

## 3.3 Frenkel Excitons

### 3.3.1 Exciton Hamiltonian

the basic form of the dye aggregate or chromophore complex (CC) Hamiltonian is

$$H_{CC} = \sum_m H_m + \frac{1}{2} \sum_{m,n} V_{mn}$$

the spatial position of the chromophores are counted by  $m$  as well as  $n$ , and  $H_m$  denotes the electron–vibrational Hamiltonian of an individual chromophore:

$$H_m = \sum_a H_{ma} |\varphi_{ma}\rangle \langle \varphi_{ma}|$$

the part  $V_{mn}$  of  $H_{CC}$  is the mutual Coulomb interaction between chromophore at site  $m$  and at site  $n$ ; it covers the interaction among electrons and nuclei:

$$V_{mn} = V_{mn}^{(\text{el-el})} + V_{mn}^{(\text{el-nuc})} + V_{mn}^{(\text{nuc-el})} + V_{mn}^{(\text{nuc-nuc})}$$

for the following it suffices to restrict the considerations to singly excited states; every chromophore is described by the electronic ground–state  $\varphi_{mg}$  and the excited electronic state  $\varphi_{me}$ ; the distance between the chromophores should be large enough to neglect electron exchange  
the CC ground state reads

$$|\phi_0\rangle = \prod_m |\varphi_{mg}\rangle$$

all possible singly excited states can be written as

$$|\phi_m\rangle = |\varphi_{me}\rangle \prod_{n \neq m} |\varphi_{ng}\rangle$$

this expansion assumes the general orthogonality relation

$$\langle \varphi_{ma} | \varphi_{nb} \rangle = \delta_{m,n} \delta_{a,b}$$

to reduce  $H_{CC}$  to the ground–state and the singly excited states we introduce respective projection operators

we obtain for the CC ground–state

$$\hat{\Pi}_0 = |\phi_0\rangle \langle \phi_0|$$

and for the singly excited states

$$\hat{\Pi}_1 = \sum_m |\phi_m\rangle \langle \phi_m|$$

both projectors can be used to introduce the following expansion

$$H_{CC} \approx \hat{\Pi}_0 H_{CC} \hat{\Pi}_0 + \hat{\Pi}_1 H_{CC} \hat{\Pi}_1 = H_0 + H_1 \equiv \mathcal{H}_0 \hat{\Pi}_0 + \mathcal{H}_1 \hat{\Pi}_1$$

we may derive

$$\langle \phi_0 | H_{CC} | \phi_0 \rangle \equiv \mathcal{H}_0 = \prod_k \langle \varphi_{kg} | \left( \sum_m H_m + \frac{1}{2} \sum_{m,n} V_{mn} \right) \prod_l |\varphi_{lg}\rangle = \sum_m H_{mg}$$

in the same way we get

$$\langle \phi_m | H_{CC} | \phi_n \rangle = \delta_{m,n} (H_{me} - H_{mg} + \mathcal{H}_0) + (1 - \delta_{m,n}) J_{mn}$$

the *excitation energy transfer coupling* has been already calculated; it takes the form

$$J_{mn} = \langle \varphi_{me} \varphi_{ng} | V_{mn} | \varphi_{ne} \varphi_{mg} \rangle \equiv \langle \varphi_{me} \varphi_{ng} | V_{mn}^{(el-el)} | \varphi_{ne} \varphi_{mg} \rangle$$

the Hamiltonian of the singly excited complex state results as

$$H_1 = \sum_m (H_{me} - H_{mg} + \mathcal{H}_0) |\phi_m\rangle \langle \phi_m| + \sum_{m,n} J_{mn} |\phi_m\rangle \langle \phi_n|$$

a detailed inspection shows that the given structure assumes a totally balanced charge distribution of electrons and nuclei (in the electronic ground as well as in the first excited state)

### Coupling to Vibrational Modes

in most cases we have to distinguish between intra-molecular and inter-molecular vibrations; for simplicity it is assumed in the following that a common set of normal mode vibrations couples to every molecule;  $R_0$  denotes the reference nuclear equilibrium configuration for which the normal mode vibrations are defined the normal mode expansion of the ground-state Hamiltonian takes the form:

$$\begin{aligned} \mathcal{H}_0 &= T_{\text{nuc}} + \sum_m U_{mg}(R) \approx T_{\text{nuc}} + \sum_m \left( U_{mg}(R_0) + \frac{1}{2} \sum_{\mu,\nu} k_{\mu\nu}^{(mg)} \Delta R_\mu \Delta R_\nu \right) \\ &= \sum_m U_{mg}^{(0)} + \sum_\xi \hbar \omega_\xi (c_\xi^+ c_\xi + 1/2) \equiv H_{\text{vib}} \end{aligned}$$

the deviations from the equilibrium nuclear configuration are denoted as  $\Delta R_\mu$ ; to get the contribution for the excited state we consider the difference  $H_{me} - H_{mg}$ ; we can restrict ourselves to the linear contribution with respect to the deviations  $\Delta R_\mu$ ; it results in:

$$\begin{aligned} H_{me} - H_{mg} &= U_{me}(R) - U_{mg}(R) \approx U_{me}^{(0)} + \sum_{\mu,\nu} k_\mu^{(me)} \Delta R_\mu - U_{mg}^{(0)} \\ &= E_m + \sum_\xi \hbar \omega_\xi g_\xi(m) (c_\xi + c_\xi^+) \end{aligned}$$

an expansion of the excitonic coupling follows as

$$J_{mn}(R) \approx J_{mn} + \sum_\xi \hbar \omega_\xi g_\xi(m, n) (c_\xi + c_\xi^+)$$

