2

Models

In this chapter, we introduce models of coupled amide vibrations in peptides and Frenkel excitons in molecular aggregates. The model Hamiltonian contains couplings between local oscillators and interaction with the environment.

2.1 Vibrations in peptides

In the following, we will discuss the Hamiltonian for the vibrations in peptides. The similar theory of Frenkel excitons in molecular aggregates is treated in Section 2.5.

The amide I vibration is well-studied in infrared experiments on peptides [Barth 2007]. It appears in the experimental spectra relatively isolated from other modes, and has a strong oscillator strength. This has two important consequences. First of all, a strong transition is advantageous for observations. Secondly, one can expect that the large transition dipole that is responsible for the infrared absorption will also lead to strong interactions between different local vibrations. Such interactions are interesting, because they lead to structural sensitivity of the observed spectrum [Miyazawa 1960; Miyazawa and Blout 1961]. Each time an amino acid is added to the protein chain, an extra amide group is formed, and each amide group contains a single amide I oscillator. The couplings between local vibrations are found from common models to be between -15 and +15 cm$^{-1}$. These couplings are small enough to make mixing with states outside the amide I band almost impossible. It is therefore often assumed that the amide I oscillators mix only with each other, but not with vibrational modes of a different character [Torii and Tasumi 1992]. However, we will see that this mixing might not be negligible. In these cases, it is necessary to explicitly consider other vibrational modes, of which amide II is particularly relevant to spectroscopy.
In this thesis, we will look at the amide I and amide II modes in peptides. The coordinates of these modes are shown in Figure 2.1. The distortions shown in the figure are the result of DFT calculations of the normal modes in the NMA-d$_7$ molecule, which is a model of a single peptide unit. The amide I vibration is mainly a stretching mode of the double bond between the carbon and oxygen atom. The amide II mode is a combination of C-N stretch, CND bend and some C-C stretch. For clarity, most examples in this chapter will consider only amide I modes. We remark that we will mostly use the notation “amide I” and “amide II” for the modes in solution, as well as in the gas phase. Because of a solvent contribution to the coupling between the two modes, the eigenmodes in a solvent are not the same as in the gas phase. We will only make this distinction explicit in Chapter 5.

### 2.2 Peptide model

To model the vibrational modes in a polypeptide, we first consider a single amide vibration, followed by a description of the interactions between the groups. Each vibrational mode can be described as an oscillator, with a coordinate that we denote $x$. The coordinate gives the extension along a normal mode, in which the $i^{th}$ atom is displaced by $x\vec{v}_i$. The scalar $x$ gives the amplitude of the normal mode, while the vectors $\vec{v}_i$ denote the normalized relative displacements of the atoms.

#### 2.2.1 Hamiltonian of a single vibration

Because the frequency of the amide vibrations, which is approximately 1600 cm$^{-1}$ for the amide I mode, is an order of magnitude larger than the thermal energy (200 cm$^{-1}$ at room temperature), we will describe these vibrations in a quantum mechanical model. Furthermore, the interactions between modes are much smaller than the vibrational frequency. In that case, the number of vibrational quanta in the system is a conserved quantity. In third-order nonlinear optical techniques, only states with
zero, one, or two vibrational quanta play a role. In the description of a single vibration, we therefore only need to include the ground state and the first and second excited states. The energy differences between these states can be described with two parameters, which are chosen to be the energy of the first excited state, denoted \( \epsilon \), and the anharmonicity \( A \), which is the shift of the energy of the doubly excited state from \( 2\epsilon \) (all energies are expressed relative to the ground state energy). This model leads to the Hamiltonian for a single vibrational oscillator,

\[
H_S = \epsilon b^\dagger b - \frac{A}{2} b^\dagger b^\dagger b b,
\]

where \( b \) and \( b^\dagger \) are the Bose operators that annihilate or create a vibrational quantum. The subscript \( S \) indicates that the Hamiltonian includes only the degree of freedom of the selected amide vibration (the “system” mode).

For a weakly anharmonic oscillator, the creation and annihilation operators can be expressed in terms of the vibrational coordinate \( x \) in the harmonic approximation. The dynamics of the vibrational motion are governed by the atomic masses and the inter-atomic forces. For small displacements of the atoms (typical displacements in a vibrational mode are a few percent of the bond lengths), the potential energy can be expanded in the coordinate \( x \). In a fourth-order expansion for a single coordinate, the energy becomes

\[
H_S = \frac{p^2}{2m} + \frac{k_2}{2} x^2 + k_3 x^3 + k_4 x^4,
\]

