

## 2. Dissipative quantum dynamics

Complex biological systems, like the photosynthetic units of bacteria or plants, usually consist of several pigment molecules, which form aggregates, embedded in a protein environment. Within a quantum mechanical treatment it is practically impossible to take all degrees of freedom (DOFs) of such large systems explicitly into account. Note that there exist highly efficient methods, e.g., the multiconfiguration time-dependent Hartree method (MCTDH) [38], to treat the quantum dynamics of isolated systems, e.g., the intra-molecular dynamics of the aforementioned pigment molecules. The recently developed multilayer expansion of MCTDH [39, 40] facilitates the treatment of systems with a few thousand DOFs, which is sufficient to handle small systems within an environment. This approach requires a discretization of the spectral density, cf. Sec. 2.3, and is therefore restricted in its applicability. An application of the MCTDH approach to the dissipative quantum dynamics of a light-harvesting system is given in Ref. [41]. However, it is preferable to reduce the dimensionality of the problem considering only few relevant DOFs, which provide insights into the physical processes, explicitly and to treat all other DOFs as a heat bath interacting with the system DOFs via an energy exchange. According to this separation the Hamiltonian of the full system is given by

$$H = H_s + H_b + H_{s-b}, \quad (2.1)$$

where  $H_{s/b}$  denotes the system/bath Hamiltonian and  $H_{s-b}$  the interaction between the system and the bath. The separation allows one to solve the quantum mechanical equations of motion for the relevant system DOFs considering the influence of the bath DOFs exactly or approximately.

In the following section the Hamiltonian describing aggregates of pigment molecules embedded in a protein environment will be discussed. Further, two different sets of equations of motion for the reduced density matrix, namely the QME and the in principle exact HEOM will be introduced in Sec. 2.2. Both incorporate the influence of the bath via a spectral density function. The latter and its connection to the Hamiltonian, as well as some models for the spectral density, will be discussed in Sec. 2.3. Finally, the optical response function formalism, which connects the time evolution of the density matrix to the optical spectra of the system, will be briefly introduced in Sec. 2.4.

## 2.1. Hamiltonian

The system Hamiltonian,  $H_s$ , of an aggregate consisting of  $N_{\text{agg}}$  monomers is given by the Frenkel exciton Hamiltonian. It is based on the assumption that the interacting monomers, which form the aggregate, retain their chemical identity. According to this assumption the monomeric adiabatic states  $|m_a\rangle$  can be used to construct diabatic aggregate states, which are coupled due to the inter-monomeric Coulomb coupling (CC). Here,  $a = g, e, \dots$  labels the adiabatic monomeric electronic state and  $m = 1, \dots, N_{\text{agg}}$  denotes the monomer. The aggregate states can be classified according to the number of electronic excitations within the aggregate. Considering only one excited state,  $a = e$ , per monomer, the aggregate ground state  $|g\rangle$  and the one-exciton states  $|e_m\rangle$  are given by

$$|g\rangle = \prod_m |m_g\rangle \quad (2.2)$$

and

$$|e_m\rangle = |m_e\rangle \prod_{n \neq m} |n_g\rangle. \quad (2.3)$$

Higher-order excitations, such as the excitation of higher monomeric adiabatic states, e.g., the  $S_n$  states of pigment molecules, or multiple

excitations within the aggregate, can be incorporated analogously into the description. Including only the ground and one-exciton states, the Frenkel Hamiltonian is given by

$$\begin{aligned}
 H_{\text{agg}} &= H(g)|g\rangle\langle g| + \sum_m H_m(e_m)|e_m\rangle\langle e_m| \\
 &\quad + \sum_{m,n} J_{mn}(e_m, e_n)|e_m\rangle\langle e_n| + H_{\text{int}} \\
 &= H_s^{(0)} + H_s^{(1)} + H_{\text{int}}
 \end{aligned} \tag{2.4}$$

with the zero- and one-exciton parts

$$H_s^{(0)} = H(g)|g\rangle\langle g| \tag{2.5}$$

and

$$H_s^{(1)} = \sum_m H_m(e_m)|e_m\rangle\langle e_m| + \sum_{m,n} J_{mn}(e_m, e_n)|e_m\rangle\langle e_n|, \tag{2.6}$$

respectively. The coupling elements  $J_{mn}(e_m, e_n)$  represent the interaction between different one-exciton states and  $H_{\text{int}}$  describes, e.g., the interaction of the system with external fields.

