)} | \hat{V}_{SE} | \eta^{(n)} \rangle | e \rangle|^2}{(F_\eta^{(n)} - F_0^{(n)}) + (\varepsilon_e - \varepsilon_g)} - \sum_{n,\eta} \frac{|\langle e | \langle 0^{(n)} | \hat{V}_{SE} | \eta^{(n)} \rangle | g \rangle|^2}{(F_\eta^{(n)} - F_0^{(n)}) - (\varepsilon_e - \varepsilon_g)} + \ldots. \quad (2.49) \]

Based on the similarity of the individual perturbation expansion terms with the molecule’s static charge distribution and polarizability (2.13), (2.14), we can provide the physical interpretation of the individual terms in expression above, Eq. (2.49). The first line of the Eq. (2.49) corresponds to the difference in the pigment-environment electrostatic interaction for the pigment in the excited and in the ground state. The second line, of the Eq (2.49), corresponds to the situation
when the pigment in the ground (excited) state induces a polarization on the environment molecule which is then interacting back with the pigment. The same interpretation is true also for the last line, where the polarization is induced by the pigment transition density.

2.5.4.2 Transition dipole

The same procedure can be followed also for the transition dipole of the two level chromophore interacting with its environment. Transition dipole of the chromophore interacting with the environment is defined as

$$\vec{\mu}_{GE} = -\sum_i \langle G | \vec{r}_i | E \rangle,$$

(2.50)

where $|G\rangle$ and $|E\rangle$ are the ground and exited states of the chromophore including the environment, and $\vec{r}_i$ correspond to all the electronic coordinates (chromophore + environment). The ground and the excited state of the coupled chromophore can be obtained by using the perturbation expansion in the chromophore-environment interaction, Eq. (2.3). Following the same procedure as for the energy shift, the transition dipole is obtained in the form of

$$\vec{\mu}_{GE} = \vec{\mu}_{ge}^{(A)} - 2\sum_{n,\eta} \left( \frac{F^{(n)}_\eta - F^{(n)}_0}{\left(F^{(n)}_\eta - F^{(n)}_0\right)^2 - (\varepsilon_e - \varepsilon_g)^2} \right) \vec{\mu}_{g\eta}^{(n)} + \ldots$$

(2.51)

Here $\vec{\mu}_{ge}^{(A)}$ is the transition dipole moment of the chromophore in vacuum and $\vec{\mu}_{g\eta}^{(n)}$ is the transition dipole moment between the ground state and the excited state $\eta$ on the environment molecule $n$. The physical interpretation of the second term in the last line of above expression (Eq. (2.51)) follows from the similarity with the quantum definition of the dynamic polarizability, Eq. (2.14). It can be therefore interpreted as an induced dipole in the environment by the vacuum transition density of the chromophore. The total transition dipole for the chromophore embedded in the environment is then the sum of the chromophore vacuum transition dipole and the dipole induced in the environment.

2.5.4.3 Resonance coupling

For the resonance coupling calculation (Section 2.5.2) we assume a system of two chromophores interacting with their environment, described by the Hamiltonian and interaction operator in the form of the Eq. (2.35). For the simplicity, we also assume only two level chromophores, but the procedure can be generalized to more excited states. Due to the possible degeneracy of the chromophore’s excited states (for homodimer), the degenerate perturbation approach should be used for the calculation of the system eigenstates and energies $E_i$ in Eq. (2.37).
As described in the Section 2.2.3, the total Hamiltonian has to be reordered into the new unperturbed part and the perturbation \( \hat{H} = \mathcal{H}_0 + \mathcal{V} \) as
\[
\mathcal{H}_0 = \hat{H}_A + \hat{H}_B + \hat{H}_E + \sum_{i,j \in \{e,g\}} \left( \langle ij, 0 | \hat{V} | ij, 0 \rangle \right) | ij, 0 \rangle \langle ij, 0 |,
\]
\[
\mathcal{V} = \hat{V} - \sum_{i,j \in \{e,g\}} \left( \langle ij, 0 | \hat{V} | ij, 0 \rangle \right) | ij, 0 \rangle \langle ij, 0 |.
\] (2.52)
The unperturbed Hamiltonian \( \mathcal{H}_0 \) contains the interaction between the unperturbed chromophore excited states. First, the eigenfunctions of the unperturbed Hamiltonian \( \mathcal{H}_0 \) are obtained from the variation approach resulting in the new basis functions for the perturbation expansion in \( \mathcal{V} \). The diagonalization of \( \mathcal{H}_0 \) results in the mixing of the chromophore’s excited states and shifting the transition energies, whereas the rest of the basis functions remain the same. Therefore the only basis functions which are changed correspond to the one chromophore excited and the other in the ground state:
\[
|1, 0 \rangle = c_{A1} |eg, 0 \rangle + c_{B1} |ge, 0 \rangle,
\]
\[
|2, 0 \rangle = c_{A2} |eg, 0 \rangle + c_{B2} |ge, 0 \rangle.
\] (2.53)
Here \( c_{Ai} \) are expansion coefficients obtained from the diagonalization of the \( \mathcal{H}_0 \).

The states \( |eg, 0 \rangle \) and \( |ge, 0 \rangle \) are removed from the summation because they are not longer the basis functions. The interaction energy is then extracted from the resulting eigenstate energies of the full system using the Eq. (2.37).

### 2.5.5 Poisson-Boltzmann method

The Poisson-Boltzmann method [28] is based on the perturbation expansion presented in the previous section 2.5.4; however, in this approach the individual terms in the expansion are treated in the classical approximation of the environment. The type of the classical approximation is chosen according to the property of interest. The electrostatic properties of the environment are described by the ground state atomic charges (Section 2.4.3). On the other hand, the dielectric properties of the environment are described by the polarizable dielectric continuum with individual pigments located in vacuum cavities inside the dielectric.

The resonance coupling between two chromophores is only affected by the dielectric properties of the environment. The individual chromophores are represented as a set of the TrEsp (Section 2.4.3) atomic charges \( q^{(A)}_I(g,e) \), which were
calculated for the isolated chromophores in the vacuum. The resonance coupling between two chromophores embedded in the environment then corresponds to the vacuum atomic transition charges (TrEsp charges) of one chromophore in the electrostatic potential of the TrEsp charges of the other chromophore. The electrostatic potential induced by the set of the TrEsp charges in the presence of the dielectric environment \( \Phi_{ge}^{(A)}(\vec{r}) \) is obtained as a solution of the Poisson Boltzmann equation

\[
\nabla \left( \varepsilon_0 \varepsilon_r (\vec{r}) \nabla \Phi_{ge}^{(A)}(\vec{r}) \right) = -4\pi \sum_{I \in A} q_I^{(A)}(g,e) \delta \left( \vec{r} - \vec{R}_I \right) + \kappa^2(\vec{r}) \Phi_{ge}^{(A)}(\vec{r}) , \quad (2.55)
\]

where \( \varepsilon_r(\vec{r}) \) corresponds to the relative permittivity of the dielectric at the position \( \vec{r} \), and \( \varepsilon_r(\vec{r}) = 1 \) inside the chromophore cavity. The quantity \( \Phi_{ge}^{(A)}(\vec{r}) \) is the electrostatic potential at position \( \vec{r} \) induced by the set of the transition charges \( q_I^{(A)}(g,e) \), Eq. (2.25), at the position \( \vec{R}_I \) of the chromophore \( A \). The \( \kappa^2(\vec{r}) \) is the position dependent inverse Debye length, which is related to the ionic strength \( I(\vec{r}) \) of the environment by

\[
\kappa^2(\vec{r}) = \frac{8\pi F I(\vec{r})}{\varepsilon_0 \varepsilon_r(\vec{r}) k_B T},
\]

where \( F \) is the Faraday’s constant. The interaction energy is then calculated as a Coulomb interaction of the potential of the chromophore \( A \) embedded in the environment with the vacuum TrEsp transition charges of the chromophore \( B \) as

\[
J_{AB} = \sum_J \Phi_{ge}^{(A)}(\vec{R}_J) q_J^{(B)}(g,e) ,
\quad (2.56)
\]

where \( \Phi_{ge}^{(A)}(\vec{R}_J) \) is obtained by the numerical solution of the Poisson Boltzmann equation (2.55).

The transition energy shift induced by the environment has two contributions. The first contribution comes from the different electrostatic interaction of the chromophore with the environment, for the chromophore in the ground state and in the excited state. The other part comes from the different polarization of the environment by the chromophore in the ground and in the excited state. This contribution can also be interpreted as a difference in solvation energy for the chromophore in the ground and in the excited state. The transition energy shift reads as

\[
\Delta E_{g\rightarrow e} = \sum_{I \in A} \sum_{J \in E} \left( q_I^{(A)}(e,e) - q_I^{(A)}(g,g) \right) q_J^{(E)}(g,g) \frac{(\vec{R}_I - \vec{R}_J)}{\left| \vec{R}_I - \vec{R}_J \right|} - \frac{1}{2} \sum_{J \in A} \left[ \Phi_{ee}^{(A)}(\vec{R}_J) - \Phi_{gg}^{(A)}(\vec{R}_J) \right] q_J^{(A)}(g,g) ,
\quad (2.57)
\]

where \( \Phi_{ee}^{(A)}(\vec{R}_J) = \Phi_{gg}^{(A)}(\vec{R}_J) - \sum_{I \in A} q_I^{(A)(a,b)}(\vec{R}_J) / \left| \vec{R}_I - \vec{R}_J \right| \) contains only contributions from the environment effects.

The total transition dipole of the chromophore embedded in the environment is obtained as a sum of the transition dipole of the isolated chromophore and the dipole induced in the environment (usually represented as induced charges on the cavity surface), which corresponds to the environmental contribution to the transition dipole.
Figure 2.3: (a) In the Poisson-Boltzmann method, environment is described as a homogeneous dielectric with the relative permittivity $\varepsilon_r$ and the chromophores are located in the vacuum cavities. (b) In the Polarizable continuum model, the dielectric properties are modeled by the induced charges on the cavity surface and the mutual polarization of the chromophore and the environment is obtained from the self consistent procedure.

2.5.6 Polarizable continuum model

The polarizable continuum model \[29, 30\] (PCM) is very similar to the Poisson Boltzmann method. The environment is also described classically as a polarizable dielectric and the whole system is treated as individual chromophores inside vacuum cavities in the dielectric. In contrast to the Poisson Boltzmann model, in PCM approach the environment is included in the QC calculation of the chromophore properties. Within this approach the transition dipole and the transition energies including the environment effects are already obtained from QC calculation.

Mutual polarization of the chromophore and the surrounding dielectric is in PCM model obtained by following self consistent scheme. First the ground and excited state properties are calculated for the chromophore in vacuum. This yields the ground state, the excited state and also the transition electron densities. Then we include the polarizable dielectric and calculate charges on the cavity surface induced by the vacuum charge distribution. The induced charges describe the response of the dielectric to the static charge distribution of the molecule. The effect of the dielectric is then included into the QC calculation of the chromophore as an external electrostatic field of the induced charges on the cavity surface. Then the new electronic densities are obtained from the QC calculation with the external electric field. These electronic densities induce new surface charges which are then again included into the QC calculation of the chromophore. This procedure is repeated until the convergence of the induced charges is achieved.

The PCM models are very popular nowadays due to their efficiency and accuracy in describing homogeneous environments, where no strong specific solvent-solute interactions are present. This method describes the effects of the dielectric environment on the chromophore properties better than the Poisson Boltzmann method, because it allows the chromophore’s electrons to adjust to the new environment. However, the induced positive charges on the cavity surface are not shielded by the electrons as for example the nuclei charges are. This might lead to
larger distortions of the electron density, compared to the treatment of the environment as individual molecules, or even to the leakage of the chromophore electrons into the dielectric. This is the major disadvantage of the PCM method. The PCM method can also be used only for the uniform 3D dielectric environment, which will exclude layers, membranes and other relevant biological environments from the calculation.

2.5.7 Harmonic oscillator model

The harmonic oscillator (HO) model is based, same as the both previous methods, on perturbation expansion of the system-environment interaction, described in Section 2.5.4. However, in this approach we preserve the quantum nature of the environment. The direct calculation of all the environment eigenstates needed in the expansion (2.49), (2.51) and (2.54) is computationally impossible for the systems containing more then few molecules. In order to keep the system solvable, the environment atoms (or molecules) are approximated as harmonic oscillators. This approach is based on approximation of the correct electronic potential \( \sim \frac{1}{r} \) around the minimum by harmonic potential for the fixed molecular geometry. The full interacting system is then described by the Hamiltonian, Eq. (2.35), with

\[
\hat{H}_E = \sum_n \frac{p^2_n}{2m_n} + \frac{1}{2} m_n \omega_n^2 r_n^2,
\]

\[
V_{n,n'} = \frac{q_n (g,g) q_{n'} (g,g)}{|\vec{R}_{nn'}|^3} + q_n q_{n'} \left( \frac{\vec{r}_n \cdot \vec{r}_{n'}}{|\vec{R}_{nn'}|^3} - 3 \frac{(\vec{r}_n \cdot \vec{R}_{nn'}) (\vec{r}_{n'} \cdot \vec{R}_{nn'})}{|\vec{R}_{nn'}|^5} \right), \tag{2.58}
\]

where \( \vec{R}_{nn'} = \vec{R}_{n'} - \vec{R}_n \) and \( \vec{R}_n \) is the position of the harmonic oscillator \( n \), \( q_n \) corresponds to the oscillating charge, and \( q_n (g,g) \) to the total ground state charge of the harmonic oscillator. The first term in the interaction energy between two oscillators \( V_{n,n'} \) corresponds to the Coulomb interaction of the static ground state charges. The second term, in Eq. (2.58), corresponds to the interaction between two induced dipoles. For the sake of simplicity, we are not considering self polarization of the environment HO by ground state charges \( q_n (g,g) \) of the other HOs. To each harmonic oscillator we can assign polarizability \( \alpha_n \), which describes its response to an external electric field. The polarizability is defined by the Eq. (2.13), where only the ground to first excited state transitions are allowed for HO, yielding

\[
\alpha_n = \frac{q_n^2}{m_n \omega_n^2}. \tag{2.59}
\]

Exactly the same polarizability is also obtained for a classical harmonic oscillator.