where \( m \) is the effective mass, \( p \) is the momentum, \( k_2 \) is the spring constant, \( k_3 \) is the cubic anharmonicity and \( k_4 \) is the quartic anharmonicity. The harmonic frequency is \( \tilde{\omega} = \sqrt{k_2/m} \). Introducing bosonic creation and annihilation operators by \( x = \sqrt{\hbar/(2m\tilde{\omega})}(b^\dagger + b) \) and \( p = i\sqrt{m\bar{\omega}}\hbar/(b^\dagger - b) \), and making the approximation that the anharmonicities are much smaller than the frequency, one obtains the Hamiltonian in Eq. 2.1, with parameters \( \epsilon = \hbar \tilde{\omega} + 3k_4\hbar^2/k^2 \) and \( A = -3k_4\hbar^2/k^2 \). Treating the anharmonicity as a small parameter relative to the excitation energy, we have ignored all terms with a different number of creation and annihilation operators. Furthermore, the (renormalized) zero point energy has been substracted. Renormalization effects from the cubic and higher order terms in the Hamiltonian can be absorbed in \( \epsilon \) and \( A \), which we will consider as parameters of the theory. In the amide vibrations that we will discuss the ratio of the quartic anharmonicity over the harmonic frequency is typically \( A/\epsilon \approx 1/100 \), and the weakly anharmonic oscillator model is applicable.

### 2.2.2 Fluctuating oscillator Hamiltonian for coupled vibrations

Because the \( \alpha \)-carbon atom hardly moves in the amide I mode, the individual modes on each amide group form a good basis set [Torii and Tasumi 1992]. We find that this statement also holds for the amide II mode (See Section 6.3.1). Bilinear coupling between the basis modes, labeled with \( n \) and \( m \), gives rise to an interaction term in the Hamiltonian of the form \( J_{nm} b_n^\dagger b_m \), where \( J \) is a symmetric matrix (See Figure 2.2
for an illustration of the variables in the amide I subspace). Here, we assume that $J_{nm} \ll \epsilon$, and therefore include only the resonant terms (typical couplings in the amide I band are in the order of $10 \text{ cm}^{-1}$, two orders of magnitude smaller than the excitation energy). Also, we do not include nonlinear interactions in our model.

The vibrational modes in the Hamiltonian are not isolated, but interact with the rest of the peptide, as well as the solvent. We consider all the other degrees of freedom to form an environment for the vibrational modes studied in the experiment. Using the same approximations as in the intrapeptide interactions, the interaction with the environment can be expanded in the oscillator coordinates as

$$H_{SB} = \sum_{nm} X_{nm} b_n^\dagger b_m, \quad \text{(2.3)}$$

where the $X_{nm}$ are operators on the environment degrees of freedom. Here, we have only included the quadratic term in the system coordinates. Linear terms, which lead to dephasing and additional population relaxation, will be treated phenomenologically. Higher order terms in the interaction can lead to fluctuations in the anharmonicities. However, any static shifts in the anharmonicity can be included in the parameter $A$ in Eq. 2.1. Furthermore, fluctuations in the anharmonicities are known to have little effect on peptide spectra [Jansen and Knoester 2006a].

In a semiclassical limit, the system-bath interaction can be replaced by a time-dependent potential. The interaction term in the resulting Hamiltonian becomes $H_{SB}(t) = \sum_{nm} \xi_{nm}(t) b_n^\dagger b_m$, where the $\xi(t)$ variables denote a time-dependent stochastic process. The complete model Hamiltonian, often called the fluctuating oscillator
2.2: Peptide model

Hamiltonian, becomes

\[ H = \sum_n (\epsilon + \xi_{nn}(t)) b_n^\dagger b_n + \sum_{n \neq m} (J_{nm} + \bar{\xi}_{nm}(t)) b_n^\dagger b_m - \frac{A}{2} \sum_n b_n^\dagger b_n^\dagger b_n b_n. \] (2.4)

Because the complete Hamiltonian (Eq. 2.4) conserves the number of excitations, its matrix elements can be classified as a ground state, a manifold of one-quantum states, a two-quantum manifold etcetera. The one-quantum manifold contains states which are linear combinations of the one-quantum states of the individual oscillators. For a system with \( N \) oscillators, there are \( N \) such one-quantum states. Two types of states mix to form the two-quantum manifold. First, the \( N \) two-quantum states of the individual oscillators (called overtones) contribute. These states mix with the combination states, in which the one-quantum states on two different oscillators are excited. There are \( N(N - 1)/2 \) such combination states, bringing the total number of states in the two-quantum manifold to \( N(N + 1)/2 \). The nature of the collective one- and two-exciton states is determined by the competition of the coupling between the oscillators with the interactions with the environment. We now turn to a discussion of the coherent couplings, to which two mechanisms contribute: electrodynamic through-space coupling, and mechanical through-bond coupling.