we denote the excited state Hamiltonian as

$$H_1 = H_{\text{ex}} + H_{\text{ex-vib}} + H_{\text{vib}} \hat{\Pi}_1$$

the first part corresponds to the electronic (excitonic) contributions

$$H_{\text{ex}} = \sum_{m,n} \left( \delta_{m,n} E_m + (1 - \delta_{m,n}) J_{mn} \right) |\phi_m\rangle \langle \phi_n|$$

the coupling to vibrational coordinates is described by

$$H_{\text{ex-vib}} = \sum_{m,n} \sum_{\xi} \hbar\omega_{\xi} \tilde{g}_{\xi}(m,n) (c_{\xi} + c_{\xi}^{\dagger}) |\phi_m\rangle \langle \phi_n|$$

with

$$\tilde{g}_{\xi}(m,n) = \delta_{m,n} g_{\xi}(m) + (1 - \delta_{m,n}) g_{\xi}(m,n)$$

### Change to an Exciton Representation

introduction of exciton states is achieved as

$$|\alpha\rangle = \sum_m C_{\alpha}(m) |\phi_m\rangle$$

the exciton Hamiltonian becomes diagonal

$$H_{\text{ex}} = \sum_{\alpha} \hbar\Omega_{\alpha} |\alpha\rangle \langle \alpha|$$

and the exciton vibrational coupling reads

$$H_{\text{ex-vib}} = \sum_{\alpha,\beta} \sum_{\xi} \hbar\omega_{\xi} \tilde{g}_{\xi}(\alpha,\beta) (c_{\xi} + c_{\xi}^{\dagger}) |\alpha\rangle \langle \beta|$$

the coupling constant follows as

$$\tilde{g}_{\xi}(\alpha,\beta) = \sum_{m,n} C_{\alpha}^*(m) \tilde{g}_{\xi}(m,n) C_{\beta}(n) = \sum_m C_{\alpha}^*(m) g_{\xi}(m) C_{\beta}(m) + \sum_{m \neq n} C_{\alpha}^*(m) g_{\xi}(m,n) C_{\beta}(n)$$

### Linear and Regular Chain of Dye Molecules

we consider a linear chain of  $N_{\text{mol}}$  identical molecules with

$$E_m \rightarrow E_0$$

$$J_{mn} = (\delta_{m,n+1} + \delta_{m,n-1}) J \quad (1 < m < N_{\text{mol}})$$

$$J_{1n} = \delta_{2,n} J \quad J_{N_{\text{mol}}n} = \delta_{N_{\text{mol}}-1,n} J$$

the exciton energies become

$$\hbar\Omega_{\alpha} = E_0 + 2J \cos \alpha \quad \alpha = \frac{\pi j}{N_{\text{mol}} + 1} \quad j = 1, \dots, N_{\text{mol}}$$

and the expansion coefficients read

$$C_{\alpha}(m) = \sqrt{\frac{2}{N_{\text{mol}} + 1}} \sin(\alpha m)$$

to estimate  $J$  we use the version based on the dipole–dipole coupling

$$J = \frac{d_1 d_2}{R^3}$$

if the transition dipole moments are given in Debye and the Distance in Ångstroem we arrive at

$$J = \frac{d_1[\text{D}] d_2[\text{D}]}{(R[\text{Å}])^3} 0.625 \text{ eV}$$

## 3.4 The Nonequilibrium Statistical Operator and the Density Matrix

### 3.4.1 The Density Operator

elementary quantum mechanics → a *complete description* of a system is only possible if a set of observables exists from which all physical quantities can be measured simultaneously

a set of commuting operators  $\{\hat{A}_\alpha\}$  has to exist, i.e., the following relation has to be fulfilled

$$[\hat{A}_\alpha, \hat{A}_{\alpha'}]_- = \hat{A}_\alpha \hat{A}_{\alpha'} - \hat{A}_{\alpha'} \hat{A}_\alpha = 0$$

if for the considered system the maximal number of such operators is known, a *complete* description can be accomplished

the system is described by a *pure state*

if the complete measurement of all  $\hat{A}_\alpha$  has not been carried out, for example, because the complete set of observables is principally unknown → the state of the quantum system has to be described as a *statistical mixture* of pure states  $|\Psi_\nu\rangle$

the probability for a single state to be in the mixture will be denoted by  $w_\nu$ ; the states  $|\Psi_\nu\rangle$  are assumed to be ortho-normalized, and therefore the  $w_\nu$  must satisfy the relation

$$\sum_\nu w_\nu = 1$$

the expectation value of an observable becomes

$$\langle \hat{O} \rangle = \sum_\nu w_\nu \langle \Psi_\nu | \hat{O} | \Psi_\nu \rangle$$

introduction of the *density operator* (the statistical operator)

$$\hat{W} = \sum_\nu w_\nu |\Psi_\nu\rangle \langle \Psi_\nu| = \hat{W}^+$$

simple notation of the expectation value of any observable using the *trace formula*

$$\langle \hat{O} \rangle = \text{tr}\{\hat{W}\hat{O}\}$$

the abbreviation “tr” is defined as the trace with respect to the matrix formed by all matrix elements which are determined in a complete orthonormal basis  $|a\rangle$

$$\text{tr}\{\bullet\} = \sum_a \langle a | \bullet | a \rangle$$

therefore we have

$$\text{tr}(\hat{W}\hat{O}) = \sum_{a,\nu} w_\nu \langle a | \Psi_\nu \rangle \langle \Psi_\nu | \hat{O} | a \rangle = \sum_{a,\nu} w_\nu \langle \Psi_\nu | \hat{O} | a \rangle \langle a | \Psi_\nu \rangle = \sum_\nu w_\nu \langle \Psi_\nu | \hat{O} | \Psi_\nu \rangle$$

taking two arbitrary operators  $\hat{O}$  and  $\hat{P}$  it is easy to proof

$$\text{tr}\{\hat{O}\hat{P}\} = \text{tr}\{\hat{P}\hat{O}\}$$

this property is called *cyclic invariance* of the operator arrangement  
note also

$$\text{tr}\{\hat{W}\} = 1$$

example: the canonical density operator for thermal equilibrium

$$\hat{W}_{\text{eq}} = \frac{1}{\mathcal{Z}} e^{-H/k_B T} = \frac{1}{\mathcal{Z}} \sum_{\alpha} e^{-E_{\alpha}/k_B T} |\alpha\rangle\langle\alpha|$$