The diagonal terms of the aggregate Hamiltonian are, according to the definition of the exciton states, Eq. (2.2) and Eq. (2.3), given by

$$H(g) = \sum_m H(m_g) \tag{2.7}$$

and

$$H_m(e_m) = H(m_e) + \sum_{n \neq m} H(n_g). \tag{2.8}$$

Here,  $H(m_g)$  and  $H(m_e)$  denote the Hamiltonian of the adiabatic monomeric ground and excited state of monomer  $m$ , respectively. The diabatic aggregate states depend on the set  $\{R\} = (R_1, \dots, R_{N_{\text{agg}}})$  of all intra-molecular nuclear coordinates, i.e.  $|g\rangle = |g(\{R\})\rangle$  and  $|e_m\rangle = |e_m(\{R\})\rangle$ . This is due to the parametric dependence of the

monomeric adiabatic states on the monomeric set of intra-molecular nuclear coordinates  $R_m = (\vec{R}_{m,1}, \vec{R}_{m,2}, \dots)$ , i.e.  $|m_g\rangle = |m_g(R_m)\rangle$  and  $|m_e\rangle = |m_e(R_m)\rangle$ . Note that the intra-molecular vibrations are separated from the inter-molecular vibrations. The latter, as well as the vibrations of the protein environment and their influence on the system, can be conveniently described by the bath and the system-bath Hamiltonian. The dependence of the diabatic aggregate states on the intra-molecular nuclear DOFs can be treated implicitly by including the intra-molecular vibrations into the heat bath as well, or explicitly, e.g., by the shifted oscillator model [31]. In the former case the on-diagonal terms  $H(g)$  and  $H_m(e_m)$  are given by the bare electronic state energies  $E_g$  and  $E_{e_m}$ , respectively. However, in the latter case the electronic state energies need to be supplemented by a contribution representing the change of the potential energy with respect to  $\{R\}$  and the corresponding kinetic energy contribution. The corresponding on-site elements of the system Hamiltonian are given by

$$H(g, \{R\}) = E_g + U_g(\{R\}) + T_g(\{R\}) \quad (2.9)$$

and

$$H_m(e_m, \{R\}) = E_{e_m} + U_{e_m}(\{R\}) + T_{e_m}(\{R\}). \quad (2.10)$$

A second order Taylor expansion of the potential energy  $U(\{R\})$  around its minimum with respect to  $\{R\}$  in combination with a normal mode transformation yields the frequently used harmonic oscillator model, i.e.

$$H(g, \{q\}) = E_g + \frac{1}{2} \sum_m \sum_{\xi} \left( p_{\xi,m}^{(g)2} + \omega_{\xi,m}^{(g)2} q_{\xi,m}^{(g)2} \right) \quad (2.11)$$

and

$$\begin{aligned} H_m(e_m, \{q\}) = & E_{e_m} + \frac{1}{2} \sum_{n \neq m} \sum_{\xi} \left( p_{\xi,n}^{(g)2} + \omega_{\xi,n}^{(g)2} q_{\xi,n}^{(g)2} \right) \\ & + \frac{1}{2} \sum_{\xi} \left( p_{\xi,m}^{(e)2} + \omega_{\xi,m}^{(e)2} q_{\xi,m}^{(e)2} \right). \end{aligned} \quad (2.12)$$

Here,  $p_{\xi,m}^{(a)}$  denotes the momentum and  $\omega_{\xi,m}^{(a)}$  the harmonic frequency associated with the  $\xi$ th mode of monomer  $m$ , being in the electronic state  $a$ , in normal mode space  $\{q\}$ . Note that the normal coordinates are mass-weighted and that  $\hbar = 1$  here and in the following. It is convenient to define the normal modes in the corresponding monomeric ground states  $|m_g\rangle$  and project all vibrational properties of the aggregate states  $|g\rangle$  and  $|e_m\rangle$  onto this basis. Assuming additionally that there are no changes in the curvature of the oscillator potentials yields the shifted oscillator model. In the limit of the aforementioned approximations the on-site Hamiltonian is given by

$$H(g, \{q\}) = E_g + \frac{1}{2} \sum_m \sum_{\xi} \left( p_{\xi,m}^2 + \omega_{\xi,m}^2 q_{\xi,m}^2 \right) \quad (2.13)$$