2.2.3 Electrodynamic coupling

To find the electrodynamic interaction between two modes, we write the Coulomb energy in terms of the charge densities of the two modes (on different peptide groups), which we assume to be non-overlapping. The charge density \( \rho \) on mode \( n \) depends on the spatial coordinate \( R_n \) and on the extension of the normal mode \( x_n \). The Coulomb energy is

\[ E_C(x_n, x_m) = \frac{1}{4\pi\varepsilon_0} \int \int d\tilde{R}_n d\tilde{R}_m \frac{\rho(\tilde{R}_n, x_n) \rho(\tilde{R}_m, x_m)}{|\tilde{R}_n - \tilde{R}_m|}. \] (2.5)

To find the bilinear coupling term, we expand the Coulomb energy in the normal mode extensions \( x_n \) and \( x_m \). The bilinear coupling is given by the expansion coefficient

\[ J_{nm} = \left[ \frac{\partial^2}{\partial x_n \partial x_m} E_C(x_n, x_m) \right]_{x_n = x_m = 0}. \] (2.6)

This coupling is found from the transition dipole formula [May and Kühn 2000] if the distance between the units is big enough. For closely spaced oscillators, multipole effects may be important. We will now discuss the transition dipole coupling and the transition charge coupling formulas.

Transition dipole coupling

The electrodynamic coupling gives the change in the interaction between charge clouds when a vibrational mode is stretched. If two units are far away from each
other, the change in a charge cloud can be approximated by its dipole part (assuming that this is nonzero, which is by definition the case for a dipole-allowed IR active mode) [Torii and Tasumi 1992]. Denoting coordinates measured from the center of the \(n\)th unit by \(\vec{r}_n\), the charge density in a single unit becomes\(^1\)

\[
q(\vec{r}_n, x_n) = q(\vec{r}_n, 0) + q_n \delta(\vec{r}_n - x_n \vec{v}_n) - q_n \delta(\vec{r}_n + x_n \vec{v}_n).
\]  

(2.7)

The transition dipole vector is defined in terms of the charges \(q_n\) as \(\vec{\mu}_n = 2q_n \vec{v}_n\), and is given by the derivative of the dipole \(\vec{M}\) with respect to the coordinate of the transition as

\[
\vec{\mu}_n = \left[ \frac{\partial}{\partial x_n} \vec{M} \right]_{x_n=0} := \left[ \frac{\partial}{\partial x_n} \int d\vec{r} q(\vec{r}, x_n) \right]_{x_n=0}.
\]  

(2.8)

To find the interaction between two units \(n\) and \(m\), we assume that their centers are separated by a vector \(\vec{R}_{nm}\). Coordinates within each unit are denoted by \(\vec{r}_n\) and \(\vec{r}_m\). The Coulomb energy resulting from the interaction between unit \(n\) and unit \(m\) becomes

\[
4\pi\varepsilon_0 E_C = C + \frac{q_n q_m}{|\vec{R}_{nm} + x_n \vec{v}_n - x_m \vec{v}_m|} + \frac{q_n q_m}{|\vec{R}_{nm} - x_n \vec{v}_n + x_m \vec{v}_m|} - \frac{q_n q_m}{|\vec{R}_{nm} + x_n \vec{v}_n + x_m \vec{v}_m|} - \frac{q_n q_m}{|\vec{R}_{nm} - x_n \vec{v}_n - x_m \vec{v}_m|},
\]  

(2.9)

where the term \(C\) contains all contributions which do not include both \(x_n\) and \(x_m\). The assumption of well separated charge clouds implies \(|x_n \vec{v}_n| + |x_m \vec{v}_m| \ll |\vec{R}_{nm}|\).

Using the expansion

\[
\frac{1}{|\vec{R} + \vec{v}|} = \frac{1}{|\vec{R}|} + (\vec{v} \cdot \vec{v}) \frac{1}{|\vec{R}|} + \frac{(\vec{v} \cdot \vec{v})^2}{2 |\vec{R}|^3} + \frac{(\vec{v} \cdot \vec{R})^2}{2 |\vec{R}|^3} + \frac{3 (\vec{v} \cdot \vec{R})^2}{2 |\vec{R}|^5},
\]

(2.10)

we find for the terms bilinear in \(x_n\) and \(x_m\)

\[
4\pi\varepsilon_0 E_C = C' + q_n q_m \left( \frac{4 x_n x_m \vec{v}_n \vec{v}_m}{|\vec{R}_{nm}|^3} - \frac{12 x_n x_m (\vec{v}_n \cdot \vec{R}_{nm}) (\vec{v}_m \cdot \vec{R}_{nm})}{|\vec{R}_{nm}|^5} \right).
\]

(2.12)

Taking the derivatives with respect to \(x_n\) and \(x_m\), the coupling in the dipole approxi-

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\(^1\)The charges do not necessarily remain constant when the transition coordinate is stretched, and in principle we should replace \(q_n\) by \(q_n + xd\dot{q}_n\), et cetera. However, the transition charges \(dq\) cancel in the final expression for the transition dipole coupling.
2.2: Peptide model

Imitation is given by the transition dipole formula,

\[ J_{nm} = \frac{1}{4\pi\varepsilon_0} \left( \frac{\vec{\mu}_n \cdot \vec{\mu}_m}{|\vec{R}_{nm}|^3} - \frac{3(\vec{\mu}_n \cdot \vec{R}_{nm})(\vec{\mu}_m \cdot \vec{R}_{nm})}{|\vec{R}_{nm}|^5} \right). \] (2.13)

The transition dipole vectors are given by Eq. 2.8 and the vector \( R_{nm} \) connects the centers of the transition dipoles on units \( n \) and \( m \).