Within the harmonic approximation of the environment, the transition energy shift of the chromophore due to the interaction with the coupled identical harmonic oscillators reads as

\[
\Delta E_{g\rightarrow e} = \sum_n \sum_{I \in A} \frac{\left( q^{(I)}_I (e,e) - q^{(I)}_I (g,g) \right)}{|\vec{R}_I - \vec{R}_n|} q_n (g,g) + 2 \sum_{I \in A} \sum_n \frac{q^{(I)}_I (g,e) q_n (g,g)}{|\vec{R}_I - \vec{R}_J| \left( \varepsilon^{(I)}_e - \varepsilon^{(I)}_g \right)}
\]

39
and the combined electric field from the induced dipoles on all the other HOs, charges $q$, and so on. The total dipole moment of the chromophore charge distribution. The second order induced dipole moments can be written as

$$
\Delta = (\varepsilon^{(A)}_e - \varepsilon^{(A)}_g) / \hbar \omega
$$

where $\Delta$ is the ratio between the chromophore and the HO excitation energies, and $\bar{\mu}^{(2)}_{n}(a,b) = \sum_{i} \bar{\mu}^{(2)}_{n}(a,b)$ are the total induced dipole moments on the environment HO. The individual orders of the dipole moments induced by the chromophore, in Eq. (2.60), are defined by recurrent relations as

$$
\bar{\mu}^{(1)}_{n}(a,b) = \alpha_n \sum_{i \in A} \frac{q^{(A)}_i(a,b) \bar{R}_{I n}}{|\bar{R}_{I n}|^3},
$$

$$
\bar{\mu}^{(2)}_{n}(a,b) = \alpha_n \sum_{i \in A} \frac{q^{(A)}_i(a,b) \bar{R}_{I n}}{|\bar{R}_{I n}|^3},
$$

$$
\varepsilon^{(i-1)}_{ind}(\bar{R}_{n}) = \sum_{\eta'} \left( 3 \left( \frac{\bar{\mu}^{(i-1)}_{n}(a,b) \cdot \bar{R}_{n'}}{|\bar{R}_{n'}|^3} - \frac{\bar{\mu}^{(i-1)}_{n'}(a,b)}{|\bar{R}_{n'}|^3} \right) \right). \tag{2.61}
$$

The first order induced dipole moments $\bar{\mu}^{(1)}_{n}(a,b)$ are induced by the electric field of the chromophore charge distribution. The second order induced dipole moments $\bar{\mu}^{(2)}_{n}(a,b)$ are induced by the electric field of the first order dipole moments $\bar{\mu}^{(1)}_{n}(a,b)$, and so on. The total dipole $\bar{\mu}_{n}(a,b)$ of nth HO induced by the chromophore charges $q^{(A)}_i(a,b)$, is therefore induced by the total electric field at the position $\bar{R}_{n}$, which is a sum of an electric field of the chromophore’s charge distribution and the combined electric field from the induced dipoles on all the other HOs, $\varepsilon_{ind}(\bar{R}_{n})$. This system is usually treated in the limit $\Delta \to 0^+$, which corresponds to much lower chromophore excitation energy than the excitation energies of the HOs $1 \ll (\varepsilon^{(A)}_e - \varepsilon^{(A)}_g) \ll \hbar \omega$. The transition energy shift then reads as

$$
\Delta E_{g \to e} = \sum_{n} \sum_{I \in A} \left( \frac{q^{(A)}_I(e,e) - q^{(A)}_I(g,g)}{|\bar{R}_{I} - \bar{R}_{n}|} \right) q^{(A)}_n(g,g) - \frac{1}{2} \sum_{I \in A} \sum_{n} \frac{q^{(A)}_I(e,e) \left( \bar{R}_{I n} \cdot \bar{\mu}^{(1)}_{n}(e,e) \right)}{|\bar{R}_{I n}|^3} + \frac{1}{2} \sum_{I \in A} \sum_{n} \frac{q^{(A)}_I(g,g) \left( \bar{R}_{I n} \cdot \bar{\mu}^{(1)}_{n}(g,g) \right)}{|\bar{R}_{I n}|^3}, \tag{2.62}
$$

which is exactly the same as for the Poisson Boltzmann method, with the only difference in using polarizable atoms, instead of the polarizable continuum. The dipole $\bar{\mu}_{n}(g,g)$ corresponds, according to Eq. (2.61), to the dipole on nth harmonic oscillator induced by the chromophore ground state charges. The above expression, Eq. (2.62), for the transition energy shift is within the HO approximation general, and valid also for a set of the non-identical HOs representing the environment. The first term in the formula for the transition energy shift, Eq. (2.62), corresponds to the different Coulomb interaction of the chromophore with
Figure 2.4: Graphical representation of the HO approximation for system-environment interaction. The dipoles in the environment (represented by arrows) are induced by the chromophore $A$ charge distribution. (a) The electron density in the figure corresponds to the difference electron density between the ground and the excited state. Chromophore charge density interacts with the dipoles on the environment HO induced by the same charge density. (b) The transition density of the chromophore $B$ interacts with the dipoles on the environment HO induced by the transition density of the chromophore $A$.

Within the same approximations, the transition dipole of the chromophore including the environment, $\vec{\mu}_{GE}$, is simply the sum of the transition dipole of the isolated chromophore in the vacuum and the total dipole in the environment induced by the chromophore transition density (charges) as

$$\vec{\mu}_{GE} = \vec{\mu}_{ge} + \sum_n \vec{\mu}_{ind}^{n} (g,e).$$  \hspace{1cm} (2.63)

The interaction energy is obtained in the form of

$$J_{AB} = \sum_{I \in A} \sum_{J \in B} \frac{\varepsilon_{I}^{(A)} (g,e) \varepsilon_{J}^{(B)} (g,e)}{||\vec{R}_{I} - \vec{R}_{J}||} - \sum_{I \in A} \sum_{n} \varepsilon_{I}^{(A)} (g,e) \left[ \frac{\left(\vec{R}_{I} - \vec{R}_{n}\right) \cdot \vec{\mu}_{ind}^{n,B} (g,e)}{||\vec{R}_{I} - \vec{R}_{n}||^{3}} \right],$$  \hspace{1cm} (2.64)

where $\vec{\mu}_{ind}^{n,B} (g,e)$ corresponds to the total dipole moment on the environment HO induced by the transition density (charges) of the chromophore $B$. The first term of the Eq. (2.64) represents the direct interaction of the two chromophores without the environment, whereas the other term represents the interaction of the transition density of the chromophore $A$ with dipole in the environment, induced by the transition density of the chromophore $B$ (Figure 2.4b).
2.5.8 Polarizable QM/MM method

The polarizable QM/MM method [17] is a combination of harmonic oscillator approximation and polarizable continuum model. In QM/MM methods, the system of interest is described quantum mechanically, whereas the environment is described by the classical polarizable force field. The environment is treated as polarizable atoms, where every environment atom is assigned a charge and an isotropic polarizability. As in the PCM model, the environment is included into the QC calculation of the system properties as a static electric field of the environment atomic charges and induced atomic dipoles. The mutual polarization of the system and the environment atoms is obtained from the self consistent procedure, in which chromophore induces dipoles in the environment which then influence the chromophore electronic states. Polarizable QM/MM approach was successfully applied to investigation of excited state properties of many biological systems such as LH2 [31], FMO [32] or small organic molecules in water solution [33, 34].

The transition energies and dipoles for the chromophore embeded in the environment are obtained directly from the QC calculation. The interaction energy is then obtained from the Eq. (2.64), using the known induced dipoles in the environment from the QC calculation of the individual chromophores.

The complication in this approach arises, when the separation of the quantum chemical region and the classical one requires cutting a chemical bond. In order to correct for the cut bond in the QC calculation, the bond is usually replaced by the hydrogen atom or by the functional group similar to the original bond. The addition of the new atom, however, changes the mutual interaction of the system with the classical environment. This can be corrected by empirical shifting of the environment charges which are close to the added atom. This procedure is described in greater detail in [35, 36].

2.5.9 Practical notes

- When the transition density, and other derived quantities are calculated by QC methods, they should be always re-scaled to obtain the experimental transition dipole. QC usually provides the correct symmetry and structure of the electron density, however the absolute values are obtained with larger systematic errors due to the complicated form of the electron-electron interaction. Usually, it is complicated to obtain the experimental vacuum transition dipole moment directly. For these cases, the experimental vacuum transition dipole is extrapolated from the series of the dipole measurements of the chromophore in solutions with different permitivities. The re-scaling of the transition densities generally results in a better agreement with the experimental measurements.

- The transition atomic charges (TrEsp) are calculated from the optimized structure in the vacuum and then they are placed on the individual atoms of the distorted molecule from the crystal structure. This procedure results in the better agreement with experiment than if one use the charges calculated directly from the distorted crystal structure.
2.6 Spectral density

In this section we will discuss effects of system-bath coupling on the system optical and excitation transfer properties. This interaction enters to the calculation of the system optical properties through the bath correlation function, respectively through the spectral density. The spectral density describes how the changes in the bath DOF are reflected on the system properties. The spectral density is defined as a Fourier transform of the imaginary part of the energy gap correlation function $C(t)$, Eq. (1.17), as

$$C^*(\omega) = i \int_{-\infty}^{\infty} dt \Im\{C(t)\} e^{i\omega t}. \quad (2.65)$$

The standard approach to the separation of the sample Hamiltonian into the system and bath part is to include all electronic DOF into the system and all nuclear DOF into the bath. Then the spectral density describes how the change of the nuclear coordinates (system+environment) changes the transition energies of the individual chromophores.

2.6.1 Classical time evolution

The bath correlation function and the corresponding spectral density can be obtained from energy gap correlation function (Eq. (1.29)). The energy gap correlation function describes, how the transition energies on the same chromophore or between two different chromophores are correlated, when the system is subjected to thermal fluctuations in the ground state. It could be directly extracted from the known evolution of the initial density $\hat{\rho}_0(\{Q\}) = \Delta \hat{V}_m(\{Q\}) \hat{\rho}_{eq}$ for every state of interest $m$. This would however require a propagation using the Hamiltonian of the whole ensemble, the very thing we are trying to avoid, because of the large size of the bath.

The usual approach to overcome this problem is to use a classical approximation where the configuration space is sampled by molecular dynamic (MD) simulation. Applying the ergodic theorem, the trace over all the possible configurations of the system can be replaced by the averaging over the time propagation of the whole ensemble

$$C_{mn}(t) = \frac{1}{\hbar^2} \langle \Delta V_n^{I,B}(t) \Delta V_m \rangle \approx \frac{1}{\hbar^2 T} \int_0^T d\tau \Delta V_n(\tau + t) \Delta V_m(\tau). \quad (2.66)$$

Here $T$ is the total period of the system evolution, which should be large enough to allow the system to sample the whole conformation space. The $\Delta V_m(t) = \Delta V_m\left(\{Q_t\}\right)$ corresponds to the value of the energy gap $\Delta V_m$ for the configuration of the system at the time $t$.

The time evolution of the system coupled to the thermal bath can be obtained from classical MD simulations. In MD simulations the propagation of the system is recovered from the numerical integration of the Newton’s equations of motion for each atom of the system. The atoms move on an empirical potential energy surface described by the classical force-field, which provides a simple prescription how to construct the potential energy surface. The temperature is introduced in MD propagation by using thermostat, which is responsible for re-scaling of atom velocities to obtain the correct canonical distribution. The classical propagation
with the MD simulation is very fast and can also be used for the large systems such as pigment-protein complexes embedded in membrane and dissolved in solution. For every time-step of the system evolution, the snapshot of the molecular structure is obtained. The known structure is then used for the QC calculation of the transition energies of the chromophore system, including the environmental effects (as described in Section 2.5). These transition energies correspond to energy gap $\Delta V_m$ in Eq. (2.66). The known time evolution of the transition energies is then used for the calculation of the classical correlation function.

The classical energy gap correlation function $C_{cl}(t)$, obtained from the combined MD evolution and the QC calculation of the transition energies, is a real quantity. However, the correct quantum correlation function, Eq. (1.29), needed for the correct description of the system optical and excitation transfer properties, is a complex quantity. Problem of the real correlation function is that it does not fulfill the fluctuation-dissipation theorem, Eq. (1.19). In order to use the classical correlation function for the description of the system excited state properties, it needs to be transformed into the quantum one. There are several possible transformations [37]:

- **Standard approximation**
  \[
  C' (\omega) = \int_{-\infty}^{\infty} dt \, C_{cl} (t) e^{i\omega t}
  \]  
  (2.67)

- **Harmonic approximation**
  \[
  C'' (\omega) = \frac{\beta \hbar \omega}{2} \int_{-\infty}^{\infty} dt \, C_{cl} (t) e^{i\omega t}
  \]  
  (2.68)

- **Schofield’s approximation scheme**
  \[
  C (\omega) = \exp \left( \frac{\beta \hbar \omega}{2} \right) \int_{-\infty}^{\infty} dt \, C_{cl} (t) e^{i\omega t}
  \]  
  (2.69)

- **Egelstaff’s approximation scheme**
  \[
  C (t) = C_{cl} \left( \sqrt{t (t + i \beta \hbar)} \right)
  \]  
  (2.70)

For every specified transformation exist a system, for which it is exact. All of these approximations fulfill the fluctuation dissipation theorem, Eq. (1.19), however, it is not clear which approximation should be used for the studied biological pigment protein systems. The usual approach is to fit the classical correlation function with the dampened oscillators in form $C_{cl} (t) \approx \sum_i c_i e^{-\gamma_i t} + \sum_j \tilde{c}_j \cos (\omega_j t) e^{-\gamma_j t}$ and then use the Standard approach (2.67) for the transformation of the classical correlation function into the quantum one.