for the ground state and by

$$\begin{aligned} H_m(e_m, \{q\}) = & E_{e_m} + \frac{1}{2} \sum_{\xi} \left( p_{\xi,n}^2 + \omega_{\xi,n}^2 q_{\xi,n}^2 \right) \\ & + \frac{1}{2} \sum_{\xi} \sum_{n \neq m} \left( p_{\xi,m}^2 + \omega_{\xi,m}^2 (q_{\xi,m} - d_{\xi,m})^2 \right) \end{aligned} \quad (2.14)$$

for the excited states, respectively. Here,  $d_{\xi,m}$  represents the shift of the excited state oscillator along  $q_{\xi,m}$  with respect to the ground state potential energy surface. Introducing intrinsic harmonic oscillator variables, i.e.

$$\tilde{p}_{\xi,m} = \sqrt{\frac{1}{\omega_{\xi,m}}} p_{\xi,m} \quad (2.15)$$

and

$$\tilde{q}_{\xi,m} = \sqrt{\omega_{\xi,m}} q_{\xi,m}, \quad (2.16)$$

yields

$$H(g, \{\tilde{q}\}) = E_g + \sum_m \sum_{\xi} \frac{\omega_{\xi,m}}{2} \left( \tilde{p}_{\xi,m}^2 + \tilde{q}_{\xi,m}^2 \right) \quad (2.17)$$

and

$$\begin{aligned}
 H_m(e_m, \{\tilde{q}\}) = & E_{e_m} + \sum_{n \neq m} \sum_{\xi} \frac{\omega_{\xi,n}}{2} \left( \tilde{p}_{\xi,n}^2 + \tilde{q}_{\xi,n}^2 \right) \\
 & + \sum_{\xi} \frac{\omega_{\xi,m}}{2} \left( \tilde{p}_{\xi,m}^2 + (\tilde{q}_{\xi,m} - \tilde{d}_{\xi,m})^2 \right). \quad (2.18)
 \end{aligned}$$

The dimensionless shift  $\tilde{d}_{\xi,m}$  can be expressed by the Huang-Rhys factor  $S_{\xi,m} \equiv \tilde{d}_{\xi,m}^2/2$ , which is often used to characterize the coupling between electronic and vibrational DOFs. Expanding Eq. (2.18) using the definition of  $S_{\xi,m}$  yields

$$\begin{aligned}
 H_m(e_m, \{\tilde{q}\}) = & E_{e_m} + \sum_{\xi} \sum_n \frac{\omega_{\xi,n}}{2} \left( \tilde{p}_{\xi,n}^2 + \tilde{q}_{\xi,n}^2 \right) \\
 & - \sum_{\xi} \omega_{\xi,m} \sqrt{2S_{\xi,m}} \tilde{q}_{\xi,m} + \sum_{\xi} \omega_{\xi,m} S_{\xi,m}. \quad (2.19)
 \end{aligned}$$

Note that the last sum represents the reorganization energy associated with the relaxation within the excited state after a vertical transition from the ground to the excited state and is thus related to the Stokes shift in linear spectroscopy.

The interaction between configurations of the aggregate, where the excitation is located on different sites of the aggregate, i.e. between different one-exciton states, is in general (in terms of the monomeric adiabatic states) given by the Coulomb integral

$$J_{mn}(m_a n_b, n_c m_d) = \int d\vec{r} d\vec{r}' \frac{\mathfrak{N}_{m_a, m_d}(\vec{r}) \mathfrak{N}_{n_b, n_c}(\vec{r}')}{|\vec{r} - \vec{r}'|}. \quad (2.20)$$

Here,  $\vec{r}$  denotes an electronic coordinate and  $\mathfrak{N}$  stands for the generalised molecular charge density [31] depending on the adiabatic monomeric states. Note that within the present model only elements, which describe a simultaneous excitation of one and de-excitation of another monomer, are considered. Thus, the inter-monomeric interac-

tions between two sites  $m$  and  $n$  in Eq. (2.4) are represented by the coupling elements  $J_{mn}(e_m, e_n)$ , which are given by

$$J_{mn}(e_m, e_n) = \int d\vec{r} d\vec{r}' \frac{\tilde{\mathfrak{N}}_{e_m}(\vec{r}) \tilde{\mathfrak{N}}_{e_n}(\vec{r}')}{|\vec{r} - \vec{r}'|}, \quad (2.21)$$

where  $\tilde{\mathfrak{N}}$  denotes the generalized charge density associated with the corresponding one-exciton state.