$\mathcal{Z}$  is the partition function  $\text{tr}[\exp\{-H/k_B T\}]$  ensuring proper normalization of  $\hat{W}_{\text{eq}}$   
the second part is obtained using the eigenenergies  $E_{\alpha}$  and eigenstates  $|\alpha\rangle$  of the Hamiltonian  $H$

density operator of a pure state  $|\Psi\rangle$

$$\hat{W}_{\text{pure}} = |\Psi\rangle\langle\Psi| = \hat{P}_{\Psi}$$

expansion of the state vector  $|\Psi\rangle$  with respect to the complete orthogonal basis  $|\alpha\rangle$ :

$$|\Psi\rangle = \sum_{\alpha} c_{\alpha} |\alpha\rangle .$$

introducing this expansion into the expression for the pure state density operator one obtains

$$\hat{W}_{\text{pure}} = \sum_{\alpha, \bar{\alpha}} c_{\alpha} c_{\bar{\alpha}}^* |\alpha\rangle\langle\bar{\alpha}| \neq \sum_{\alpha} |c_{\alpha}|^2 |\alpha\rangle\langle\alpha| .$$

there exists a measure which tells us whether the state is a pure state or not: *degree of coherence*

$$C = \text{tr}\{\hat{W}^2\}$$

it takes the value 1 for pure states since the statistical operator in this case is a projector

$$C_{\text{pure}} = \text{tr}\{\hat{W}_{\text{pure}}^2\} = \text{tr}\{\hat{P}_{\Psi}^2\} = \text{tr}\{\hat{P}_{\Psi}\} = \text{tr}\{\hat{W}_{\text{pure}}\} = 1$$

where the projector property  $\hat{P}_{\Psi}^2 = \hat{P}_{\Psi}$  has been used  
for a mixed state it follows that

$$\begin{aligned} C_{\text{mixed}} &= \text{tr}\{\hat{W}^2\} = \sum_{\mu, \nu} w_{\mu} w_{\nu} \text{tr}\{\hat{P}_{\Psi_{\mu}} \hat{P}_{\Psi_{\nu}}\} = \sum_{\mu, \nu} \sum_{\alpha} w_{\mu} w_{\nu} \langle\alpha|\Psi_{\mu}\rangle\langle\Psi_{\mu}|\Psi_{\nu}\rangle\langle\Psi_{\nu}|\alpha\rangle \\ &= \sum_{\mu} \sum_{\alpha} w_{\mu}^2 \langle\Psi_{\mu}|\alpha\rangle\langle\alpha|\Psi_{\mu}\rangle = \sum_{\mu} w_{\mu}^2 < 1 \end{aligned}$$

the degree of coherence becomes less than one

### 3.4.2 The Density Matrix

we consider a complete orthogonal basis of states  $|a\rangle, |b\rangle, \dots$   
the density operator can be expanded as

$$\hat{W} = \sum_{a, b} \langle a|\hat{W}|b\rangle |a\rangle\langle b|$$

the expansion coefficients are called *density matrix* and denoted by

$$\rho_{ab} = \langle a | \hat{W} | b \rangle$$

the density matrix fulfills the relation

$$\rho_{ab} = \rho_{ba}^*$$

from which one simply deduces

$$\text{Re } \rho_{ab} = \text{Re } \rho_{ba} , \quad \text{Im } \rho_{ab} = -\text{Im } \rho_{ba}$$

the diagonal elements of the density matrix are real

$$\rho_{aa} = \text{Re } \rho_{aa} .$$

one may write

$$\rho_{aa} = \langle a | \hat{W} | a \rangle = \sum_{\nu} \langle a | w_{\nu} | \Psi_{\nu} \rangle \langle \Psi_{\nu} | a \rangle = \sum_{\nu} w_{\nu} |\langle a | \Psi_{\nu} \rangle|^2 \equiv \sum_{\nu} w_{\nu} |c_a(\nu)|^2$$

with the expansion coefficients  $c_a(\nu) = \langle a | \Psi_{\nu} \rangle$

it shows that  $\rho_{aa}$  gives us the probability for the state  $|a\rangle$  being contained in the statistical mixture described by  $\hat{W}$

taking the off-diagonal matrix elements of the density operator it follows

$$\rho_{ab} = \sum_{\nu} w_{\nu} c_a(\nu) c_b^*(\nu)$$

the density matrix  $\rho_{ab}$  describes an *incoherent* superposition of contributions from different pure states

depending on the basis set  $\{|a\rangle\}$  the different terms on the right-hand side can cancel each other or give a finite  $\rho_{ab}$

the off-diagonal density matrix are also called *coherences*

since the definition of the density matrix represents a quadratic form the Schwarz inequality is valid

$$\rho_{aa}\rho_{bb} \geq |\rho_{ab}|^2$$

the representation of the statistical operator via the density matrix introduced so far is frequently termed *state representation*