Transition charge coupling

If the size of the changes in the charge clouds becomes comparable to the distance between them, the dipole approximation breaks down. A model that takes the effects of higher multipoles on the coupling into account is the transition charge coupling model. Here, we approximate the charge density by a set of point charges,

\[ \rho(\vec{r}_n, x_n) = \sum_i \delta(\vec{r}_n - \vec{r}_i(x_n))Q_i(x_n) \] (2.14)

The charges \( Q_i \) can be placed anywhere in the charge cloud, but we choose to put them on the atoms, labeled by \( i \). Both the atom positions and the charges depend on the normal mode extension \( x \). The atom positions are given by \( \vec{r}_i(x_n) = \vec{r}_i(0) + x_n\vec{v}_{ni} \), where the vectors \( \vec{v}_{ni} \) give the direction of movement of atom \( i \) in normal mode \( n \). The charges can be expanded as \( Q_i(x_n) = q_i + dq_i x_n \), with the transition charges \( dq_i = [dQ_i(x_n)/dx_n]_{x_n=0} \). Higher order terms in the expansion are irrelevant, because they will not contribute to the bilinear coupling. Performing the integrals in the expression for the coupling leads to the transition charge coupling [Hamm and Woutersen 2002; Jansen et al. 2006]

\[ J_{nm} = \frac{1}{4\pi\varepsilon_0} \left[ \frac{\partial^2}{\partial x_n \partial x_m} \sum_{ij} \frac{(q_{ni} + dq_{ni} x_n)(q_{mj} + dq_{mj} x_m)}{|\vec{r}_i(x_n) - \vec{r}_j(x_m) - \vec{R}_{nm}|} \right]_{x_n=x_m=0}. \] (2.15)

Using the expansion of atom positions \( \vec{r}_i(x_n) \) in the normal mode extension \( x_n \), the derivatives can be performed explicitly, and the transition charge coupling can be evaluated as

\[
J_{nm} = \frac{1}{4\pi\varepsilon_0} \sum_{ij} \left( \frac{dq_{ni}dq_{mj}}{|\vec{r}_{ni,mj}|} - \frac{3q_{ni}q_{mj}(\vec{v}_{ni} \cdot \vec{r}_{ni,mj})(\vec{v}_{mj} \cdot \vec{r}_{ni,mj})}{|\vec{r}_{ni,mj}|^5} \right. \\
+ \frac{dq_{ni}q_{mj}\vec{v}_{mj} \cdot \vec{r}_{ni,mj} - q_{ni}dq_{mj}\vec{v}_{ni} \cdot \vec{r}_{ni,mj} + q_{ni}q_{mj}\vec{v}_{ni} \cdot \vec{v}_{mj}}{|\vec{r}_{ni,mj}|^3},
\] (2.16)

with \( \vec{r}_{ni,mj} = \vec{r}_i(x_n) - \vec{r}_j(x_m) - \vec{R}_{nm} \). The parameters required to use this formula are available from quantum chemistry calculations on a monomer, they are given in Chapter 6. The value of the permittivity is given by \( 1/4\pi\varepsilon_0 \approx 1.16 \times 10^5 \text{ cm}^{-1} \text{Å}^2/\text{e}^2 \).
2.2.4 Nearest neighbor coupling

For interactions between amide groups that are linked by covalent bonds, the TCC model is not applicable, because mechanical coupling caused by movements of the atoms in between (through-bond coupling) is important. The mechanical interactions depend on the relative orientation of the peptide groups, and were found to vary mostly with the $\psi$ angle (See Figure 2.3) between them [Torii and Tasumi 1998]. Such through-bond couplings have been taken into account in models of amide I vibrations in peptides by performing DFT calculations on dipeptides or polypeptides [Torii and Tasumi 1998]. In Chapter 6, we extend these methods to include the amide II mode. The goal of this procedure is to write the eigenmodes in a dipeptide (which is illustrated in Figure 2.3) as a linear superposition of the eigenmodes in two NMA-d$_7$ molecules. If the dipeptide eigenmodes are denoted $|\psi\rangle$ and the NMA-d$_7$ eigenmodes as $|\phi\rangle$, the required transformation can be expressed as a 4x4 matrix $U$ which satisfies $|\psi\rangle = U|\phi\rangle$. This is achieved by expressing the dipeptide eigenstates and the NMA-d$_7$ eigenstates in the same basis set of stretch and bend vibrations, and then using a matrix reconstruction method to find the transformation between the two sets of eigenmodes. The details of the method and the resulting coupling maps will be described in Chapter 6.