### 2.6.2 Normal mode analysis

The second approach is based on the description of the environment as the harmonic bath with Hamiltonian (1.10). To build the Hamiltonian, we need to know the normal modes of the system, corresponding frequencies and also the
coupling strength of the individual modes to the system. The QC calculation of the normal modes of the whole system is impossible due to the large size of the system. However, a reasonable approximation of the QC normal modes can be obtained from the normal mode analysis (NMA) with the classical description of the nuclei using the molecular mechanic (MM). In the MM the real potential for nuclei is approximated by the one constructed from the empirical force-field. This simple potential approximation is then used for the analytical calculation of the normal modes and the corresponding frequencies. The simplicity of the potential allows us to use this procedure even for large systems, e.g. protein complexes. When the normal modes are obtained, the bath is then considered as a set of quantum harmonic oscillators with the coordinates and the frequencies from the classical NMA. From the quantum description of the bath the proper complex correlation function is obtained, as discussed in the Section 1.4, in the known form (1.22) as

\[ C_{NN}^\nu(\omega) = \pi \sum_\xi g_\xi^2(N,N) \omega_\xi^2 \left[ \delta(\omega - \omega_\xi) - \delta(\omega + \omega_\xi) \right], \quad (2.71) \]

where \( g_\xi(N,N) \) describes the coupling strength of the normal mode \( \xi \) to the electronic state \( N \), and \( \omega_\xi \) is the frequency of the normal mode. Here we have used the assumption of the bath composed of the discrete set of undampened oscillators. This corresponds to the procedure used for the calculation of the normal modes, which are calculated for the isolated pigment protein complex without the surrounding solvent or membrane. Therefore the damping of the normal modes is not included. Another possibility is to obtain the normal modes from analysis of the MD propagation including the solvent and membrane. For this case, we would obtain damping of the pigment protein complex vibrational normal modes, and the Brownian model for spectral density (1.21) could be used instead.

The coupling strength \( g_\xi(N,M) \) is within the harmonic approximation obtained as

\[ g_\xi(N,M) = \sum_I \nabla_I H_{NM}(\vec{R})|_{\vec{R} = \vec{R}(0)} \cdot \left( R_I - R_I^{(0)} \right) T_j^{(\xi)} \left( 2\omega_\xi^3 \hbar \right)^{-\frac{1}{2}}, \quad (2.72) \]

where \( \nabla_I H_{NM}(\vec{R}) \) is the gradient of the Hamiltonian operator element \( H_{NM}(\vec{R}) = \langle N \| H \| M \rangle \) in electronic states \( |N\rangle \) of the whole system (including the environment). The \( \left( R_I - R_I^{(0)} \right) \) corresponds to a displacement, in Cartesian coordinates, of atom \( I \) form the optimal geometry \( \vec{R}^{(0)} \), and \( T_j^{(\xi)} \) is the transformation matrix between the Cartesian \( (R_I) \) and the normal mode coordinates \( q_\xi \). The transformation matrix is obtained from the classical NMA and it is defined as

\[ \left( \vec{R}_j - \vec{R}_j^{(0)} \right) = \sum_\xi T_j^{(\xi)} \sqrt{m_\xi} \hat{q}_\xi, \quad (2.73) \]

where \( m_\xi \) is the reduced mass of the normal mode \( \xi \). All the parameters for the coupling strength \( g_\xi(N,M) \), except of the Hamiltonian gradient, are calculated from the classical NMA of the whole system. The Hamiltonian gradient in the system optimal geometry \( \nabla_I H_{NM}(\vec{R})|_{\vec{R} = \vec{R}^{(0)}} \) can be obtained as the derivative of the system energy including the environment effects with respect to the atomic
coordinates. This gradient is usually obtained during the calculation of the excited state properties for the system in the optimal geometry. The methods, which are used for calculation of the excited state energies for system coupled to its environment (Section 2.5), can therefore be also used for the energy gradient calculation. The detailed derivation of the system-bath coupling strength, Eq. 2.72 and the transformation into the normal mode coordinates, Eq. 2.73, is presented in the Attachment A.1.
3. Effects of Higher Excited States on Optical Properties of Chromophore system

This chapter introduces the work presented in Paper I, where we investigate relation between Frenkel exciton model [20] (FEM) and QC methods for calculation of excited state properties. Understanding the correspondence between the well established methods of QC and FEM can provide a starting point for improvements of the FEM and for a more extensive use of QC methods in structure based parametrization of the FEM. In Chapter 2 we introduced basic concepts of calculation of resonance couplings between chromophores and construction of FEM Hamiltonian from the structural information. Here, we discuss correspondence between standard Frenkel exciton formalism and configuration interaction QC method [39] with only single excited states (CIS), for description of molecular electronic states, and we propose a straightforward full configuration interaction (FCI) extension of the FEM. Although the extension of standard FEM provides only small correction to optical properties for molecular dimers of standard photosynthetic pigments, we show that for large closely packed aggregates it might result in a noticeable shift of absorption spectra and change of the total oscillator strength of a single exciton band of the aggregate.

3.1 Interpigment resonance coupling

In the standard FEM of molecular aggregates, individual molecules are described by their ground and excited states. When no differential overlap between electronic states of individual molecules is present, the FEM Hamiltonian of the aggregate is constructed in the site basis (Section 1.5), where the collective ground state is constructed as a Hartree product of ground states of individual molecules. Similarly, the collective singly excited states are constructed as Hartee products of states where single molecule is in excited state whereas the rest of the molecules is in ground state. The doubly excited states correspond to states where two distinct molecules are in the excited states and so on.

Like in configuration interaction (CI) method, the FEM improves the ground and excited states, not by improving the molecular orbitals of the individual molecules, but rather by combination of electronic states taken from a certain orthonormal basis of states, in our case the site basis. In standard FEM of molecular aggregates, only interactions inside excited state manifold with the same number of excitations are considered. This result in block separation of the system Hamiltonian. Single excited states can be then treated independently of the ground and the higher excited states. The same is true for double and higher excited state manifolds. The single exciton basis (1.26) is then unitary transformation of a site basis where only single chromophore is excited. This implies the same total oscillator strength of the single exciton block for a interacting chromophore system as for set of noninteracting separated chromophores.

For neutral and non-polar molecules, interaction between manifolds which dif-
fer only in single excitation is small and can be neglected (Section 2.4). However interaction between manifolds which differ by two excitations is the same as interaction between states within the singly excited state manifold, as presented in Section 2.4 on a simple example of ground state interaction with doubly excited state. Although the values of the coupling between states of different exciton manifolds are the same as the values of coupling between states within the same manifold, the effect of the inter-band coupling is much smaller due to large energetic distance of the bands (Section 2.4.4).

3.2 Optical properties

In optical spectroscopy, the electronic ground state and the first exciton band plays the predominant role. For non-linear spectroscopy of the third order we need to also include doubly excited states. All of these states are also coupled to the higher excited states, which need to be included into the calculation of transition energies and dipoles. There are two limits in which system-bath interaction is discussed in Frenkel exciton model, week and strong system-bath coupling (Section 1.5). The weak regime correspond to the case where the coupling between individual states and the resulting delocalization of the electronic states is undisturbed by the interaction with bath. In the strong system-bath interaction regime the delocalization is disturbed by the system-bath interaction and localized states should be used instead. In this regime the effects of the interaction between different exciton manifolds will be largely suppressed by interaction with the bath and it is therefore expected that standard FEM will deliver correct results. We will therefore focus on the weak system-bath coupling case where the delocalization of the electronic states is important for correct description of the system.

Because there is no interaction between manifolds with odd and even number of excitations, the system Hamiltonian is separated into two blocks, and ground and singly excited states can be treated separately. The interaction of the ground state with higher excited states results in lowering the ground state energy. The lowering of the energy is expected also for the singly excited states. We cannot therefore predict the shift of the spectra without considering all the interactions. The resulting shift of the transition energy is therefore dependent on the parameters of the system. Due to the different nuclear potential for molecule in the ground and excited state, the mixing of the ground with double excited states results in a change of the ground state potential, which leads to reorganization of the bath with respect to the standard FEM.

3.3 Results

The couplings between electronic states from different exciton manifolds are the same as couplings between states within the single excited manifold, which are already present in standard FEM. Within the developed approach the standard FEM Hamiltonian can be simply expanded to account for the interaction with higher excited states without the need to calculate any additional interaction elements. Now we will discuss effects of the interaction with higher excited states
on model molecular dimer and carotenoid aggregate.

### 3.3.1 Spectroscopy of molecular dimer

Assuming homodimer, the change of the excitation energy due to the interaction of the ground and doubly excited state reads

$$
\Delta E_{g \rightarrow e} = E_{g \rightarrow e} \left( \frac{1}{2} \sqrt{1 + \left( \frac{J}{E_{g \rightarrow e}} \right)^2} - \frac{1}{2} \right)
$$

where $J$ is resonance coupling between singly excited states and $E_{g \rightarrow e}$ is excitation energy for the monomer. For bacteriochlorophyll typical values of transition energy and resonance couplings are $E_{g \rightarrow e} = 12500\text{cm}^{-1}$ and $J = 100\text{cm}^{-1}$, respectively. Using these values we obtain shift of the transition energy just about $0.2\text{cm}^{-1}$. This is too small to observe any effects of the higher excited states in photosynthetic systems. For a carotenoid dimer, assuming Astaxanthin with $E_{g \rightarrow e} = 20700\text{cm}^{-1}$ and resonance coupling $J = 1000\text{cm}^{-1}$, we obtain a shift of $12\text{cm}^{-1}$. This is also rather small value, however, in closely packed aggregates the effects of the higher excited states are enhanced. We also investigated the effects of higher excited states on linear and 2D Fourier transformed spectra of the model carotenoid dimer. Including the higher excited states results in a change of the peak intensity ratio for the single excited states and also of the total intensity of the spectra. Effects on the lineshape and reorganization energy due to the renormalization of the bath were negligible for a realistic set of parameters. The magnitude of the effects is dependent on both magnitude of the resonance coupling and mutual orientation of the molecular transition dipole moments. Although the absolute magnitudes of the effects of inter-band coupling are rather small, if one uses the spectra to fit the unknown value of the resonance coupling from 2D spectra, it would lead to clearly different results depending on whether the inter-band coupling is neglected or not.

### 3.3.2 Spectroscopy of molecular aggregates

The effects of the inter-band coupling on properties of molecular aggregate are demonstrated on absorption spectra for aggregate of carotenoid molecules, where the effects discussed for molecular dimer are enhanced due to the number of involved molecules. For our study we have chosen aggregate of 15 carotenoids in water solution as a smallest aggregate which could reasonably well represent the experimental absorption spectra of Ref. [40]. Molecular dynamic (MD) simulation was used for sampling of the aggregate conformational space to obtain aggregate structures needed for absorption spectra calculation. We have run several MD trajectories starting from random and tightly packed configurations. Tightly packed configurations were created by applying additional restriction on initial carotenoid position to keep all molecules around the center of the simulation box. The MD simulation was performed using GROMACS [41, 42, 43] package and explicit water solvent with periodic boundary conditions. Carotenoid molecules were described using GAFF forcefield with RESP [26] charges. For simulation we used NpT ensemble with temperature 300K and pressure 1bar with 2fs timestep.
Figure 3.1: Absorption spectra of the Astaxanthin in DMSO solution (black dashed line), which correspond to absorption spectra of Astaxanthin monomer (solid line), and for high water concentration (red dashed line) which results in formation of aggregates. The simulated absorption spectra (solid line) well correspond to the experimental one.

for numerical integration of Newton equations of motion. During 40ns equilibration carotenoid aggregates were formed due to the hydrophobic interaction of π-conjugated chain of the carotenoids. After the equilibration, short MD simulation was performed to sample the aggregate structural conformations from which absorption spectra were calculated (Figure 3.1). The simulated absorption spectra well represent the experimental spectra well and they explain the observed spectral shift due to the aggregation and forming H-type aggregates in water solution.

To investigate the effects of the inter-band coupling we choose a random aggregate structure from the equilibrated MD simulation. The resonance couplings between the allowed singly excited ($S_2$) states were calculated by TDC method (2.4.2) with transition densities from TD-DFT QC calculation. The resulting absorption spectrum is shown in Figure 3.2. Including singly and doubly excited states into the FEM Hamiltonian (CISD) results in a shift of the absorption spectrum to the higher frequencies compared to the standard FEM. This shift is expected because of the interaction of the ground state with doubly excited states, the ground state energy is lowered while the singly excited states remain the same because no additional interaction is included. Including all states up to triply excited states (CISDT) into the FEM Hamiltonian results in a shift of the singly excited states and the whole spectrum is shifted to lower transition energies by about 200 cm$^{-1}$ with respect to standard FEM. Including the quadruply (CISDTQ) and higher excited states had only negligible effect on the absorption spectra.