if eigenstates of some Hamiltonian are used it is also called *energy representation* using eigenstates of the coordinate operator

$$|s\rangle = \prod_j |s_j\rangle ,$$

with coordinate  $s_j$  for the  $j$ th degree of freedom of the system, consequently, the *coordinate representation* of the statistical operator reads

$$\rho(s, \bar{s}) = \langle s | \hat{W} | \bar{s} \rangle$$

### 3.4.3 Equation of Motion for the Density Operator

the probabilities  $w_\nu$  represent our reduced knowledge about the state of the system the state vectors  $|\Psi_\nu\rangle$  of the mixed state evolve in time according to the time–dependent Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} |\Psi_\nu\rangle = H |\Psi_\nu\rangle$$

although any individual state of the mixture changes in time there is no change whatsoever in the amount of our knowledge about the system

the probabilities  $w_\nu$  are constant ( $w_\nu \neq w_\nu(t)$ )

accordingly the time–dependent density operator has the following form

$$\hat{W}(t) = \sum_\nu w_\nu |\Psi_\nu(t)\rangle \langle \Psi_\nu(t)|$$

to derive an equation of motion we note

$$\hat{W}(t) = \sum_\nu w_\nu U(t, t_0) |\Psi_\nu(t_0)\rangle \langle \Psi_\nu(t_0)| U^\dagger(t, t_0) = U(t, t_0) \hat{W}(t_0) U^\dagger(t, t_0) .$$

taking the time derivative of this expression it follows

$$\frac{\partial}{\partial t} \hat{W}(t) = -\frac{i}{\hbar} (H \hat{W}(t) - \hat{W}(t) H) \equiv -\frac{i}{\hbar} [H, \hat{W}(t)]_-$$

this equation of motion for the density operator  $\hat{W}$  is called *Liouville–von Neumann* or *Quantum Liouville*; for its solution we have to establish an initial condition

$$\hat{W}(t_0) = \hat{W}_0$$

we give the Liouville–von Neumann equation in the state representation ( $\langle a|H|b\rangle = H_{ab}$ )

$$\frac{\partial}{\partial t} \rho_{ab} = -\frac{i}{\hbar} \sum_c (H_{ac} \rho_{cb} - H_{cb} \rho_{ac}) \equiv -i \frac{H_{aa} - H_{bb}}{\hbar} \rho_{ab} - \frac{i}{\hbar} \sum_{c \neq a} H_{ac} \rho_{cb} + \frac{i}{\hbar} \sum_{c \neq b} H_{cb} \rho_{ac}$$

the difference of the diagonal matrix elements of the Hamiltonian defines the transition frequencies  $\omega_{ab} = (H_{aa} - H_{bb})/\hbar$ , whereas the off–diagonal matrix elements describe the inter–state coupling

there exists an alternative notation of the Liouville–von Neumann equation using the concept of *superoperators*

$$\mathcal{L}\bullet = \frac{1}{\hbar} [H, \bullet]_- .$$

we see that the Liouville–von Neumann equation can be written as

$$\frac{\partial}{\partial t} \hat{W}(t) = -i \mathcal{L} \hat{W}(t) ,$$

with the solution

$$\hat{W}(t) = e^{-i \mathcal{L}(t-t_0)} \hat{W}(t_0)$$

the exponential function of the superoperator is defined via the respective power expansion

one can introduce the time–evolution superoperator as follows:

$$\mathcal{U}(t, t_0) = e^{-i \mathcal{L}(t-t_0)} .$$

it gives

$$\hat{W}(t) = \mathcal{U}(t, t_0) \hat{W}(t_0) = U(t, t_0) \hat{W}(t_0) U^\dagger(t, t_0) .$$

### 3.4.4 The Reduced Density Operator and the Reduced Density Matrix

to put the idea of the reduced density matrix into a rigorous frame the starting point will be

$$H = H_S + H_{S-R} + H_R$$

a complete basis in the state space of the reservoir is written as  $|\alpha\rangle$  then the *reduced density operator* follows as

$$\hat{\rho}(t) = \sum_{\alpha} \langle \alpha | \hat{W}(t) | \alpha \rangle = \text{tr}_R \{ \hat{W}(t) \}$$

next we take a basis  $|a\rangle$  in the state space of the system and define the *reduced density matrix*

$$\rho_{ab}(t) = \langle a | \hat{\rho}(t) | b \rangle$$

the following relation has to be fulfilled

$$\text{tr}_S \{ \hat{\rho}(t) \} \equiv \sum_a \rho_{aa}(t) = 1$$

it is easily confirmed if we note that

$$\text{tr} \{ \hat{W}(t) \} = 1$$

an equation of motion for the reduced density matrix is derived by starting from the respective operator equation for the reduced density operator from the Liouville–von Neumann equation we obtain

$$\begin{aligned} \frac{\partial}{\partial t} \hat{\rho}(t) &= \text{tr}_R \left\{ \frac{\partial}{\partial t} \hat{W}(t) \right\} = -\frac{i}{\hbar} \text{tr}_R \left\{ \left[ H_S + H_{S-R} + H_R, \hat{W}(t) \right]_- \right\} \\ &= -\frac{i}{\hbar} [H_S, \hat{\rho}(t)]_- - \frac{i}{\hbar} \text{tr}_R \left\{ \left[ H_{S-R} + H_R, \hat{W}(t) \right]_- \right\} \end{aligned}$$

the commutator notation for the reduced density operator is not possible for the contributions proportional to  $H_{S-R}$  and  $H_R$

to calculate the commutator with  $H_R$  we take into account the cyclic invariance of the trace; as a result the term proportional to  $H_R$  vanishes and the equation of motion for the reduced density operator follows as

$$\frac{\partial}{\partial t} \hat{\rho}(t) = -\frac{i}{\hbar} [H_S, \hat{\rho}(t)]_- - \frac{i}{\hbar} \text{tr}_R \{ [H_{S-R}, \hat{W}(t)]_- \}$$

we realize that this is not yet a closed equation for reduced density operator; because of the appearance of  $H_{S-R}$  in the commutator on the right–hand side it still contains the total density operator