2.3 Sum over states limit

A clear, although simplified, description of the dynamics generated by the Hamiltonian (Eq. 2.4) can be obtained by separating the environment-induced fluctuations into a fast and a slow contribution on the time scale of the experiment. The fast fluctuations average out during the experiment, and lead to exponential damping of the reduced density matrix [Kubo et al. 1985; Boyd 1992; Sung and Silbey 2001],

$$\dot{\rho}_{nm}(t) = -i [H', \rho(t)]_{nm} - \gamma_{nm}\rho_{nm}(t) \tag{2.17}$$

The damping constants $\gamma$, which are the result of the fast fluctuations, determine the homogeneous line width of the infrared spectra (see Section 3.4). Slow fluctuations lead to a constant environment for a molecule during the experiment. The environment is, however, different for each molecule in an ensemble and the calculated response must be averaged over the different states of the environment. This
mechanism is called static disorder. Its effect on the spectra is a sum of separate contributions, and is consequently known as inhomogeneous broadening.

In the case of a single oscillator in each amide group the Hamiltonian, which explicitly includes the slow fluctuations, is given by

\[ H' = \sum_n (\epsilon + \zeta_{nn}) b_n^\dagger b_n + \sum_{n \neq m} (J_{nm} + \zeta_{nm}) b_n^\dagger b_m - \frac{A}{2} \sum_n b_n^\dagger b_n b_n. \] (2.18)

Here, \( \epsilon \) is the average energy of amide I vibrations. The shifts in energy \( \zeta_{nm} \) have become time-independent stochastic variables. The properties of these variables are given by a probability distribution.

Because, in each realization of the stochastic variables, the Hamiltonian is now a constant operator, it can be diagonalized to find the energy eigenstates. The ground state |0\rangle is obviously the state with no excitations. One-quantum eigenstates can be found by diagonalizing the one-quantum matrix in the site basis. The basis states are given by |n\rangle = b_n^\dagger |0\rangle, and the one-quantum matrix elements in this basis are

\[ H'_{nm} = (\epsilon + \zeta_{nn}) \delta_{nm} + (J_{nm} + \zeta_{nm})(1 - \delta_{nm}). \] (2.19)

The eigenstates of the one-quantum Hamiltonian are found by solving the system \( H'_{nm} u_n = E_u u_n \), where \( u_n \) denotes the projection of the eigenstate |u\rangle on site \( n \) (\( u_n = \langle u | n \rangle \)), and \( E_u \) is the energy of state |u\rangle. Matrix elements of the transition dipole between the ground state and the one-exciton states are then given by \( \bar{\mu}_u = \sum_n u_n \bar{\mu}_n \).

A site basis for the two-quantum states is given by

\[ |nm\rangle = \frac{1}{\sqrt{1 + \delta_{nm}}} b_n^\dagger b_m^\dagger |0\rangle. \] (2.20)

The square root factor ensures that the states with two excitations on the same vibration - the overtones - are correctly normalized. As an example, we will give the matrix of two-quantum states in a trimer. If we order the basis in such a way that the overtones |nm\rangle appear before the combination states |nm\rangle, a basis for the two-quantum states in a trimer is |11\rangle, |22\rangle, |33\rangle, |12\rangle, |13\rangle, |23\rangle. The two-quantum Hamiltonian matrix in this basis is

\[
\begin{pmatrix}
2\epsilon + 2\zeta_{11} - A & 0 & 0 & \sqrt{2}(J_{12} + \zeta_{12}) & \sqrt{2}(J_{13} + \zeta_{13}) & 0 \\
0 & 2\epsilon + 2\zeta_{22} - A & 0 & \sqrt{2}(J_{12} + \zeta_{12}) & 0 & \sqrt{2}(J_{23} + \zeta_{23}) \\
0 & 0 & 2\epsilon + 2\zeta_{33} - A & 0 & \sqrt{2}(J_{13} + \zeta_{13}) & \sqrt{2}(J_{23} + \zeta_{23}) \\
\sqrt{2}(J_{12} + \zeta_{12}) & \sqrt{2}(J_{12} + \zeta_{12}) & 0 & 2\epsilon + \zeta_{11} + \zeta_{12} & \sqrt{2}(J_{21} + \zeta_{21}) & J_{12} + \zeta_{12} \\
\sqrt{2}(J_{13} + \zeta_{13}) & 0 & \sqrt{2}(J_{13} + \zeta_{13}) & J_{23} + \zeta_{23} & J_{23} + \zeta_{23} & J_{12} + \zeta_{12} \\
0 & \sqrt{2}(J_{23} + \zeta_{23}) & \sqrt{2}(J_{23} + \zeta_{23}) & J_{12} + \zeta_{12} & J_{12} + \zeta_{12} & 2\epsilon + \zeta_{22} + \zeta_{33}
\end{pmatrix}
\] (2.21)