The Coulomb integral, Eq. (2.21), can be evaluated, e.g., by employing a transition dipole approximation, assuming that the separation of the monomers is large compared to the spatial extension of the transition density [31]. However, more elaborate methods, such as the transition density cube [5], the transition charge from electrostatic potential method [42], or time-dependent tight-binding-based density functional theory [43], facilitate the calculation of more accurate Coulomb coupling matrix elements.

The diabatic one-exciton aggregate Hamiltonian, Eq. (2.6), can be transformed to an adiabatic representation via diagonalization of its potential energy part. This leads to a set of adiabatic (delocalized) states  $|\alpha\rangle$  which are connected to the diabatic states via the components  $c_{\alpha,m}$  of the eigenvectors of the diabatic Hamiltonian, i.e.

$$|\alpha\rangle = \sum_m c_{\alpha,m} |e_m\rangle. \quad (2.22)$$

For example, for an electronic dimer system the energy of the adiabatic excited states is given by [31]

$$E_{1,2} = \frac{E_{e_1} + E_{e_2}}{2} \mp \frac{1}{2} \sqrt{(E_{e_1} - E_{e_2})^2 + 4J_{12}^2}. \quad (2.23)$$

Note that the adiabatic levels are numbered according to their energy in increasing order, i.e. the level with the lowest energy is labelled with 1, the second lowest with 2 and so forth. The aggregate ground state  $|g\rangle$  is the same in both representations as there exists no coupling to the one-exciton states.

The last term in Eq. (2.4) describes interactions with external fields. In dipole approximation  $H_{\text{int}}$  is given by

$$H_{\text{int}} = -d\mathfrak{E}(t), \quad (2.24)$$

for the interaction with an external laser field assuming that the field  $\vec{\mathfrak{E}}(t)$  and the transition dipole moment  $\vec{d}$  exhibit a constant orientation with respect to each other, i.e.

$$\vec{d} \cdot \vec{\mathfrak{E}}(t) = c \cdot |d| |\mathfrak{E}(t)|. \quad (2.25)$$

Here,  $c$  denotes an orientation factor, which is assumed to be included in the definition of  $d$  in Eq. (2.24). The aggregate dipole operator with the site-dependent dipole transition strength  $d_{e_m, g}$  is given by

$$d = \sum_m d_{e_m, g} |e_m\rangle \langle g| + \text{h.c.} \quad (2.26)$$

Under certain conditions all kinds of environments, even those that contain anharmonic effects, can be described by an effective harmonic bath [32]. However, the specific form of the bath as well as of the system-bath Hamiltonian depends on the underlying model. First, consider the case that only the DOFs of the environment contribute to the bath. This is the case if the intra-molecular nuclear DOFs can be neglected, e.g., if their coupling to the electronic DOFs is negligible or if they are included in the system explicitly. The Hamiltonian of the environmental DOFs,  $H_{\text{b}}^{(\text{I})}$ , is given by

$$H_{\text{b}}^{(\text{I})} = \sum_i \frac{\omega_i}{2} (\tilde{p}_i^2 + \tilde{x}_i^2). \quad (2.27)$$

Here,  $\omega_i$  denotes the harmonic frequency and  $\tilde{x}_i$  the corresponding bath coordinate. If the intra-molecular vibrations contribute to the bath, it is convenient to separate the bath Hamiltonian into an intra-molecular and an environmental part, i.e.

$$H_{\text{b}}^{(\text{II})} = H_{\text{b}}^{(\text{int})} + H_{\text{b}}^{(\text{env})}. \quad (2.28)$$



The intra-molecular part,  $H_b^{(\text{int})}$ , is given by, cf. Eq. (2.19),

$$H_b^{(\text{int})} = \sum_m \sum_\xi \frac{\omega_{\xi,m}}{2} \left( \tilde{p}_{\xi,m}^2 + \tilde{q}_{\xi,m}^2 \right) \quad (2.29)$$

and the environmental part by Eq. (2.27). Thus, the full bath Hamiltonian reads

$$H_b^{(\text{II})} = \sum_m \sum_\xi \frac{\omega_{\xi,m}}{2} \left( \tilde{p}_{\xi,m}^2 + \tilde{q}_{\xi,m}^2 \right) + \sum_i \frac{\omega_i}{2} \left( \tilde{p}_i^2 + \tilde{x}_i^2 \right). \quad (2.30)$$

The system-bath interaction Hamiltonian,  $H_{\text{s-b}}$ , depends in general on the system and bath operators. However, it can be decomposed into a product of arbitrary functions of system and bath operators, i.e.