Including the coupling with the higher excited states results in redistribution of the transition dipole moment and lowering the total oscillator strength of
the single exciton band (Section 2.4.4). The calculated lowering of the oscillator strength by 12% compared to monomeric spectra obtained for aggregate structures sampled by MD simulation is consistent with experimental decrease of 10% (calculated from the absorption spectra of Ref. [40]).

Although the inter-band excitonic coupling has only small influence on dimer spectral properties, the effects are greatly enhanced for tightly packed aggregates. Dominant effects of the higher excited states are the spectral shift and change in the total oscillator strength of the aggregate. We have found only minor changes due to the renormalization of the system-bath interaction. The convergence of the configuration interaction with the number of multiply excited bands is found to be fast, however, taking only doubly excited states does not provide a good estimate of the effects.

In the context of photosynthesis, the configuration interaction will play only minor role in the chlorophyll based pigment-protein antenna complexes. This is due to the weak to moderate couplings and relatively small number of pigments in these systems. One system which, due to its size and close packing of pigments, can potentially show significant band shifts due to the interaction with the higher excited states, is the chlorosome of green sulfur bacteria [44].
4. Excitation Energy Transfer in Rylene Dyads

This chapter introduces the work presented in Paper II, where we investigate optical properties and excitation energy transfer in rylene dyads. First we briefly present the most important properties of rylene molecules and introduce two studied members of the rylene dyads. The studied molecules present two limiting cases of strong excitonic coupling, dyad with parallel arrangement of donor and acceptor transition dipoles, and weak excitonic coupling regime, dyad with orthogonal arrangement of the transition dipoles of the donor and acceptor. Then we explain the origin of the observed unexpectedly fast excitation energy transfer in the orthogonal dyad, where no energy transfer is allowed according to the standard FEM. We demonstrate that vibronic model, with excitonic couplings obtained from combined MD and QC methods, can represent the experimental optical spectra and excitation energy transfer for both week (orthogonal dyad) and strong (parallel dyad) coupling regime quantitatively well. The vibronic model therefore represents the method of choice for investigation of optical properties of rylene molecules and its derivatives.

4.1 Rylene dyads

Rylene dyads show high fluorescence quantum yield and photostability and their applications range from laser dyes [5, 6], fluorescence probes [1] to organic photovoltaic [8, 9]. The family of rylene molecules shows similar spectral features and similar properties. For example, the studied molecules: perylene, terrylene and their chemical derivatives, commonly enjoy a strong modulation of a central transition by an intramolecular stretching vibrational mode around 1300-1400cm$^{-1}$. The fluorescence lifetime of these molecules is around 5 ns and quantum yield is near unity. Broad variability of geometric arrangements of rylene in dyads implies large variations of intramolecular coupling magnitude. Therefore, there is a need for unified approach, which would be applicable to broad range of rylene dyads and correctly interpolates between both week and strong intermolecular coupling regimes. We show that removing the most pronounce intramolecular vibrational mode from a bath and treating it on the equal footing as the electronic degrees of freedom, so-called vibronic model, significantly reduces the system-bath interaction. Within the vibronic model, the system-bath interaction for rylene dyads is weak enough for the Redfield theory to be used for the description of excitation energy transfer even for the cases with small intermolecular couplings.

To demonstrate the validity of this model, we investigate interplay of excitation transfer and vibrational relaxation for two different arrangements of rylene molecules, with parallel and orthogonal orientation of the transition dipoles. For the dyad with parallel arrangement of the transition dipoles (parallel dyad) of the donor (S-13-OBISI M) and the acceptor (terylene), i.e. large intermolecular coupling, fast excitation energy transfer with time constant of 0.5 ps is observed. Redfield theory is expected to provide correct description of excitation energy transfer for this regime. In the dyad with orthogonal arrangement of the tran-
sition dipoles (orthogonal dyad) of the donor (perylene) and acceptor (benzoperylene), according to the standard FEM there should be no excitation energy transfer between individual monomers allowed, because of negligible resonance coupling in equilibrium geometry. However, unexpectedly fast excitation transfer, with transfer time of 13 ps, is experimentally observed. From temperature dependence of the transfer times, it was proposed that thermal fluctuations distorts the optimal orthogonal geometry and allow the excitation energy transfer. Yet no rigorous quantitative calculations of these effects were done to convincingly prove this mechanism.

4.2 Computation details

4.2.1 Resonance coupling

For calculation of resonance coupling for studied rylene dyads, the spacer molecule was replaced by methyl group, yielding two separated molecules. For every molecule separately, excited state energies and transition densities were obtained from TDDFT calculations with CAM-B3LYP functional and 6-311G(p,d) basis set. The resonance coupling between donor and acceptor was calculated by applying TDC method (Section 2.4.2) with transition densities from the separated molecules.

4.2.2 Orthogonal dyad

To rule out all possible mechanisms of excitation transfer originating from the equilibrium geometry, we investigated bridge assisted excitation transfer, structure reorganization in the excited state of the dyad and solvent induced changes of the optimal dyad geometry. In the bridge assisted excitation energy transfer, the energy transfer between donor and acceptor is mediated through excited states of the bridge molecule. This type of transport requires strong interaction between excited state of the bridge molecule and excited states of the both donor and acceptor. Due to the unfavorable geometric orientation of the donor, bridge and acceptor molecule no electronic state on the bridge molecule, which would strongly interact with both donor and acceptor molecule, was found. We can therefore exclude this contribution to the excitation energy transfer. Other
Figure 4.2: Results from normal mode analysis of resonance coupling dependence on vibrational coordinate. a) Dependence of the resonance coupling on dyad structure distortion along normal mode coordinate. b) Visualization of structure changes along each normal mode.

possible mechanism is based on the reorganization of the dyad structure in the excited state before the energy transfer occurs. However, even optimal structure for the electronic excited state exhibits the perfect orthogonal arrangement of the transition dipoles. The same is true when solvent effects are included into geometry optimization through PCM model.

The next step was to investigate thermally induced geometry fluctuations as a possible source of the excitation energy transfer, by applying normal mode analysis of the dyad. The normal modes were calculated using Gaussian 09 [47] quantum chemistry package with B3LYP DFT functional and 6-311G(p,d) basis set. The high frequency normal modes correspond to stretching vibrations which do not change the orthogonal arrangement of the dyad and therefore it is unlikely that they would affects the resonance coupling between the donor and acceptor. The low frequency normal modes correspond to bending and torsion of the dyad and therefore changing the mutual orientation of the transition dipole moments of the donor and acceptor. The low frequency normal modes are also more thermally populated at the room temperature than the high frequency ones and therefore higher displacements along the normal mode coordinates are probable. This makes them good candidates for the geometry changes which could trigger the energy transfer. For the five lowest vibrational normal modes, suggested also in the previous study of Ref. [45], resonance coupling for dyad geometries along the normal mode coordinate was calculated with TDDFT method and CAM-B3LYP with 6-311G(p,d) basis set (Figure 4.2). The thermal averaging of the resonance couplings for the room temperature performed over the discrete set of molecular geometries, yields negligible mean value of the coupling and variance \( \sqrt{\langle J^2 \rangle} = 3 \text{cm}^{-1} \). The effective resonance coupling \( J_{\text{eff}} = \sqrt{\langle J^2 \rangle} \) between donor and acceptor obtained from the normal mode analysis of the lowest vibrational modes is insufficient to explain the observed fast excitation energy transfer.

In order to realistically account for the thermal and solvent induced fluctuations, MD simulation was used to sample the dyad’s fluctuating geometry. MD simulation was performed using AMBER [48] molecular dynamics package. The
terylene dyad was parametrized by GAFF force field with RESP \cite{26} charges, whereas parameters for the toluene solvent were acquired from Ref. \cite{49}. After initial 10 ns equilibration of the terylene dyad in toluene at room temperature (300K), the fluctuating geometry was sampled along MD trajectory of sufficient length of 40 ps. The resonance coupling distribution calculated for MD geometries with TDC method is shown in Figure 4.3b. The coupling distribution is roughly symmetric around $J = 0$, yielding negligible average coupling $\langle J \rangle = 0.5 (\pm 0.6) \text{cm}^{-1}$ and variance $J_{eff} = \sqrt{\langle J^2 \rangle} = 19 \text{cm}^{-1}$. The effective coupling $J_{eff}$ obtained from MD simulation corresponds well to the coupling of 17cm$^{-1}$ predicted by fitting of the experimental results.

To investigate the reason, why the normal mode analysis is insufficient to describe the coupling fluctuations and the resulting excitation energy transfer, we performed detailed analysis of the MD simulation. For every geometry from the MD simulation we projected the change of the dyad geometry into normal mode displacements from the optimal geometry. This is realized by the following scheme: First we transform out the coordinate change connected with translation and rotation motion of the dyad. Then we calculate Cartesian displacements of the atomic coordinates from the optimal geometry $\Delta \mathbf{R}_t = \mathbf{R}_t - \mathbf{R}_{opt}$, where $\mathbf{R}_t$ is 3N dimensional coordinate vector for the MD geometry at time $t$ with...
N being the number of atoms in the molecule. The Cartesian displacements $\Delta \mathbf{R}_t$ are then transformed into the normal mode displacements $\Delta \mathbf{q}_t$ yielding a single realization of the normal mode displacement for every normal mode. When this procedure is applied to a long MD simulation, resulting statistics of the normal mode displacements can be used to obtain probability distribution of the normal mode displacements along each normal mode. We can then compare the predicted harmonic normal mode distribution with the one obtained from the MD simulation to investigate effects of anharmonic potential surfaces (Figure 4.4). Repeating the procedure for MD simulations at different temperatures we can clearly see the temperature dependence of the anharmonicity effects. The effects of the anharmonic potential surface are presented on one of the low frequency normal modes of the orthogonal dyad on Figure 4.4. At low temperatures, the system does not have enough energy to sample the whole potential surface and therefore remains in the vicinity of the optimal geometry, where the potential is approximately harmonic. For this case, the predicted harmonic distribution of $\Delta \mathbf{q}$ is consistent with the results from MD simulation (Figure 4.4a-b). When the temperature is higher, the system has more energy to overcome potential barriers and sample the anharmonic part of the potential surface. As a result, double well potential signatures can be identified on the $\Delta \mathbf{q}$ distribution from the MD simulation (Figure 4.4c-d). When the thermal energy is much higher then the potential barrier, the double well potential can be approximated by "harmonic" potential, however, with different frequency and minimum. As a result, the $\Delta \mathbf{q}$ distribution from the MD simulation is shifted compared to the harmonic one (Figure 4.4e).

The projection analysis can be also applied to the short MD simulation, which was used to calculate the coupling fluctuations, to investigate which normal modes are responsible for the high coupling values. From this analysis we were not able to identify single normal mode which would be responsible for the large fluctuation of the coupling. Rather then by single normal mode, the coupling fluctuations are caused by a collective motion of many normal modes. These results suggest that
large number of normal modes would have to be included into the calculation, to obtain the correct variance of the coupling form the normal mode analysis.

### 4.2.3 Parallel dyad

For the parallel rylene dyad, the coupling fluctuations were calculated from MD simulation, following the same scheme as for the orthogonal dyad. The distribution of the resonance coupling calculated for MD geometries is shown in Figure 4.3c. The coupling distribution is symmetric around the mean value $\langle J \rangle = \sqrt{\langle J^2 \rangle} = 247\text{cm}^{-1}$. For the parallel dyad the effects of the coupling fluctuations are negligible in comparison to the average value of the coupling. We can therefore describe the optical and transfer properties of the parallel rylene dyad with resonance coupling obtained for dyad in the optimal geometry.

### 4.3 Optical properties

The effective resonance coupling values for both configurations of rylene dyads were used to calculate absorption and fluorescence spectra, and to simulate the excitation energy transfer. The linear and nonlinear spectra were calculated in standard response formalism for vibronic dimer described in Ref. [50]. The vibronic model was parametrized to yield quantitative agreement with measured absorption spectra of monomeric compounds. For the simulation of the transient absorption signal we account for the selective pump pulse excitation by weighting the transition dipole moments by laser pulse intensity at given frequency as suggested in [51]. Both the simulated linear spectra (4.5) and the transient absorption signal (4.6) corresponds well to the experimental measurements.

![Figure 4.5](image)

**Figure 4.5**: Experimental (solid line) and simulated (dashed line) fluorescence (red) and absorption (blue) spectra for the (a) orthogonal and the (b) parallel rylene dyad. Green dashed line represents a direct sum of the absorption spectra of donor and acceptor.
4.4 Results

In Paper II, we show that the observed unexpectedly fast excitation energy transfer in orthogonal dyad can be explained by thermally induced fluctuations of the dyad structure. From the combined MD simulation, TD-DFT quantum chemistry calculation and TDC method for the calculation of the resonance coupling, we obtain quantitative agreement with couplings predicted by fitting of the experimental results. Our analysis clearly demonstrates that including the thermal fluctuations through normal mode analysis of the few lowest normal modes yields insufficient value of the coupling. From the analysis of MD simulations we found two possible reasons. The first is the need to include large number of normal modes into the analysis, and the second is a possible role of anharmonic potential. Applying the Lilliefors test on coupling distribution for the orthogonal dyad, we found significant deviations from the normal (Gaussian) distribution. We assign this difference to anharmonicity of the potential surface, which was found by the analysis of MD simulation. We also show that applying the vibronic model for description of optical and transfer properties, with resonance couplings obtained by combined MD and QC methods, can interpolate correctly between regimes with small and large intermolecular resonance couplings in rylene dyads. This is supported by the good quantitative agreement of the simulated absorption spectra and the transient absorption signal with experimental measurements for rylene dyads with parallel and orthogonal arrangement of the transition dipole moments.