Diagonalization of this matrix gives the two-exciton eigenstates and their energies. Transition dipoles between a one-quantum state |u\rangle and a two-quantum state |w\rangle are given by \( \bar{\mu}_{ww} = \langle w | \bar{\mu} | u \rangle = \sum_{nm} w_{nm} u_{n} \langle nm | \bar{\mu} | p \rangle \). Different energies and dipoles will be found in each realization of the stochastic variables, and the observables must be averaged over realizations.
2.4 Numerical integration of the Schrödinger equation

Although spectra calculated with the sum over states method match experimental data well [Hamm et al. 1998; Woutersen and Hamm 2001b], the model is not completely satisfactory. It is not straightforward to include the dynamics inside the amide I bands during the waiting time in a 2DIR experiment, which is outside the perturbative regime. Furthermore, the validity of the separation into slow (inhomogeneous) and fast (homogeneous) fluctuations is doubtful. From MD simulations, much has been learned about the fluctuations $\xi_{nm}(t)$. They describe the effect of the environment on the oscillator frequencies and their couplings. Once the state of the environment is known from MD simulations, preparametrized maps can be used to find a trajectory of the fluctuations [Kwac and Cho 2003a; Schmidt et al. 2004; Jansen and Knoester 2006a]. We have extended these methods to create dual mode maps for the effect of the environment on the amide I and II frequencies and the coupling between them. These maps will be presented in Chapter 6.

The dynamics of a system described with a time-dependent Hamiltonian are found from the time-dependent Schrödinger equation,

$$i \frac{d}{dt} \psi(t) = H(t) \psi(t). \quad (2.22)$$

In essence, by replacing the bath operators with time-dependent variables, one obtains a stochastic theory of the system-environment interaction [Kubo et al. 1985]. Assuming that the fluctuations are ergodic, the $\xi_{nm}(t)$ variables in Eq. 2.4 can be interpreted as a stochastic process. Non-ergodic fluctuations must be handled by additional averaging over configurations. For linear interaction with a harmonic bath, the stochastic process is Gaussian, and the dynamics can be calculated with a cumulant expansion [Kubo et al. 1985; Mukamel 1983; Sung and Silbey 2001; Cho 2001]. However, this theory is only applicable to Gaussian fluctuations, and has not been developed to include nonadiabatic relaxation in the modeling of a 2DIR experiment.

In general, the Schrödinger equation can be solved formally with a time ordered (denoted $T$) exponential of the Hamiltonian,

$$\psi(t) = U(t; t_0) \psi(t_0) = T e^{-i \int_{t_0}^{t} d\tau H(\tau)} \psi(t_0). \quad (2.23)$$

The time propagation can be computed by taking time steps of length $\delta t$, which must be short compared to the time scale of the fluctuations. The propagator during each small time step is found by explicitly evaluating the matrix exponent with a constant Hamiltonian. The propagator for longer times is given as the product of all the short time propagations,

$$\psi(t) \approx T \prod_{n=0}^{(t-t_0)/\delta t} e^{-iH(t_0+n\delta t)\delta t} \psi(t_0). \quad (2.24)$$

In each time step, the exponential term is a matrix, which can be expressed in the site basis. The rotation matrices at different times do not commute, and the time ordering
symbol implies that matrices at later time should appear to the left. In this way, a numerical integration of the Schrödinger equation (NISE) is performed [Jansen et al. 2004; Torii 2006; Jansen and Knoester 2006b].

The propagation of two-quantum matrix elements of the Hamiltonian, which is the most time-consuming step in calculations on large systems, follows in principle directly from Eq. 2.24. It can be simplified by separating the the harmonic part of the propagation from the anharmonic part [Paarmann et al. 2008]. The anharmonic part of the Hamiltonian is denoted $H^{\text{ah}}$, while the remaining harmonic part is $H^{(h)}$. The complete time propagation is generated by the sum of these two Hamiltonian operators, which do, in general, not commute. However, for small anharmonicities, the anharmonic contribution to the propagator is varying slowly in time. With good accuracy we can use the factorization [Suzuki 1985; de Raedt 1987]

$$U^{(2)}((n+1)\delta t; n\delta t) = U^{\text{ah}}(\delta t/2)U^{(h)}((n+1)\delta t; n\delta t)U^{(\text{ah})}(\delta t/2) + O(\delta t^3) \quad (2.25)$$

in each time step with length $\delta t$. The propagation of a two-quantum wave function is formally given by $\psi^{(2)}(t) = U^{(2)}(t; t_0)\psi^{(2)}(t_0)$.