#### Approximate Equations of Motion for the Reduced Density Operator and the Reduced Density Matrix

the effect of the environment can be accounted for by a superoperator  $\mathcal{D}$  acting on the reduced density operator

$$-\frac{i}{\hbar} \text{tr}_R \{ [H_{S-R}, \hat{W}(t)]_- \} = -\mathcal{D} \hat{\rho}(t) \equiv -\hat{A} \hat{\rho}(t) - \hat{\rho}(t) \hat{B} - \sum_j \hat{C}_j \hat{\rho}(t) \hat{D}_j$$



the last part of this formula indicates the most general action of the superoperator when represented by different ordinary operators (acting from the left as well as from the right);

we introduce the density matrix where the states  $|a\rangle$  are considered as eigenstates of  $H_S$  with energy  $\hbar\omega_a$ ; the equation of motion can be written as ( $\omega_{ab} = \omega_a - \omega_b$ )

$$\frac{\partial}{\partial t}\rho_{ab}(t) = -i\omega_{ab}\rho_{ab}(t) - \sum_{c,d} R_{ab,cd}\rho_{cd}(t)$$

the action of the superoperator  $\mathcal{D}$  is replaced by the so-called *Redfield tensor*  $R_{ab,cd}$ ; there exist several theories calculating  $R_{ab,cd}$ ; we will quote the most simple version

$$\sum_{c,d} R_{ab,cd}\rho_{cd} = \delta_{a,b} \sum_c (k_{a\rightarrow c}\rho_{aa} - k_{c\rightarrow a}\rho_{cc}) + (1 - \delta_{a,b}) \frac{1}{2} \sum_c (k_{a\rightarrow c} + k_{b\rightarrow c})\rho_{ab}$$

it is based on a decoupling of diagonal and off-diagonal density matrix elements ; the diagonal elements obey a rate equation with transition rates  $k_{a\rightarrow c}$  and  $k_{c\rightarrow a}$ ; the off-diagonal elements follow from an equation including transition frequencies as well as dephasing rates

$$\gamma_{ab} = \frac{1}{2} \sum_c (k_{a\rightarrow c} + k_{b\rightarrow c})$$

they are responsible for the exponential decay of the off-diagonal density matrix elements (the coherences) with increasing time;

the transition rates and, thus, the dephasing rates can be calculated based on a concrete expression for the system-reservoir coupling  $H_{S-R}$ ;

### 3.4.5 Density Matrix Equations for Excitons

we note the definition of the reduced density operator

$$\hat{\rho}(t) = \text{tr}_{\text{vib}}\{\hat{W}(t)\}$$

the exciton density matrix follows as

$$\rho_{\alpha\beta}(t) = \langle\alpha|\hat{\rho}(t)|\beta\rangle$$

the equations of motion take the form

$$\frac{\partial}{\partial t}\rho_{\alpha\beta}(t) = -i\Omega_{\alpha\beta}\rho_{\alpha\beta}(t) - \sum_{\gamma,\delta} R_{\alpha\beta,\gamma\delta}\rho_{\gamma\delta}$$

the approximation which decouples diagonal and off-diagonal density matrix elements reads here:

$$\sum_{\gamma,\delta} R_{\alpha\beta,\gamma\delta}\rho_{\gamma\delta} \approx \delta_{\alpha\beta} \sum_{\gamma} (k_{\alpha\rightarrow\gamma}\rho_{\alpha\alpha} - k_{\gamma\rightarrow\alpha}\rho_{\gamma\gamma}) + (1 - \delta_{\alpha\beta})\Gamma_{\alpha\beta}\rho_{\alpha\beta}$$

the dephasing rates are

$$\Gamma_{\alpha\beta} = \frac{1}{2} \sum_{\gamma} (k_{\alpha\rightarrow\gamma} + k_{\beta\rightarrow\gamma})$$

although a direct theory exist which leads to the density matrix equations as well as to the transition rates, the latter can also be directly deduced from the *Golden Rule* formula; it is based on the given form of the exciton vibrational coupling; next we present respective computations; the normal mode vibrational states are abbreviated as  $\chi_M$  for the initial state (note  $M = \{M_\xi\}$ ), and as  $\chi_N$  for the final state of the transition; related energies, for example, are

$$\omega_M = \sum_{\xi} M_{\xi} \omega_{\xi}$$

we introduce the thermal distribution  $f(\omega_M)$  for the initial vibrational state and obtain the total rate as

$$k_{\alpha \rightarrow \beta} = \frac{2\pi}{\hbar^2} \sum_{M,N} f(\omega_M) |\langle \alpha | \langle \chi_M | H_{\text{ex-vib}} | \chi_N \rangle | \beta \rangle|^2 \delta(\Omega_{\alpha} + \omega_M - \Omega_{\beta} - \omega_N)$$

standard manipulations give first

$$k_{\alpha \rightarrow \beta} = \frac{1}{\hbar^2} \int dt e^{i\Omega_{\alpha\beta}t} \sum_{M,N} f(\omega_M) \langle \alpha | \langle \chi_M | e^{i\omega_M t} H_{\text{ex-vib}} e^{-i\omega_N t} | \chi_N \rangle | \beta \rangle \langle \beta | \langle \chi_N | H_{\text{ex-vib}} | \chi_M \rangle | \alpha \rangle$$