Figure 4.6: Comparison of the simulated and the experimental excitation dynamics for the (a) orthogonal and the (b) parallel rylene dyad.
5. Fluorographene with Impurities as a Biomimetic Light-Harvesting Medium

Primary processes in photosynthesis, such as light harvesting and excitation energy transfer, are extensively studied and to a great extend also understood even on a molecular level. Using the knowledge acquired from the study of the biological light harvesting complexes, we propose an artificial light harvesting antenna based on disordered fluorographene (FG). We show by quantum chemical (QC) calculations that graphene-like impurities on the FG surface can act as quasi-molecules, embedded in a pure FG environment, similar to natural pigments. The same as pigments in natural light harvesting complexes, the FG impurities can act as centers for light absorption and the spatial excitation energy transfer. We show that organized system of impurities may lead to efficient excitation energy transfer across the FG sheet. In this chapter we introduce the work presented in the Paper III, show basic concepts of the FG based light harvesting antenna and summarize its most important properties. We investigate effects of the FG environment and the spatial orientation of the impurities on resonance couplings and the resulting excitation energy transfer.

5.1 Fluorographene biomimetic antenna

In natural light harvesting complexes, quantum efficiency of the photon absorption and excitation energy transfer to the reaction center is under optimal conditions close to one. The very high efficiency of the primary processes is a consequence of the fast excitation energy transfer and dissipation of the excess energy, and the long life-time of excited states of the individual chromophores. The fast excitation energy transfer is a result of the well defined structure of the chromophore systems and its interaction with the surrounding protein environment. However, natural light harvesting antennas are more then to high efficiency of the excitation transfer optimized to a robust function in wide range of external conditions. Under the high light intensity conditions the photoprotective mechanisms
Figure 5.2: Fluorographene structure: (a) Hexagonal cell of fluorographene lattice. (b) Side view of fluorographene lattice (c) Two perylene-like impurities on the fluorographene lattice.

suppress the excitation energy transfer considerably to reduce a photochemical damage, resulting in efficiency of the incident light to useful energy conversion of only few percent. However when the aim is to collect as much excitation energy as possible, the selective design principles of natural light harvesting systems can be used in artificial systems. Systems inspired by light harvesting strategies in natural photosynthetic systems provide a road for achieving efficient harvesting of solar energy which is alternative to the more standard photovoltaic concepts.

The ideal light harvester in addition to the efficiency of the excitation energy transfer must enjoy other important properties such as a photo-chemical and thermal stability, robustness of electronic and transfer properties under wide range of external conditions and sensitivity to a broad range of wavelengths in the solar spectrum. We propose fluorinated graphene, fluorographene (CF), - 1:1 ratio of fluorine to carbon, as a promising medium for light harvesting. Fluorographene (FG) is a thermally stable insulator with large optical energy gap above 3eV which makes it transparent to almost entire solar spectrum [52]. However, when some adjacent fluorine atoms are removed from the material, isles of graphene with different shapes could form on the FG lattice, e.g. perylene like impurities (Figure 5.2). Comparison of QC ground state energies of optimized structures of FG sheet with impurities, fluorine vacancies, revealed that the compact impurities are more stable and energetically favorable than more disordered impurities (Figure 5.3). This is in agreement with previous findings [53], where it is proposed that fluorine atoms tend to dissociate in the vicinity of already formed fluorine vacancy due to the lower formation free energy.

Formation of \( \pi \)-conjugated graphene-like impurities in otherwise \( \sigma \)-bonded structure of pure FG, leads to formation of \( \pi \)-molecular electronic orbitals, which are energetically inside the FG band gap and spatially well confined in the area of the impurity. Due to the localization of the \( \pi \)-conjugated states, the lowest optical transitions should be also well localized on the impurity. This was confirmed by QC calculations of excited state properties of the perylene-like and anthanthrene-like impurities in FG (Figure 5.4). QC calculation also revealed a correspondence between \( \pi \)-molecular orbitals and transition densities for FG sheet with a single impurity and the impurity-like molecule in the vacuum (Figure 5.4). The correspondence with the isolated molecules, together with the localization of the
molecular orbitals, allows us to treat the impurities in FG as a quasi-molecules (moleculoids) embedded in a pure FG environment, the same way as pigments are treated in natural light harvesting complexes. Similarly as pigments in natural light harvesting complexes, individual impurities in FG can acts as a centers for absorption of incoming light and transfer of the excitation energy across the FG sheet, triggered by the interaction with other impurities.

We demonstrate that when the impurities (impurities in FG) are placed next to each other, separated by the minimum one layer of fluorinated carbon atoms, they exhibit negligible differential overlap of the $\pi$-conjugated electronic orbitals, i.e. negligible electron transfer. They generally satisfy the conditions for treatment with Frenkel exciton model [20]. We also show how certain arrangements of even a few moleculoids on the FG lattice lead to a more efficient energy transfer between two collections of moleculoids playing the roles of donor and acceptor of excitations. We demonstrate the idea of excitation energy transfer and occurrence of energy funneling in a model light harvesting antenna made up from perylene and anthanthrene moleculoids. Perylene and anthanthrene are the smallest symmetric aromatic hydrocarbons built out of hexagonal (benzen) rings which have the excitation energies smaller than the FG energy gap and the lowest electronic excited state allowed for the optical excitation. They represent perhaps the smallest moleculoids to be employed in constructing interesting model light-harvesting antenna. Larger moleculoids may turn out to be more suitable for construction of a practical antenna. However, for computational reasons, smaller moleculoids are more apt for the present proof of the principle.
Figure 5.4: Transition density between electronic ground state and the lowest electronically excited state obtained from quantum chemistry calculation for isolated perylene molecule (a), perylene moleculoid on fluorographene (b), anthanthrene molecule (c) and anthanthrene moleculoid on fluorographene (d). Transition density is represented as iso-surface with density value of 0.0008.

5.2 Calculation details

FG clusters with impurities were created from finite FG sheets in ideal periodic geometry (C-C distance 1.594Å) leaving always at least three rows of fluorinated graphene between the moleculoid and the edges of the FG sheet, to minimize the effects of its finite dimension. The geometry of the structure was then optimized at DFT level with BLYP functional with LANL2DZ double zeta valence basis in Gaussian09 quantum chemistry package. During the geometry optimization, positions of border atoms were kept frozen to mimic the effects of the infinite sheet, which does not allow such a large structure deformation as a finite cluster does. The excited state properties were calculated within TDDFT approach with $\omega$B97XD functional and LANL2DZ double zeta valence basis. The combination of the methods for the geometry optimization and calculation of the excited properties was chosen, based on extensive study presented in supporting informations of the Paper III, as a combination which provides the best agreement with experiment, for excited state properties of broad range of aromatic hydrocarbons. Aromatic hydrocarbons were chosen as a testing set due to the structure similarity with $\pi$-conjugated impurities which can be formed on the FG surface.

5.3 Parametrization of Frenkel exciton model

To determine the parameters of the Frenkel exciton Hamiltonian, and to verify that properties of the moleculoids are as expected, we employ QC methods, specified above, to sections of FG sheets with model impurities. Transition energies and dipoles were calculated for fluorographene clusters with single perylene or anthanthrene moleculoids and compared with the vacuum properties of the corresponding perylene and anthanthrene molecules. In vacuum, we use the geometry of an isolated defect optimized within the FG sheet, with added hydrogens after the optimization to replace missing bonds between the impurity and the FG.
Figure 5.5: (a) Resonance couplings calculated by quantum chemistry from excited states splitting for two mutual orientations (parallel and serial) of dipole moments with various distances between the centers of perylene moleculoids. Linearity confirms the validity of dipole-dipole approximation. (b) Effective relative permittivity of fluorographene as a function of distance between two perylene moleculoids with both parallel and serial transition dipole moments. The positions of the added hydrogens were optimized keeping all carbons frozen in the FG geometry. Transition dipoles for the isolated molecules are always smaller than the ones corresponding to moleculoids in the FG sheet, however, direction of the transition dipole moment is the same for both cases. The transition energies are lower for the moleculoids in FG than for molecules in vacuum. For calculation of resonance couplings $J$ between moleculoids, we use scaled dipole-dipole dipole approximation

$$J_{ij} = \kappa \frac{\vec{d}_i \cdot \vec{d}_j - 3 (\vec{d}_i \cdot \hat{r})(\vec{d}_j \cdot \hat{r})}{r^3},$$

where $\vec{d}_i$ is the transition dipole moment between the ground and the first excited state of the moleculoid $i$ in vacuum, and $\hat{r}$ is the unit vector along $\vec{r}_{ij}$. The scaling factor $\kappa$ represents the effect of the FG environment on the interaction, which can be also understood as the inverse of the relative permittivity $\varepsilon_{eff} = 1/\kappa$ of the FG sheet.

To verify the validity of this approximation we compare the resonance couplings $J_{ij}$ calculated from Eq. (5.1) with the resonance couplings obtained from QC methods for few distances between two perylene moleculoids. According to the Frenkel exciton model, the resonance coupling for symmetric homodimer can be calculated as the half of the excited state splitting. For this calculation it is crucial to use symmetric structures to have exactly the same interaction with the FG environment for both impurities. We use this approach because there is no other straightforward way how to include the unknown effects of the FG into the calculation of the resonance coupling by the standard methods such as transition TDC (2.4.2) or Poisson-TrEsp (2.5.5) method. We then use Eq. (5.1) to calculate the relative permittivity, for every mutual configuration of the moleculoids, needed to obtain the correct QC resonance coupling within the dipole dipole approximation (Figure 5.5b). We estimate the average scaling factor for the FG
Figure 5.6: Distance dependence of resonance coupling enhancement in the fluorographene compared to the vacuum. a) Quantum chemistry calculation of the resonance coupling for perylene impurities in fluorographene divided by the resonance coupling for the corresponding molecules in vacuum. b) Classical interpretation of the distance dependent resonance coupling enhancement, by the representation of the fluorographene sheet as a dielectric slab. The blue line represents the ratio between potentials calculated for point charge in dielectric slab \( \Phi_{\text{slab}}^{\varepsilon_r=2} \) and for homogeneous dielectric \( \Phi_{\text{dielectric}}^{\varepsilon_r=2} \) both with the same relative permittivity \( \varepsilon_r = 2 \). The red dotted line corresponds to the ratio between potentials calculated for the point charge in vacuum and in the homogeneous dielectric.

The same distance dependent enhancement can be seen on comparison of QC resonance couplings calculated for perylene moleculeoids and QC resonance couplings calculated for the corresponding perylene molecules in vacuum, at exactly the same position and geometry as the moleculeoids in FG. (Figure 5.6a). The possible origin of the distance dependence of the relative permittivity \( \varepsilon_{\text{eff}} \) can be demonstrated on simple example of point charge in dielectric slab (Figure 5.6b). For the close distance from the point charge, shielding of the environment is the same as for a homogeneous dielectric. However, with increasing distance from the point charge, the electrostatic potential is approaching the potential of the point charge in vacuum. With this simple model we can qualitatively explain the origin of the distance dependence of the ratio between resonance coupling in FG and in vacuum, by simple representation of the moleculeoid transition density as point atomic charges and FG environment as a dielectric slab. Quantitative explanation requires atomic description of fluorographene environment, which is presented in the next chapter.
5.4 Excitation energy transfer

In order to demonstrate the central ideas behind our proposed artificial light-harvesting systems, we construct several examples of artificial antennae for energy transport from a donor molecule to an energetically lower acceptor molecule. We choose the donor (D) moleculoid to be of the perylene type, and the acceptor (A) moleculoid of the anthanthrene type, with excitation energies $E_D = 22354 \text{ cm}^{-1}$ and $E_A = 21736 \text{ cm}^{-1}$, respectively, obtained from QC calculations. The energy gap between D and A ensures thermodynamically that preferential donor to acceptor energy transfer occurs, because a larger than $k_B T$ energy gap has to be crossed (for temperature $T$ around 300 K). The transition dipole moments calculated for these moleculoids are 6.30 D and 6.55 D, respectively, obtained from QC.

To model the environmental influence, we assume that the environment has an overdamped Brownian oscillator spectral density $J(\omega) = \frac{2\lambda\gamma}{\omega^2 + \gamma^2}$, where $\lambda$ and $\gamma$ are reorganization energy and inverse correlation time, respectively. We take $\gamma = 1/60 \text{ fs}^{-1}$ in all calculations, and vary the reorganization energy to obtain the range of achievable transfer times. Within this model of the environment we investigate excitation energy transfer between perylene donor and anthanthrene acceptor for different mutual distances and orientations. We also study the role of a middle-exciton conveyor aggregate (M), which could aid the excitation in crossing the energy gap between the donor and the acceptor by increasing a density of states inside the energy gap. We present the effect of the middle conveyor on two examples of possible structure of light harvesting antenna, Loop and Square antenna (Figure 5.7). In structures without M aggregate, the D aggregate was shifted to the same distance from A, where M originally was, to keep the same distance between A and the closest aggregate. The population dynamics was cal-
culated by numerically exact hierarchical equation of motion (HEOM) starting from a unity population on the donor aggregate. For both examples of the light harvesting antenna, the excitation energy transfer is considerably faster when M is present. We also compared energy transfer rate between the two antennae in order to assess the role of geometry. Loop antenna shows faster energy transfer over the whole values of reorganization energy compared to the Square antenna. The differences are considerable, meaning that the orientation of dipole moments can hugely influence the dynamics. Therefore, the impurity orientation seems to be a major factor for the optimized antenna.