The calculation of the diagonal anharmonic propagator is trivial, and the harmonic propagator is given by the sum of permutations of one-quantum propagators,

$$U^{(h)}_{m'n'n'mn} = \langle m'n'|U^{(h)}|mn\rangle = \frac{1}{\sqrt{1+\delta_{m'n'}}} \frac{1}{\sqrt{1+\delta_{mn}}} \left( U^{(1)}_{m'm}U^{(1)}_{n'n} + U^{(1)}_{m'n}U^{(1)}_{n'm} \right). \quad (2.26)$$

The indices refer to the site basis, and the prefactors ensure correct normalization of overtones. This expression can be found by a direct expansion of the matrix exponential and the evaluation of each term (See Appendix 2A), or by diagonalizing the one-quantum Hamiltonian. Its advantage is the avoidance of the direct calculation of matrix exponentials of the two-quantum Hamiltonian, which leads to considerably faster simulations.

2.5 Molecular aggregates

A second system, which we will discuss in Chapter 7 is the molecular aggregate at low temperature. The model for a linear aggregate is illustrated in Figure 2.4.

Much of the formalism described before is applicable to molecular aggregates. However, instead of vibrations, the excitations are now Frenkel excitons. Multiple excitation of the same mode on a single molecule is forbidden by the Pauli exclusion principle. Therefore, each molecule can be described as a two-level system. Electrodynamic interactions between the molecules are generally modeled with the transition dipole coupling model. At low temperature, the energy gaps of the two-level systems in a glassy surrounding material feel the effect of an environment which is static on the timescale of the experiment [Fidder et al. 1991a]. The Frenkel exciton model combined with this static disorder has been successful in explaining the linear absorption [Bednarz et al. 2003; Heijs et al. 2005b], fluorescence [Bednarz et al. 2003; Malyshev et al. 2007] and pump-probe spectra [Fidder et al. 1993] of molecular
Figure 2.4: Illustration of the model of a linear molecular aggregate in a glassy surrounding material at low temperature. Each chromophore molecule has a different environment, which leads to variations in the energy gap between its ground and excited states.

Aggregates at low temperatures. The Hamiltonian including static disorder has the same form as in Eq. 2.18, which we rewrite as

\[
H = \sum_n (\epsilon + \xi_{nn}) c_n^+ c_n + \sum_{n \neq m} (J_{nm} + \xi_{nm}) c_n^+ c_m. \tag{2.27}
\]

The \(c\) and \(c^+\) operators act on a two-level system, which implies the commutation relations \([c_m, c_n^+] = \delta_{nm} (1 - 2c_n^+ c_n)\). As before, \(n\) and \(m\) label the molecules, \(\epsilon\) is the average energy gap and \(J\) are the bilinear interactions. The \(\xi\) variables model the static shifts in frequencies and couplings (although the latter are often not included in the model) arising from the interaction with the environment.

The one-quantum matrix elements of the Hamiltonian are the same as in the case of vibrational oscillators, given in Eq. 2.19. Because double excitation of a monomer is forbidden, anharmonicity does not play a role. However, an effective anharmonicity arises from the Pauli exclusion principle (This can, in fact, be understood by taking the limit of the anharmonicity to minus infinity in Eq. 2.4.). The basis for the two-quantum states contains \(N(N - 1)/2\) states, which gives the number of possible ways two quanta can be spread over the \(N\) oscillators. In the example of a trimer, with a two-quantum basis chosen as \(|12\rangle, |13\rangle, |23\rangle\) (where \(|nm\rangle = c_n^+ c_m^+ |0\rangle\)), the two-quantum Hamiltonian matrix is

\[
\begin{pmatrix}
2\epsilon + \xi_{11} + \xi_{22} & J_{23} + \xi_{23} & J_{13} + \xi_{13} \\
J_{23} + \xi_{23} & 2\epsilon + \xi_{11} + \xi_{33} & J_{12} + \xi_{12} \\
J_{13} + \xi_{13} & J_{12} + \xi_{12} & 2\epsilon + \xi_{22} + \xi_{33}
\end{pmatrix}.
\tag{2.28}
\]

Diagonalization of the one- and two-quantum Hamiltonians produces the eigenstates in each realization of the static disorder. In calculations, observables are found after an average over realizations.
Appendix 2A Harmonic two-exciton propagator

Given the quadratic Hamiltonian with bosonic operators \( b \) and \( b^\dagger \),

\[
\hat{H} = \sum_{nm} H_{nm} b_n^\dagger b_m,
\]

the propagator for one-exciton states is

\[
U_{pp'}^{(1)} = \langle p | \exp(-i\hat{H}t)|p' \rangle = \langle \exp(-iHt) \rangle_{pp'}.
\]

\( H \) is the one-quantum matrix of the operator \( \hat{H} \), it has matrix elements \( H_{nm} \). The indices \( n \) and \( m \), as well as \( p \) and \( q \), label the individual oscillators.