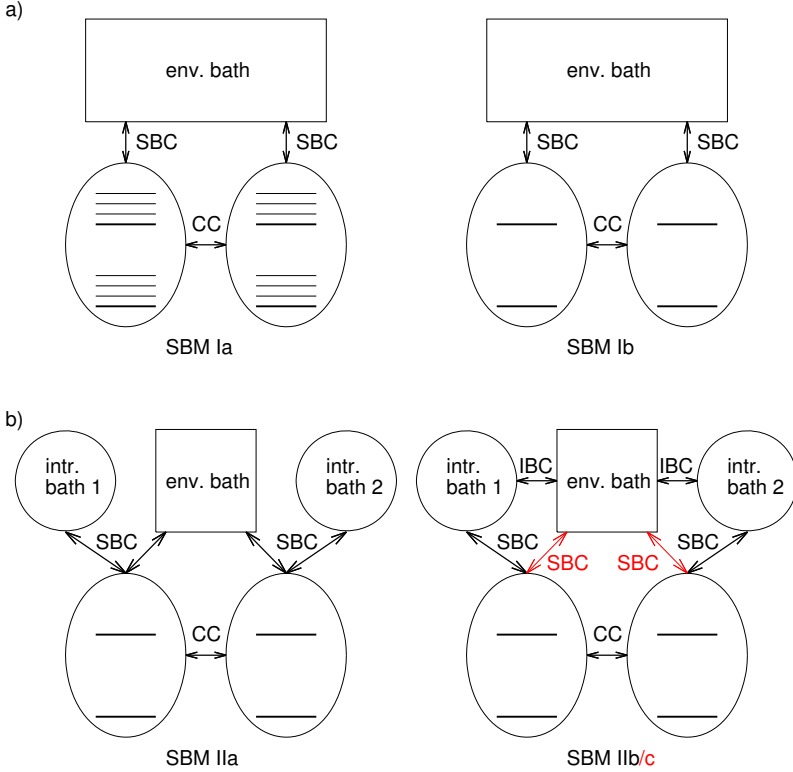
$$H_{\text{s-b}} = \Phi_b(X) K_s(Q), \quad (2.31)$$

with no loss of generality. A linear Taylor expansion of the bath function  $\Phi_b(X)$  and of the system function  $K_s(Q)$  yields the widely used Caldeira-Leggett model [44] for the system-bath Hamiltonian

$$H_{\text{s-b}} = \sum_j \sum_\zeta c_{j,\zeta} X_j Q_\zeta. \quad (2.32)$$

Here,  $X_j$  denotes an harmonic oscillator position operator and  $Q_\zeta$  an operator representing a part of the system. Note that the linear expansion with respect to the system operators restricts the description to energy gap fluctuations in the system. An expansion of  $K_s(Q)$  up to higher orders of  $Q$  would take additional effects into account, e.g., a modulation of the curvature of the potential energy surface [45].

The general form of the Caldeira-Leggett system-bath Hamiltonian, Eq. (2.32), needs to be adjusted according to the bath and system-bath models (SBMs). Note that the same bath configuration leads in combination with different SBMs to a different dynamics of the system.



**Figure 2.1.:** Schematic view of the system-bath models (SBM) for a dimer system. **(a)** In SBM Ia/b the DOFs of the two monomers are coupled to the environmental DOFs by the system-bath coupling (SBC) and to each other via the Coulomb coupling (CC). SBM Ia and b differ in the description of the system. In the former the intra-molecular vibrations are included in the system, whereas they are neglected in the latter. **(b)** The intra-molecular vibrations are treated as separated bath. In contrast to SBM IIa, where the environmental bath is not coupled to the intra-molecular one, there exists an inter-bath coupling (IBC) in SBM IIb/c.

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