5.5 Results

In this work, we present the idea of utilizing graphene-like defects (impurities) in fluorographene for light energy harvesting and spatial excitation energy transfer. We show that π-conjugated impurities in FG, exhibit properties which are remarkably molecule-like, hence can be treated as individual molecules embedded in FG environment. The quantum chemistry methods were used to parametrize Frenkel exciton model, which was used for simulation of the excitation energy transfer. We construct several model antennae and show that for reasonable range of system-environment coupling strengths (measured by reorganization energy) we obtain energy transfer rates which would result in high quantum yields in presence of expected losses. We thus expect that construction of efficient artificial light-harvesting antennae using fluorographene impurities is feasible.

A broader concept of impurity based antennae includes the possibility to tune antenna properties by combination of different types of impurities. Larger impurities are expected to absorb light on longer wavelengths and similar designs could thus be translated to different wavelength regions for simultaneous light-harvesting of different sections of solar spectrum. The concept of π-conjugated isles in 2D materials is not restricted to fluorographene. Other 2D materials, e.g. other modifications of graphene, may provide similar opportunities. Obviously first guess would be graphane and materials using other halogen atoms – these seem however not to be stable without further modifications. The idea is also not restricted to a single sheet. The prospect of building membrane with several interacting 2D sheets and impurities interacting in three dimensions is also worth investigating.

Recently, we have identified naturally occurring candidate impurities in the band of nearly pure fluorographene by single molecule spectroscopy. Single molecule measurements confirm the "molecular" character of the naturally occurring impurities in the fluorographene, and they show excited state lifetimes of the impurities around 3ns, which is large enough to allow the excitation transfer in the fluorographene based light harvesting antenna.
6. Role of the Dynamic Polarizability on Static Excited State Properties

In the two previous chapters we showed, how interaction of system with its environment is important for excitation energy transfer and optical properties of embedded systems. For rylene dyads with orthogonal arrangement of transition dipoles, thermal fluctuations trigger excitation energy transfer within the dyad, whereas for fluorographene systems, interaction of impurities with pure fluorographene environment leads to enhancement of resonance couplings between the impurities. Correct description of system-environment interactions is crucial for interpretation of experimental results and understanding the underlying molecular processes of light harvesting, excitation energy transfer or nonphotochemical quenching mechanisms. This chapter provides an introduction to the Paper IV, where we present a new method, quantum polarizable atom model, for treating environmental effects on excited state properties of embedded systems. Quantum polarizable atom model provides more general description of the environmental effects than the widely used polarizable QM/MM approach, accounting also for frequency dependent atomic polarizabilities. First, we introduce basic ideas behind the quantum polarizable atom model of the environment. We show that the classical polarizable atom model used in the polarizable QM/MM can be obtained as a limiting case of the present model. This enables us to pinpoint approximations and assumptions about the system inherent to the classical polarizable atom description of the environment. Then we apply the quantum polarizable atom model to investigate effects of the FG sheet on excited state properties of impurities on FG surface, discussed in the previous chapter. Quantum polarizable atom model quantitatively well describes all the observed effects of the FG environment on exited state properties of the impurities and provides computationally very efficient and reliable alternative to the full quantum chemical (QC) approach. Comparison of quantum polarizable atom model with the full QC calculation and standard polarizable QM/MM on disordered fluorographene clusters revealed the need to use frequency dependent atomic polarizabilities to properly account for the environment effects on both transition energy shifts and interaction energies for FG systems.

6.1 Theory

The environmental effects play a crucial role in photochemistry and photophysics of embedded molecular systems. In complex systems with many chromophores, environment influences excited state properties and dynamics in variety of ways. Different environment of otherwise symmetric chromophore structure leads to an asymmetric electron transfer \[^{15}\] or change in environment conformations leads to different excitation energy pathways, creating of traps or even quenching the excitation \[^{22}\]. This is usually accomplished by modulation of chromophore site energies and interaction energies between individual chromophores. The correct
description of the environment effects on the chromophore excited state properties is crucial for understanding the function of photochemical systems.

In the past years substantial effort was devoted to development and improvement of models that account for the environment in excited state quantum chemical calculations. These methods can be divided into quantum subsystem approaches (QM/QM), combined quantum mechanical and molecular mechanical methods (QM/MM) and polarizable continuum models (PCM). These methods are described to a greater extent in Section 2.5. Here we present a general QM/QM approach for description of the environmental effects on chromophore system inspired by [28]. We start from the properties of the isolated chromophores in vacuum, which can be obtained by standard QC methods. Our method is based on perturbation treatment of the system-environment interaction resulting in quantum polarizable atom description of the environment. The quantum polarizable atom model provides a generalization of standard classical polarizable atom model, without loss of the computational simplicity of the QM/MM approach.

We consider a pair of chromophores, denoted \( A \) and \( B \) interacting with an environment building blocks \( n \). Individual environmental building block, may be single atom or whole molecules. Localized states of individual parts of the system are denoted as \( |a_A\rangle \), \( |b_B\rangle \) and \( |\eta_n\rangle \) and stand for the states where the chromophore \( A \) is in the state \( a \), chromophore \( B \) in the state \( b \) and \( n \)th environment building block in the state \( \eta \), respectively. The respective energies are denoted as \( \varepsilon_a^{(A)} \), \( \varepsilon_b^{(B)} \) and \( F^{(n)}_\eta \). We further assume no molecular orbital overlaps between individual parts of the system. In absence of electron exchange between individual parts, we can use the basis functions in form of the Hartree product \( |ab,\eta\rangle = |a_A\rangle |b_B\rangle \prod_n |\eta_n\rangle \) to investigate the effects of the interaction with environment on chromophore properties. Hamiltonian of the individual parts of the system and the Coulomb interaction operator is presented in Section 2.5.1.

The environment building blocks are composed of individual atoms or small molecules e.g. amino-acids for the protein environment. These small molecules usually have \( \sigma \)-bond structure, resulting in higher excitation energies then \( \pi \)-conjugated chromophores i.e. impurities in FG or pigments in photosynthetic complexes. The quantum perturbation approach is therefore suitable to account for the environmental effects on chromophore excited state properties in such systems.

The main idea behind the quantum polarizable atom model is to use the perturbation expansion of the system-environment interaction operator. Then we partially sum individual terms of the expansion into simple atomic properties (atomic charges and polarizabilities), which can be parametrized by quantum chemical calculations or by fitting experimental measurements.

We will present this procedure on a single representative contribution from the first order perturbation expansion (Section 2.5.4), \( \sum_{n,\eta} |\langle a_0|V|b_\eta\rangle|^2 F^{(n)}_\eta / (\varepsilon^{(A)}_{ab} + \varepsilon^{(A)}_a) \), assuming only single chromophore embedded in the environment. This term corresponds to the interaction of the state where the chromophore \( A \) is in the electronic state \( a \) and all the environment building blocks are in the ground state, with the state where the chromophore \( A \) is in the electronic state \( b \) and single environment building block \( n \) is excited to the state \( \eta \). The \( F^{(n)}_\eta = F^{(n)}_\eta - F^{(n)}_0 \) and \( \varepsilon^{(A)}_{ab} = \varepsilon^{(A)}_b - \varepsilon^{(A)}_a \) correspond to the excitation energies of isolated environment building block
n and the chromophore A, respectively. Applying multipole expansion (Section 2.4.1) to the Coulomb interaction, the term \( \langle a, 0 | V | b, \eta_n \rangle \) can be interpreted as a chromophore transition density interacting with the transition dipole \( \mu_{\eta}^{(n)} \) of the environment building block \( n \). We obtain

\[
\langle a, 0 | V | b, \eta_n \rangle = \langle a_A | \langle 0_n | V_{A_{n_0}} | \eta_n \rangle | b_A \rangle = -\mathcal{E}_{ab}^{(A)} (R_n) \cdot \mu_{\eta}^{(n)},
\]

where \( \mathcal{E}_{ab}^{(A)} (R_n) \) is the electric field, at position of the center of the environment building block \( R_n \), generated by the chromophore transition density between the states \( a \) and \( b \). Applying the Eq. (6.1) to the investigated contribution from the perturbation expansion, yields

\[
\sum_{n, \eta_n} \frac{\langle a, 0 | V | b, \eta_n \rangle^2}{F_{\eta n}^{(n)}} = \frac{1}{2} \sum_n \mathcal{E}_{ab}^{(A)} (R_n) \left( 2 \sum_{\eta} \frac{\mu_{\eta}^{(n)} \mu_{\eta}^{(n)}}{F_{\eta n}^{(n)} + \varepsilon_{ab}^{(A)}} \right) \mathcal{E}_{ab}^{(A)} (R_n) = \frac{1}{2} E_{ab,ab}^{(n)} \left( \alpha \left( -\varepsilon_{ab}^{(A)} \right) \right),
\]

where the polarizability tensor \( \overrightarrow{\alpha}^{(n)} \) of the \( n \)th environment building block is introduced, based on the remarkable similarity with the static polarizability (introduced in the Section 2.3). For elements of the polarizability tensor \( \alpha_{ij}^{(n)} \) we generalized the definition of Ref. [23] to include dependency on the transition energy \( E \) as

\[
\alpha_{ij}^{(n)} (E) = 2 \sum_{\eta} \frac{\left( \mu_{\eta}^{(n)} \right)_{i} \left( \mu_{\eta}^{(n)} \right)_{j}}{F_{\eta n}^{(n)} - E}.
\]

The polarizability at zero frequency, \( \overrightarrow{\alpha}^{(n)} (0) \), corresponds to the static polarizability of the environment building block and \( \overrightarrow{\alpha}_{\text{dynamic}}^{(n)} (E) = \frac{1}{4} E_{ab,ab}^{(n)} \left( \alpha \left( -\varepsilon_{ab}^{(A)} \right) \right) \) to the dynamic polarizability defined in Section 2.3.

The physical interpretation of Eq. (6.2) is that the chromophore A transition density produce an electric field \( \mathcal{E}_{ab}^{(A)} (R_n) \) at the location of environment building block \( n \). This field induces a dipole moment \( \mu_{ab}^{(n)\text{ind,1}} (\alpha (E)) = \overrightarrow{\alpha}^{(n)} (E) \mathcal{E}_{ab}^{(A)} (R_n) \) on the environment building block \( n \), which then interacts back with the transition density on the chromophore A (Figure 6.2 - green green arrows).

### 6.1.1 Transition energy

We use the procedure outlined above to obtain the excitation energy shift \( \Delta E_{g \rightarrow e}^{(A)} = E_{g \rightarrow e}^{(A)} - \varepsilon_{ab}^{(A)} \) between the chromophore A embedded in the environment and in the vacuum. The \( E_{g \rightarrow e}^{(A)} \) corresponds to the transition energy of the chromophore A embedded in environment, whereas \( \varepsilon_{ab}^{(A)} \) represents the transition energy of the chromophore in vacuum. The zero and the first order contributions to the
Figure 6.1: Graphical representation of the individual terms for the excitation energy shift in the quantum polarizable atom model. Terms $E_{ele}$ and $E_{env-pol1}(\alpha(0))$ correspond to the same interaction as $E_{ge}$ and $E_{env-pol1}(\alpha(0))$, however, with the chromophore ground state charge distribution (instead of the transition density as in the case of the $E_{ele}$ and $E_{env-pol1}(\alpha(0))$, which are shown in the Figure).

The first two terms in Eq. (6.4) correspond to a difference in electrostatic interaction between the chromophore and its environment, for the chromophore in the excited and in the ground state. The next term represents scaled electrostatic interaction of the chromophore transition density with the environment. Term $\left[ E_{pol,1}^{ee,ee}(\alpha(0)) - E_{pol,1}^{gg,gg}(\alpha(0)) \right]$, in Eq. (6.4), can be interpreted as a solvation energy difference for the chromophore in the excited and in the ground state. The last term of Eq. (6.4) corresponds to the difference of solvation energies for the chromophore transition density with two different environment polarizabilities $\alpha(\varepsilon_{ab})$ and $\alpha(-\varepsilon_{ab})$.