We want to calculate the two-exciton matrix element

\[
U_{pp'qq'}^{(2)}(t) = \langle pq | \exp(-i\hat{H}t)|p'q' \rangle,
\]

where \( |pq\rangle = 1/\sqrt{1+\delta_{pq} b^\dagger_p b^\dagger_q} |0\rangle \) is a two-exciton state. The result is

\[
U_{pp'qq'}^{(2)}(t) = \frac{1}{\sqrt{1+\delta_{pq}}} \frac{1}{\sqrt{1+\delta_{p'q'}}} \left( U_{pp'}^{(1)}(t) U_{qq'}^{(1)}(t) + U_{pq}^{(1)}(t) U_{qp}^{(1)}(t) \right).
\]

The two-exciton propagator in a harmonic system is, thus, given simply as the product of one-exciton propagators. The prefactors in Eq. 2A.4 arise from the correct normalization of the overtone states. In the following, we will derive Eq. 2A.4.

To find the two-exciton propagator, we expand the exponent in Eq. 2A.3 in a Taylor series, the \( \alpha \)th term in the series is

\[
\frac{(-it)^\alpha}{\alpha!} \langle pq | \left( \sum_{nm} H_{nm} b_n^\dagger b_m \right)^\alpha |p'q' \rangle = \frac{(-it)^\alpha}{\alpha!} \langle \prod_{i=1}^\alpha H_{n_i,m_i} \rangle \langle pq | \prod_{i=1}^\alpha b_n^\dagger b_m |p'q' \rangle,
\]

where summation over the indices \( n_i \) and \( m_i \) is implied for all \( i \). We then define

\[
S^{(\alpha)}_{n_am_2...n_1m_1} = \langle pq | \prod_{i=1}^\alpha b_n^\dagger_i b_m_i |p'q' \rangle,
\]

and use the bosonic commutation relations to find the recursion relations

\[
S^{(\alpha)}_{n_am_a...n_3m_3n_2m_2n_1m_1} = S^{(\alpha-1)}_{n_am_a...n_3m_3n_2m_1} \delta_{n_2n_1} + h^{(\alpha)}_{n_am_a...n_3m_3n_2n_1m_2m_1},
\]

where

\[
h^{(\alpha)}_{n_am_a...n_3m_3n_2n_1m_2m_1} := \langle pq | b^\dagger_{n_a} b_{m_a} \ldots b^\dagger_{n_3} b_{m_3} b^\dagger_{n_2} b_{m_2} b_{m_1} |p'q' \rangle
\]

\[
= h^{(\alpha-1)}_{n_am_a...n_3m_2m_1} \delta_{m_3n_2} + h^{(\alpha-1)}_{n_am_a...n_3m_2m_2} \delta_{m_3n_1}.
\]
The zeroth order contribution \((\alpha = 0)\) to the exponent is
\[
\frac{1}{\sqrt{1 + \delta_{pq}}} \frac{1}{\sqrt{1 + \delta_{p'q}'}} \left( \delta_{pp'} \delta_{qq'} + \delta_{pq} \delta_{qp'} \right).
\] (2A.9)

The recursion relations for \(g\) and \(h\) terminate for \(\alpha\) equal to 1 or 2, and the initial values are
\[
\delta_{nm}^{(1)} = \frac{1}{\sqrt{1 + \delta_{pq}}} \frac{1}{\sqrt{1 + \delta_{p'q}'}} \left( \delta_{pp} \delta_{qq} + \delta_{pq} \delta_{qp} \right),
\]
\[+ \delta_{qq'} \delta_{nm} \delta_{p'm} + \delta_{pq} \delta_{mq} \delta_{p'n} + \delta_{p'q} \delta_{nm} \delta_{pq} \right), \] (2A.10)

\[
h_{n_2n_1,m_2m_1}^{(2)} = \delta_{n_2n_1,m_2m_1}^{(2)} = \delta_{n_2n_1,m_2m_1}^{(2)} = \frac{1}{\sqrt{1 + \delta_{pq}}} \frac{1}{\sqrt{1 + \delta_{p'q}'}} \left( \delta_{p_1n_2} \delta_{q_1m_2} + \delta_{p_2n_1} \delta_{q_2m_1} \right) \left( \delta_{p'_1m_2} \delta_{q'_2m_1} + \delta_{p'_2m_2} \delta_{q'_1m_1} \right). \] (2A.11)

After application of the recursion relations and putting together all the terms from Eq. 2A.5, we find
\[
U_{pp'qq'}^{(2)} = \sum_{\alpha=0}^{\infty} \frac{(-it)^{\alpha}}{\alpha!} (H^{\alpha})_{nm} \delta_{nm}^{(1)} - \frac{1}{2} \delta_{nm} \delta_{nm}^{(1)} + \frac{1}{\sqrt{1 + \delta_{pq}}} \frac{1}{\sqrt{1 + \delta_{p'q}'}} \left( U_{pp'}^{(1)}(t) U_{qq'}^{(1)}(t) + U_{pq}^{(1)}(t) U_{qp'}^{(1)}(t) \right), \] (2A.12)

which proves Eq. 2A.4.