this leads to

$$\begin{aligned} k_{\alpha \rightarrow \beta} &= \int dt e^{i\Omega_{\alpha\beta}t} \text{tr}_{\text{vib}} \{ \hat{R} e^{iH_{\text{vib}}t/\hbar} \sum_{\xi} \omega_{\xi} \tilde{g}_{\xi}(\alpha, \beta) (c_{\xi} + c_{\xi}^{\dagger}) e^{-iH_{\text{vib}}t/\hbar} \sum_{\zeta} \omega_{\zeta} \tilde{g}_{\zeta}(\beta, \alpha) (c_{\zeta} + c_{\zeta}^{\dagger}) \} \\ &= \sum_{\xi} \omega_{\xi}^2 |\tilde{g}_{\xi}(\alpha, \beta)|^2 \int dt e^{i\Omega_{\alpha\beta}t} \text{tr}_{\text{vib}} \{ \hat{R} (c_{\xi} c_{\xi}^{\dagger} e^{-i\omega_{\xi}t} + c_{\xi}^{\dagger} c_{\xi} e^{i\omega_{\xi}t}) \} \\ &= \sum_{\xi} \omega_{\xi}^2 |\tilde{g}_{\xi}(\alpha, \beta)|^2 \int dt e^{i\Omega_{\alpha\beta}t} ([1 + n(\omega_{\xi})] e^{-i\omega_{\xi}t} + n(\omega_{\xi}) e^{i\omega_{\xi}t}) \\ &= 2\pi \sum_{\xi} \omega_{\xi}^2 |\tilde{g}_{\xi}(\alpha, \beta)|^2 ([1 + n(\omega_{\xi})] \delta(\Omega_{\alpha\beta} - \omega_{\xi}) + n(\omega_{\xi}) \delta(\Omega_{\alpha\beta} + \omega_{\xi})) \end{aligned}$$

here we noticed that the double sum with respect to the normal mode vibrations reduces to a single sum and we took into account

$$\text{tr}_{\text{vib}} \{ \hat{R} c_{\xi}^{\dagger} c_{\xi} \} = n(\omega_{\xi}) \equiv \frac{1}{e^{\hbar\omega_{\xi}/k_B T} - 1}$$

the rate expression is further rewritten by introducing the following general type of spectral density

$$J_{\alpha\beta,\gamma\delta}(\omega) = \sum_{\xi} \tilde{g}_{\xi}(\alpha, \beta) \tilde{g}_{\xi}(\gamma, \delta) \delta(\omega - \omega_{\xi})$$

accordingly, the rate takes the form

$$k_{\alpha \rightarrow \beta} = 2\pi \Omega_{\alpha\beta}^2 [1 + n(\Omega_{\alpha\beta})] (J_{\alpha\beta,\beta\alpha}(\Omega_{\alpha\beta}) - J_{\alpha\beta,\beta\alpha}(-\Omega_{\alpha\beta}))$$

to compute this expression we need the exciton spectrum resulting in the transition frequencies  $\Omega_{\alpha\beta}$  and the set of spectral densities  $J_{\alpha\beta,\beta\alpha}(\omega)$ ; temperature enters via the

Bose–Einstein distribution  
to be more specific we approximate

$$\tilde{g}_\xi(\alpha, \beta) = \sum_m C_\alpha^*(m) g_\xi(m) C_\beta(m)$$

i.e. we neglect the contribution given by  $g_\xi(m, n)$   
it yields

$$J_{\alpha\beta, \gamma\delta}(\omega) = \sum_{m,n} C_\alpha^*(m) C_\beta(m) C_\gamma^*(n) C_\delta(n) \sum_\xi g_\xi(m) g_\xi(n) \delta(\omega - \omega_\xi)$$

this expression leads to the introduction of the spectral density

$$J_{mn}(\omega) = \sum_\xi g_\xi(m) g_\xi(n) \delta(\omega - \omega_\xi)$$

furthermore, we neglect correlations among different excited states and assume

$$J_{mn}(\omega) \approx \delta_{mn} J(\omega)$$

it follows

$$J_{\alpha\beta, \gamma\delta}(\omega) = \sum_m C_\alpha^*(m) C_\beta(m) C_\gamma^*(m) C_\delta(m) J(\omega) \equiv j_{\alpha\beta, \gamma\delta} J(\omega)$$

now, the rate can be simply written as

$$k_{\alpha \rightarrow \beta} = j_{\alpha\beta, \beta\alpha} C(\Omega_{\alpha\beta})$$

with the abbreviation

$$C(\omega) = 2\pi\omega^2 [1 + n(\omega)] [J(\omega) - J(-\omega)] \equiv 2\pi\omega^2 \left( [1 + n(\omega)] J(\omega) + n(-\omega) J(-\omega) \right)$$