The second order contribution to the chromophore excitation energy shift is obtained from the second order perturbation expansion following the same approach as for the first order. For defects with the large excitation energy compared to the electrostatic interaction of the defect with its environment, the
The term $E_{\text{a}}$ chromophore state proceeds the same way as for the excitation energy shift. The transition dipole of the chromophore embedded in the environment we can proceed the same way as for the excitation energy shift obtained as $\Delta G_{\text{a}} = \mu_{\text{ge}} \cdot (\varepsilon \cdot \alpha)$. The graphical representation of few representative terms of the excitation energy shift is shown in Figure 6.1

6.1.2 Transition dipole

For the transition dipole of the chromophore embedded in the environment we can proceed the same way as for the excitation energy shift. The transition dipole of chromophore coupled to the environment is defined as $\mu_{\text{ge}} = e \langle G | \mathbf{r} | E \rangle$, where $|G\rangle$ and $|E\rangle$ are the ground and excited states of the whole system (chromophore + environment) and $\mathbf{r}$ are electronic coordinates of all electrons (chromophore + environment). All the environmental effects are now included in the wavefunctions of the whole system ($|G\rangle$ and $|E\rangle$). These wavefunctions can be obtained from the known wavefunctions of the chromophore in vacuum, using perturbation expansion of the system-environment interaction operator. The first and the second order corrections to the transition dipole (Eq. (2.51)) $\Delta \mu_{\text{ge}} = \mu_{\text{ge}} - \mu_{\text{ge}}^{(A)}$, where $\mu_{\text{ge}}^{(A)}$ is the vacuum transition dipole, are within the same approximations as for the excitation energy shift obtained as

$$\Delta \mu_{\text{ge}}^{(1+2)} \approx \sum_n \mu_{\text{ge}}^{(n)\text{ind},1} (\mathbf{\alpha} \cdot \mathbf{\alpha})_{\text{dynamic}} (\varepsilon^{(A)}) + \sum_n \mu_{\text{ge}}^{(n)\text{ind},2} (\mathbf{\alpha} \cdot \mathbf{\alpha})_{\text{dynamic}} (\varepsilon^{(A)}) . \quad (6.6)$$

The $\mu_{\text{ge}}^{(n)\text{ind},1} (\mathbf{\alpha} \cdot \mathbf{\alpha})$ is the dipole on the environmental building block $n$ induced by the transition density of the chromophore. The difference between the transition dipole for the chromophore embedded in the environment and in the vacuum corresponds to the induced dipole on environment building blocks by the chromophore (vacuum) transition density, assuming dynamic polarizabilities (of the environment atoms) at chromophore excitation energy.
6.1.3 Resonance coupling

The resonance coupling between two chromophores can be defined in variety of ways. Here we define the resonance coupling from the excited state energy splitting as \[ |J_{AB}| = \frac{1}{2} \sqrt{(E_2 - E_1)^2 - (\tilde{\varepsilon}_B - \tilde{\varepsilon}_A)^2} \], where \( E_i \) are excited state energies of the whole interacting system (including the environment), whereas \( \tilde{\varepsilon}^{(A)} \) and \( \tilde{\varepsilon}^{(B)} \) are excited state energies of the individual chromophores with the environment. We use this definition, because it provides the correct couplings for the Frenkel exciton model (FEM), i.e. the correct eigenstates after diagonalization of the FEM hamiltonian. The validity of the used definition is discussed in Section 2.5.2.

The energies \( E_i \) of the excited states are obtained following the same procedure as for the transition energy shift. However, in the case of the two chromophore system, there is a possibility of degeneracy (or close to degenerate) of the excited states from the different chromophores, which would result in divergence of the perturbation expansion. This divergence can be avoided using degenerate state perturbation expansion (see Section 2.2.3). For homodimer, or chromophores with small difference in transition energies, the interaction energy \( J_{AB} \) up to the second order of perturbation expansion, within the same level of approximations as for the excitation energy shift, reads as

\[
J_{AB} \approx J_{AB}^{\text{vac}} + E_{\text{ge,ge}}^{(AB)} (\alpha_{\text{dynamic}} (\varepsilon_{\text{ge}})) + E_{\text{ge,ee}}^{(AB)} (\alpha_{\text{dynamic}} (\varepsilon_{\text{ge}}))
+ \left[ E_{\text{ge,gg}}^{(AB)} - E_{\text{ge,ee}}^{(AB)} \right] \left[ E_{\text{ge,gg}}^{(AB)} + E_{\text{ge,ee}}^{(AB)} + 2E_{\text{ge}}^{(A)\text{ele}} \right] \varepsilon_{\text{ge}}
\]

where \( J_{AB}^{\text{vac}} \) is the resonance coupling between two chromophores in vacuum. The environmental contribution to the interaction energy corresponds to the interaction of the chromophore \( A \) transition density with dipoles on environmental building blocks induced by the transition density of chromophore \( B \) assuming dynamic atomic polarizabilities. Graphical representation of the quantum polarizable atom model for calculation of the resonance coupling for chromophores embedded in environment is shown in Figure 6.2.

6.1.4 Classical polarizable atom model

The classical polarizable atom model (Section 2.5.8) (as used for example in polarizable atom forcefield) is obtained from the quantum polarizable atom model, outlined above, together with additional assumption of large chromophore excitation energies, compared to the electrostatic interaction of the chromophore with its environment, but still small compared to the excitation energy of environment building blocks (\( \varepsilon_{\text{ge}} \ll F_{0\eta} \)). For this case, we can neglect the frequency dependence of the polarizabilities \( F_{0\eta}^{(n)} - E \approx F_{0\eta}^{(n)} + E \approx (F_{0\eta}^{(n)})^{-1} \) and we obtain \( \alpha (E) = \alpha (-E) = \alpha (0) \). Within this approximation, the excitation energy is shifted only due to the different electrostatic interaction of the chromophore in the electronic ground and excited state with the environment and due to the different polarizations of the environment in the ground and in the
excited states. The energy shift reads as

\[
\Delta E_{g\rightarrow e} = (E_{ele}^{ee} - E_{ele}^{gg}) + \frac{1}{2} \left[ E_{pol}^{ee,ee} (\vec{\alpha} (0)) - E_{pol}^{gg,gg} (\vec{\alpha} (0)) \right] + \left[ E_{env-pol}^{ee} (\vec{\alpha} (0)) - E_{env-pol}^{gg} (\vec{\alpha} (0)) \right].
\]

(6.8)

The excitation energy shift is then no longer dependent on the chromophore transition density. The transition dipole change due to the interaction with the environment, corresponds to the dipole induced by the chromophore transition density in the environment with static polarizability as

\[
\Delta \vec{\mu}_{GE} = \sum_n \vec{\mu}_{ge}^{(n)ind} (\vec{\alpha} (0)).
\]

(6.9)

The resonance coupling between two chromophores embedded in the classical polarizable atom environment consist of vacuum interaction energy plus interaction of the chromophore transition density with the dipoles in the environment induced by the transition density of the other chromophore, using only static atomic polarizabilities

\[
J_{AB} = J_{AB}^{vac} + E_{ge,ge}^{(AB),pol} (\vec{\alpha} (0)).
\]

(6.10)
6.2 Application to fluorographene systems

In the previous chapter we introduced disordered fluorographene (FG) system as a promising medium for artificial light harvesting systems. Treatment of large FG systems with many impurities and investigation of effects of different impurities and their mutual configurations on efficiency of the excitation energy transfer is not in reach of the full QC treatment of the system. Therefore a simple and reliable approximate structure based method is needed. In the previous chapter we also discussed properties of disordered FG systems including the distance dependent enhancement of resonance couplings between impurities, compared to the resonance couplings between corresponding molecules in vacuum. It was also demonstrated that the individual impurities can be treated as molecules embedded in pure FG environment rather than as defects in perfectly periodic structure. Although the transition density of the impurity in FG is well confined in the area of the impurity, small part of the transition density is delocalized over few surrounding FG atoms. The leakage of the transition density from the impurity into the FG is proportional to the corresponding transition dipole. For forbidden transitions, the transition density is localized only on the defect whereas for transitions with large dipole moment, small part of the transition density is delocalized over few rows of surrounding FG atoms (Figure 6.3). This leakage can be interpreted as dipoles induced in FG by the impurity transition density. This conclusion is also supported by the shape of the transition density in FG area, which follows the transition dipole electric field (Figure 6.3f). This correspondence allows us to treat the impurity as a molecule, and describe the effects of the FG environment on its excited state properties with the quantum polarizable atom model.

6.2.1 Computation details

We use the quantum polarizable atom model to calculate excitation energy and transition dipole shifts together with interaction energies for "graphen-like" impurities on FG surface. The results obtained by the quantum polarizable atom model are compared with the full QC calculation of excited state properties and with the classical polarizable atom model on FG clusters with different impurity sizes, shapes and mutual orientation. For testing set we used FG clusters with perylene, anthanthrene, bisanthrene and peropyrene-like impurities. The corresponding isolated molecules are the smallest symmetric aromatic hydrocarbons which have the excitation energies smaller than the FG energy gap and the lowest electronic excited state allowed for the optical excitation. These properties makes the tested moleculoids, Ref. Paper III (Chapter 5), good candidates for centers for absorption and excitation energy transfer in FG artificial light harvesting antenna. For calculation of interaction energies between excited states of individual impurities, the symmetric clusters with two identical impurities in different distances and orientations were used. The total testing set consisted of 31 different clusters with two impurities and 22 clusters with a single impurity with sizes ranging from 400-800 atoms. For QC calculation of excited state properties we used the same procedure as described in previous chapter (5).

Within the quantum polarizable atom model, the impurities in FG are treated
Figure 6.3: Comparison of transition densities of perylene molecule in vacuum and perylene-like impurity in FG. (a) Perylene defect in FG. (b) Transition density of perylene $S_0 \rightarrow S_2$ transition in vacuum. (c) Transition density of perylene-like impurity in FG $S_0 \rightarrow S_2$ transition (without atoms). (d) Transition density of perylene $S_0 \rightarrow S_1$ transition in vacuum. (e) Transition density of perylene-like impurity in FG $S_0 \rightarrow S_1$ transition (without atoms). (f) Perylene impurity transition density together with electric field from transition density of isolated molecule (without atoms).

as molecules and the pure FG environment as individual polarizable atoms (Figure 6.4). Molecules are in this model described by their vacuum ground and excited state charge distributions (needed for the calculation of interaction terms $E_{\text{pol},\text{ee}}^{\alpha\alpha}(\alpha)$, $E_{\text{ele}}^{\text{ee}}$, ...) and the transition densities (needed for the calculation of interaction terms $E_{\text{pol}}^{(\alpha\beta),\text{pol}}(\alpha,\beta)$ and the induced dipoles $\vec{\mu}^{\text{ind}}_{\alpha\beta}(\alpha,\beta)$), which can be calculated by standard QC methods. To simplify calculation of the interaction terms in Eq. (6.4)-(6.7) the charge distribution and the transition density is represented by point atomic charges. This procedure is described in Section 2.4.3. The environment atoms are within quantum polarizable model described by point atomic charges (same as in molecular force fields for MD simulations) and by frequency dependent atomic polarizability $\vec{\alpha}(E)$. The ground state charges for the FG atoms were obtained from RESP fitting of the ground state potential of a pure FG cluster. For impurities we tested, the excitation energies
Table 6.1: Atomic polarizabilities for C-F coarse-grained atoms in atomic units

<table>
<thead>
<tr>
<th></th>
<th>in FG plane</th>
<th>perpendicular to FG</th>
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<tbody>
<tr>
<td>$\alpha (0)$</td>
<td>5.10</td>
<td>5.17</td>
</tr>
<tr>
<td>$\alpha (E)$</td>
<td>15.49</td>
<td>6.09</td>
</tr>
<tr>
<td>$\alpha (-E)$</td>
<td>0.56</td>
<td>1.70</td>
</tr>
</tbody>
</table>

were found to be much higher than their variation between individual impurities. We can therefore simplify the model and use the same polarizabilities $\alpha (E)$ for the studied clusters. In order to keep the system as simple as possible we treat the fluorographene C-F group as a single coarse-grained polarizable atom at the position of the carbon atom. Within this simplified model, the static atomic polarizabilities for the coarse-grained FG atoms are obtained from fitting static polarizabilities of small pure FG clusters of different sizes and shapes, calculated using DFT approach with $\omega$B97XD functional and LANL2DZ basis set. Assuming an isotropic polarizability in FG plane, the remaining four free parameters of the model, parallel and perpendicular polarizability $\alpha (E)$ and $\alpha (-E)$ to the FG surface, are obtained from fitting the QC interaction energies and excitation energy shifts. The resulting coarse-grained FG atomic polarizabilities are shown in Table 6.1.
6.2.2 Results

We compared quantum polarizable atom model with the full QC calculation and with the classical polarizable atom model on the testing set of fluorographene clusters with one or two impurities. The distance dependence of interaction energies for different mutual orientation of tested impurities are shown in Figure 6.5 for anthanthrene-like and perylene-like impurity. The results for the bisanthrene-like and peropyrene-like impurities can be found in the supporting information of the Paper IV. The quantum polarizable atom model can well describe enhancement of resonance couplings for impurities in FG, even for anthanthrene-like impurities with parallel configuration of transition dipoles, where the interaction energy in FG is twice larger then the interaction in the vacuum. The interaction energy and transition dipole shifts connected with moving the impurity from the vacuum (impurity-like molecule) to the FG sheet (impurity in FG) are shown in Figure 6.6. The excitation energy shifts for perylene-like impurities were calculated for two different shapes of the FG sheet around the impurity. The structure denoted as parallel is made of FG sheet elongated in the direction perpendicular to the perylene impurity transition dipole (Figure 6.7a), whereas for the structure denoted as serial in direction of the transition dipole (Figure 6.7b). Correct description of the excitation energy difference between these two cases (Figure 6.6a) confirms the validity of the quantum polarizable atom model for FG systems.

From the comparison of the classical polarizable atom model with the results from the QC calculation, it can be seen that although the classical model (MMpol) accounts for environmental effects on interaction energies and transition dipoles reasonably well, it provides wrong shifts of the transition energies (Figure 6.6). For FG systems, the best agreement with full QC calculation is obtained for the quantum polarizable atom model. The description of the environment with frequency dependent polarizabilities is therefore crucial to obtain the right description of the environment effects on the interaction energies, the transition dipoles and the excitation energy shifts for fluorographene systems.

![Figure 6.6: Single impurity environment effects. (a) Transition energy shift and (b) transition dipole shift induced by interaction with environment](image-url)
Figure 6.5: Distance dependence of resonance couplings between impurities in fluorographene. Anthanthrene impurities with (a) parallel and (b) serial arrangement of transition dipoles. Perylene impurities with (c) parallel and (d) serial arrangement of transition dipoles.

Figure 6.7: Structures for calculation of perylene excitation energy shift. (a) Perylene parallel and (b) perylene serial structure
6.3 Outlook

We showed that quantum polarizable atom model provides reliable alternative to full quantum chemical treatment of the FG based systems. The disordered fluorographene is an example of system where the description of the environment with the frequency dependent polarizabilities is needed to obtain the correct description of the environmental effects on the both transition energies and resonance couplings.