## Analysis of the Complete Redfield–Tensor

for the Redfield–tensor we may write

$$R_{\alpha\beta, \gamma\delta} = \text{Re} \int_0^\infty d\tau \left( \delta_{\alpha, \gamma} \sum_\epsilon e^{i\Omega_\epsilon \tau} C_{\delta\epsilon, \epsilon\beta}(-\tau) + \delta_{\delta, \beta} \sum_\epsilon e^{i\Omega_\gamma \tau} C_{\alpha\epsilon, \epsilon\gamma}(\tau) \right. \\ \left. - e^{i\Omega_\beta \tau} C_{\delta\beta, \alpha\gamma}(-\tau) - e^{i\Omega_\alpha \tau} C_{\delta\beta, \alpha\gamma}(\tau) \right)$$

the correlation function reads

$$C_{\alpha\beta, \gamma\delta}(\omega) = 2\pi\omega^2 [1 + n(\omega)] [J_{\alpha\beta, \gamma\delta}(\omega) - J_{\alpha\beta, \gamma\delta}(-\omega)]$$

the spectral density has been already defined;

we introduce identical simplifications as in the foregoing section and arrive at

$$C_{\alpha\beta, \gamma\delta}(\omega) = j_{\alpha\beta, \gamma\delta} C(\omega)$$

we assume  $C_{\alpha\beta, \gamma\delta}$  to be a real quantity and note

$$\text{Re} \int_0^\infty d\tau e^{i\omega\tau} C_{\alpha\beta, \gamma\delta}(\pm\tau) = \text{Re} \int \frac{d\omega'}{2\pi} C_{\alpha\beta, \gamma\delta}(\omega') \int_0^\infty d\tau e^{i(\omega \mp \omega')\tau}$$

$$= \text{Re} \int \frac{d\omega'}{2\pi} C_{\alpha\beta,\gamma\delta}(\omega') \frac{i}{\omega \mp \omega' + i\epsilon} = \frac{1}{2} C_{\alpha\beta,\gamma\delta}(\pm\omega)$$

the Redfield tensor follows as

$$R_{\alpha\beta,\gamma\delta} = \delta_{\alpha,\gamma} \frac{1}{2} \sum_{\epsilon} C_{\delta\epsilon,\epsilon\beta}(\Omega_{\delta\epsilon}) + \delta_{\delta,\beta} \frac{1}{2} \sum_{\epsilon} C_{\alpha\epsilon,\epsilon\gamma}(-\Omega_{\epsilon\gamma}) \\ - \frac{1}{2} C_{\delta\beta,\alpha\gamma}(\Omega_{\delta\beta}) - \frac{1}{2} C_{\delta\beta,\alpha\gamma}(-\Omega_{\alpha\gamma})$$

with, for example,

$$C_{\delta\beta,\alpha\gamma}(\Omega_{\delta\beta}) = 2\pi\Omega_{\delta\beta}^2 \left( \Theta(\Omega_{\delta\beta}) [1 + n(\Omega_{\delta\beta})] J_{\delta\beta,\alpha\gamma}(\Omega_{\delta\beta}) + \Theta(\Omega_{\beta\delta}) n(\Omega_{\beta\delta}) J_{\delta\beta,\alpha\gamma}(\Omega_{\beta\delta}) \right)$$

and with

$$C_{\alpha\epsilon,\epsilon\gamma}(-\Omega_{\epsilon\gamma}) = C_{\alpha\epsilon,\epsilon\gamma}(\Omega_{\gamma\epsilon}) \\ = 2\pi\Omega_{\gamma\epsilon}^2 \left( \Theta(\Omega_{\gamma\epsilon}) [1 + n(\Omega_{\gamma\epsilon})] J_{\alpha\epsilon,\epsilon\gamma}(\Omega_{\gamma\epsilon}) + \Theta(\Omega_{\epsilon\gamma}) n(\Omega_{\epsilon\gamma}) J_{\alpha\epsilon,\epsilon\gamma}(\Omega_{\epsilon\gamma}) \right)$$

the transition rates read

$$k_{\alpha \rightarrow \beta} = C_{\alpha\beta,\beta\alpha}(\Omega_{\alpha\beta}) = 2\pi\Omega_{\alpha\beta}^2 j_{\alpha\beta,\beta\alpha} \left( [1 + n(\Omega_{\alpha\beta})] J(\Omega_{\alpha\beta}) + n(-\Omega_{\alpha\beta}) J(-\Omega_{\alpha\beta}) \right) \\ \equiv 2\pi\Omega_{\alpha\beta}^2 \sum_m |C_{\alpha}(m)C_{\beta}(m)|^2 \left( [1 + n(\Omega_{\alpha\beta})] J(\Omega_{\alpha\beta}) + n(\Omega_{\beta\alpha}) J(\Omega_{\beta\alpha}) \right)$$

## Linear and Regular Chain of Dye Molecules

the spectral density should take the form

$$\omega^2 J(\omega) = j_{\nu} \omega^{\nu} e^{-\omega/\omega_c}$$

we get

$$C_{\alpha\beta,\gamma\delta}(\omega) \equiv C_{jj',ll'}(\omega) = j_{jj',ll'} C(\omega)$$

$$j_{jj',ll'} = \frac{4}{(N_{\text{mol}} + 1)^2} \sum_m \sin\left(\frac{\pi jm}{N_{\text{mol}} + 1}\right) \sin\left(\frac{\pi j' m}{N_{\text{mol}} + 1}\right) \sin\left(\frac{\pi lm}{N_{\text{mol}} + 1}\right) \sin\left(\frac{\pi l' m}{N_{\text{mol}} + 1}\right)$$

$$C(\omega) = 2\pi j_{\nu} |\omega|^{\nu} e^{-|\omega|/\omega_c} \left( \theta(\omega) \frac{e^{\hbar\omega/k_B T}}{e^{\hbar\omega/k_B T} - 1} + \theta(-\omega) \frac{1}{e^{-\hbar\omega/k_B T} - 1} \right)$$

$$\hbar\Omega_{\alpha\beta} \equiv \hbar\Omega_{jl} = 2J \left( \cos\left(\frac{\pi j}{N_{\text{mol}} + 1}\right) - \cos\left(\frac{\pi l}{N_{\text{mol}} + 1}\right) \right)$$