The quantum polarizable atom model provides a generalization of the polarizable QM/MM approach and the next logical step in a more precise description of the environment effects. This approach might be particularly useful for systems where standard approaches fails to explain the observed experimental behavior, especially for the systems where the excitation energy of the chromophore is not negligible compared to the excitation energy of environment building blocks. The present approach is in general not limited to the second order approximation, and it offers obvious pathways towards its extension and improvements.

Based on similarity of present quantum polarizable atom model with the polarizable QM/MM approach, we suggest an improvement of both methods by treating the environment with frequency dependent atomic polarizabilities and include the mutual system-environment polarization using self the consistent procedure, as it is implemented for the polarizable QM/MM scheme.
Conclusion

In this thesis we have focused on structure based calculations of optical and excitation transfer properties of complex molecular systems. With the recent advances in optical spectroscopy, these methods became very important for interpretation of observed spectra and for understanding of the underlying molecular processes. In this work we show how structure based methods such as quantum chemistry (QC) methods and molecular dynamics (MD) simulation can be used for parametrization of the Frenkel exciton Hamiltonian, to obtain optical properties of large (embedded) systems.

In the first part of the thesis we related Frenkel exciton model (FEM) with configuration interaction QC method. Based on this relation we suggest an extension of the standard FEM to account for interaction with higher excited states (inter-band excitonic coupling), which corresponds to the full configuration interaction approach in QC. Then we investigated effects of this interaction on model dimer and carotenoid aggregate in water solution. The most important effects of the interaction with the higher excited states are spectral shifts, redistribution of peak intensities and changes of the total oscillator strength of the single exciton manifold. We concluded that for the model dimer, representing two interacting carotenoids the effects of the higher excited states on most of the spectral properties are negligible. Although the inter-band excitonic coupling has only small influence on dimer spectral properties, the effects are greatly enhanced for larger tightly packed aggregates. By including the inter-band excitonic coupling in calculation of absorption spectra of carotenoid aggregates in water solution, we explained the experimentally observed decrease of the total oscillator strength in the absorption spectra upon the aggregation.

Then we used structure based methods to investigate excitation energy transfer in rylene dyads with orthogonal and parallel arrangement of transition dipoles of donor and acceptor. The unexpectedly fast excitation energy transfer in orthogonal dyad was explained by thermal fluctuations of the dyad structure from perfectly orthogonal geometry. From combined molecular dynamics and quantum chemistry methods we obtained effective coupling which was in agreement with value predicted from the fitting of the experimental results. We showed that normal mode analysis of few lowest normal modes, suggested in previous studies, yields insufficient resonance coupling to explain the observed transfer. From the analysis of the MD simulation we identified two possible reasons. The first is the need to include large number of normal modes into the analysis and the second is a possible role of anharmonic potential, which is also supported by the deviation of resonance coupling distribution from normal (Gaussian) distribution. For parallel dyad, it was found that thermal fluctuations have only negligible effects on effective resonance coupling and therefore, the resonance coupling for optimal geometry can be safely used for simulation of optical properties of this dyad. We also demonstrated that the vibronic model model of rylene dyad, with resonance couplings obtained by combined MD and QC methods, provides quantitative agreement with experimental spectra for both dyads. The vibronic model can therefore correctly interpolate between regimes with small (orthogonal dyad) and large (parallel dyad) intermolecular resonance couplings in rylene dyads, which
makes it the method of choice for investigation of optical properties of rylene molecules and its derivatives.

Methodology developed and tested on molecular aggregates related to photosynthesis can be applied to design artificial systems. In the second part of the thesis, we proposed disordered fluorographene (FG) as a promising medium for artificial light harvesting antenna. By QC calculations we confirmed our original idea that graphene-like impurities on FG surface, fluorine vacancies, can be used as centers for excitation energy transfer in FG based antenna. QC calculations also revealed remarkable molecule-like character of the π-molecular orbitals and the lowest optical transitions of the π-conjugated impurities in FG. For the calculation of optical properties, this makes the impurities treatable as individual molecules embedded in pure FG environment. We investigated excitation energy transfer in model artificial antenna created from impurities in FG sheet and confirmed that construction of efficient artificial light-harvesting antenna from fluorographene impurities is feasible.

In the last part of the thesis we introduces the quantum polarizable atom model a new method for including environmental effects on the excited state properties of embedded systems. Within this approach the environment is described as polarizable atoms with frequency dependent polarizabilities. We showed that the widely used polarizable QM/MM method can be obtained as a limiting case of the quantum polarizable atom model. The quantum polarizable atom model was successfully applied to calculation of interaction energies, site energy shift and transition dipole shifts for impurities in FG, yielding good quantitative agreement with the full QC results. Comparison of QC results with the classical polarizable atom model revealed the need to use frequency dependent polarizabilities to properly account for environment induced excitation energy shifts in FG based systems.

In summary, this thesis provides a comprehensive view on structure based methods for calculation of optical and excitation energy transfer properties. The selected examples of molecular systems show the strength of these methods in investigating molecular mechanisms of photo-induced processes and relate it with optical properties. Based on this work we propose several improvements of Frenkel exciton model for calculation of optical properties and introduce new method for including environmental effects on excited state properties for embedded systems.


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<th>Description</th>
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<tbody>
<tr>
<td>DFT</td>
<td>density functional theory</td>
</tr>
<tr>
<td>DOF</td>
<td>degrees of freedom</td>
</tr>
<tr>
<td>FEM</td>
<td>Frenkel exciton model</td>
</tr>
<tr>
<td>FG</td>
<td>Fluorographene</td>
</tr>
<tr>
<td>HO</td>
<td>harmonic oscillator</td>
</tr>
<tr>
<td>MD</td>
<td>molecular dynamics</td>
</tr>
<tr>
<td>MM</td>
<td>molecular mechanics</td>
</tr>
<tr>
<td>PCM</td>
<td>polarizable continuum model</td>
</tr>
<tr>
<td>QC</td>
<td>quantum chemistry</td>
</tr>
<tr>
<td>QM</td>
<td>quantum mechanics</td>
</tr>
<tr>
<td>RESP</td>
<td>restrained electrostatic potential</td>
</tr>
<tr>
<td>TDC</td>
<td>transition density cube</td>
</tr>
<tr>
<td>TDDFT</td>
<td>time-dependent density functional theory</td>
</tr>
<tr>
<td>TrEsp</td>
<td>Transition charges from electrostatic potential</td>
</tr>
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II Vladislav Sláma, Sayeh Rajabi and Tomáš Mančal. Fluorographene with Impurities as a Biomimetic Light-Harvesting Medium, *arXiv 1801.08509*, submitted to *Scientific Reports*


A. Attachments

A.1 Construction of Harmonic Bath Hamiltonian

For the description of the system we use the Born-Oppenheimer approximation which allows us to separate the electronic and nuclear motion. Hamiltonian of the whole system within the Born-Oppenheimer approximation reads as

$$\hat{H} = \hat{T} \otimes 1_{el} + \sum_{MN} H_{MN}(\vec{R}) |M \rangle \langle N|, \quad (A.1)$$

where $| N \rangle$ are the electronic states and $H_{NN}(\vec{R})$ correspond to the nuclear potential at position $\vec{R}$, described by $3N$ dimensional vector, where $N$ is a number of atoms in the system. The quantity $H_{NM}(\vec{R})$ represents the coordinate dependent coupling between individual states, and $\hat{T}$ is the nuclear kinetic operator. The Hamiltonian element $H_{MN}(\vec{R})$ can be expanded in the form of the Taylor series around the optimal geometry as

$$H_{MN}(\vec{R}) = H_{MN}(\vec{R}^{(0)}) + \sum_{I} \frac{\partial H_{MN}(\vec{R})}{\partial R_{I}} |_{\vec{R} = \vec{R}^{(0)}} \cdot (\hat{R}_{I} - R_{I}^{(0)})$$

$$+ \frac{1}{2!} \sum_{I} \sum_{J} \frac{\partial^{2} H_{MN}(\vec{R})}{\partial R_{I} \partial R_{J}} |_{\vec{R} = \vec{R}^{(0)}} \cdot (\hat{R}_{I} - R_{I}^{(0)}) (\hat{R}_{J} - R_{J}^{(0)}) + \ldots, \quad (A.2)$$

where $\vec{R}^{(0)}$ correspond to the optimal ground state geometry of the whole system. For the ground state, the second term in the expansion $\left( \frac{\partial H_{GG}(\vec{R})}{\partial R_{I}} \right) |_{\vec{R} = \vec{R}^{(0)}}$ vanishes, because the first derivation of the energy surface in minimum is zero. The first nonzero term in the expansion $A.2$ for the ground state, $H_{ij}^{(0)} = \sum_{\xi} \frac{\partial^{2} H_{GG}(\vec{R})}{\partial R_{i} \partial R_{j}} |_{\vec{R} = \vec{R}^{(0)}}$, is called a hessian matrix. The hessian matrix describes the change of the energy connected with a displacement of the system from the optimal geometry. By diagonalization of the hessian matrix the normal modes of the system are obtained as

$$\sum_{I,J} T_{ij}^{(\xi)} H_{ij} T_{j}^{(\xi)} = \delta_{\xi \xi} \hbar \omega_{\xi},$$

$$\left( \hat{R}_{j} - R_{j}^{(0)} \right) = \sum_{\xi} T_{j}^{(\xi)} \sqrt{m_{\xi}} \hat{q}_{\xi}, \quad (A.3)$$

where $T_{j}^{(\xi)}$ is the transformation matrix between the Cartesian and the mass weighted normal mode coordinates. The $\hat{q}_{\xi}$ and $\omega_{\xi}$ correspond to the normal mode coordinates and frequencies, respectively, and $m_{\xi}$ is the reduced mass of the normal mode $\xi$. In the normal mode coordinates, the kinetic operator is defined as $T = \sum_{\xi} \frac{\hat{p}_{\xi}^{2}}{2m_{\xi}}$ where $p_{\xi}$ is the normal mode momentum. The transformation of the electronic ground state Hamiltonian element into the normal mode coordinates results in

$$\langle G | \hat{H} | G \rangle = H_{GG}(\vec{R}^{(0)}) + \sum_{\xi} \left( \frac{\hat{p}_{\xi}^{2}}{2m_{\xi}} + \frac{1}{2} m_{\xi} \omega_{\xi}^{2} \hat{q}_{\xi}^{2} \right) + \ldots$$

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where we use the dimensionless normal mode coordinate \( \hat{Q}_\xi \) and momentum \( \hat{P}_\xi \) introduced in Section 1.6, and \( \varepsilon_G \) corresponds to the ground state energy of the system in the optimal geometry. The same transformation into the ground state normal modes can also be done for the excited states. For the excited states, the linear term in the Hamiltonian expansion (A.2) is generally non-vanishing. When transformed into the ground state normal mode coordinates, the linear term reads as

\[
\sum_I \frac{\partial H_{MN}(\vec{R})}{\partial R_I} \mid_{\vec{R} = \vec{R}^{(0)}} \cdot (\hat{R}_I - R_I^{(0)}) = \sum_\xi g_\xi (M, N) \hbar \omega_\xi \hat{Q}_\xi,
\]

where \( g_\xi (M, N) \) is the dimensionless coupling strength of the system to the bath coordinate.

Generally the excited states might have different normal modes and frequencies than the ground state. Within the Frenkel exciton model, which is used for description of the optical and excitation energy transfer properties, it is assumed that all the exited states have the same normal modes and frequencies (the same hessian matrix). Within this approximation, combination of Eq. (A.5) and (A.2) yields the Hamiltonian elements in the form of

\[
\langle N | \hat{H} | N \rangle = H_{NN}(\vec{R}^{(0)}) + \sum_\xi \hbar \omega_\xi g_\xi (N, N) \hat{Q}_\xi + \sum_\xi \frac{\hbar \omega}{4} \left( \hat{P}_\xi^2 + \hat{Q}_\xi^2 \right) + \sigma \left( Q^2 \right),
\]

\[
\langle N | \hat{H} | M \rangle = H_{NM}(\vec{R}^{(0)}) + \sum_\xi \hbar \omega_\xi g_\xi (N, M) \hat{Q}_\xi + \sigma \left( Q^2 \right).
\]

Here \( H_{NN}(\vec{R}^{(0)}) = \varepsilon_N \) corresponds to the energy of the system in the electronic state \( N \) in the ground state geometry (vertical transition energy), and \( H_{NM}(\vec{R}^{(0)}) = J_{NM} \) corresponds to resonance coupling between the states \( N \) and \( M \) for the system in the ground state optimal geometry. The coupling strength for the ground state is zero \( g_\xi (G, G) = 0 \), which follows from the discussion above. When harmonic approximation is used, all the terms with higher then the second order in the coordinate \( Q_\xi \) are neglected. In the Frenkel exciton model, it is also assumed only bi-linear coupling, where all the system-bath interaction terms with higher then linear dependence on the normal mode coordinate \( Q_\xi \) are neglected. Applying these approximations to our system (A.6), yields

\[
\langle N | \hat{H} | N \rangle = \varepsilon_N + \sum_\xi \hbar \omega_\xi g_\xi (N, N) \hat{Q}_\xi + \sum_\xi \frac{\hbar \omega}{4} \left( \hat{P}_\xi^2 + \hat{Q}_\xi^2 \right)
\]

\[
\langle N | \hat{H} | M \rangle = J_{MN} + \sum_\xi \hbar \omega_\xi g_\xi (N, M) \hat{Q}_\xi
\]

This results in the Hamiltonian operator for the system with harmonic bath in the form used in Section 1.3.