$$\equiv -J \sin\left(\frac{\pi(j+l)}{2(N_{\text{mol}} + 1)}\right) \sin\left(\frac{\pi(j-l)}{2(N_{\text{mol}} + 1)}\right)$$

initial condition

population of a particular exciton level  $\alpha_0$

$$\hat{\rho}(0) = |\alpha_0\rangle\langle\alpha_0|$$

it gives

$$\rho_{\alpha\beta}(0) = \delta_{\alpha\beta}\delta_{\alpha,\alpha_0}$$

population of a particular site  $m_0$

$$\hat{\rho}(0) = |m_0\rangle\langle m_0| = \sum_{\alpha,\beta} C_{\alpha}^*(m_0)C_{\beta}(m_0)|\alpha\rangle\langle\beta|$$

it gives

$$\rho_{\alpha\beta}(0) = C_{\alpha}^*(m_0)C_{\beta}(m_0)$$

the populations follows as

$$P_{\alpha}(0) = |C_{\alpha}(m_0)|^2 = \frac{2}{N_{\text{mol}} + 1} \sin^2\left(\frac{\pi j m_0}{N_{\text{mol}} + 1}\right)$$

### 3.5 Linear Absorption of a Chromophore Complex

optical properties of molecular systems are characterized via the macroscopic polarization (dipole density)

$$\mathbf{P}(\mathbf{r}, t) = \frac{1}{\Delta V(\mathbf{r})} \sum_{m \in \Delta V} \mathbf{d}_m(t)$$

the macroscopic polarization at the absence of inhomogeneous broadening reads

$$\mathbf{P}(\mathbf{r}, t) = n_{\text{mol}} \mathbf{d}(\mathbf{r}; t)$$

here,  $n_{\text{mol}}$  denotes the volume density of the considered molecules, and  $\mathbf{d}_m(t)$  is the expectation values of the  $m$ 'th molecule dipole operator; since inhomogeneous broadening has been neglected we take the quantity  $\mathbf{d}(\mathbf{r}; t)$  which, first, is independent on the spatial position; however, the electric field–strength depends on  $\mathbf{r}$ , and just this dependence enters the expectation value;

to obtain a formula for the linear absorption coefficient

$$\alpha(\omega) = \frac{4\pi\omega}{nc} \text{Im}\chi(\omega)$$

we have to establish a linear relation between the electric field–strength and the polarization:

$$\mathbf{P}(\mathbf{r}, t) = \int d\bar{t} \hat{\chi}^{(1)}(t, \bar{t}) \mathbf{E}(\mathbf{r}, \bar{t})$$

the dipole operator expectation value follows as

$$\mathbf{d}(\mathbf{r}; t) = \text{tr}\{\hat{W}(t)\hat{\mu}\}$$

here, the time–dependence of the statistical operator  $\hat{W}(t)$  is determined by the time–dependent Hamiltonian

$$H(t) = H_{\text{mol}} + H_{\text{field}}(t)$$

therefore we have to write

$$U(t, t_0) = \hat{T} \exp\left(-\frac{i}{\hbar} \int_{t_0}^t dt' H(t')\right)$$

i.e. the time–evolution operator appears as a time–ordered quantity;

to carry out a perturbation theory with respect to the molecule–field coupling it is more appropriate to introduce the  $S$ –operator according to

$$U(t, t_0) = U_{\text{mol}}(t - t_0) S(t, t_0) \equiv e^{-iH_{\text{mol}}(t-t_0)/\hbar} \hat{T} \exp\left(-\frac{i}{\hbar} \int_{t_0}^t dt' H_{\text{field}}^{(I)}(t')\right)$$

note the use of the *interaction representation* for  $H_{\text{field}}$  (as well as  $\hat{\mu}$ ):

$$H_{\text{field}}^{(I)}(t) = U_{\text{mol}}^+(t - t_0) H_{\text{field}}(t) U_{\text{mol}}(t - t_0)$$

accordingly the expectation value of the dipole operator reads

$$\begin{aligned} \mathbf{d}(\mathbf{r}; t) &= \text{tr}\{U(t, t_0) \hat{W}_{\text{eq}} U^+(t, t_0) \hat{\mu}\} = \text{tr}\{\hat{W}_{\text{eq}} U^+(t, t_0) \hat{\mu} U(t, t_0)\} \\ &= \text{tr}\{\hat{W}_{\text{eq}} S^+(t, t_0) \hat{\mu}^{(I)}(t) S(t, t_0)\} \end{aligned}$$

the statistical operator  $\hat{W}_{\text{eq}}$  describes thermal equilibrium present before the application of the external field; the different contributions in powers of the field–strength may be obtained by a power expansion of  $S(t, t_0)$ ;

### 3.5.1 Dipole–Dipole Correlation Function

to expand  $d(\mathbf{r}; t)$  up to the first order in the field–strength we note

$$S(t, t_0) \approx 1 + S^{(1)}(t, t_0)$$

with

$$S^{(1)}(t, t_0) = -\frac{i}{\hbar} \int_{t_0}^t dt' H_{\text{field}}^{(1)}(t')$$

we insert this approximation into the formula for  $d(\mathbf{r}; t)$  and obtain (the zeroth–order term does not contribute because of the absence of a macroscopic dipole density in the equilibrium)

$$\begin{aligned} \mathbf{d}(\mathbf{r}; t) &\approx \text{tr}\{\hat{W}_{\text{eq}}[1 + S^{(1)+}(t, t_0)]\hat{\mu}^{(I)}(t)[1 + S^{(1)}(t, t_0)]\} \\ &\approx \frac{i}{\hbar} \int_{t_0}^t dt' \text{tr}\left\{\hat{W}_{\text{eq}}[H_{\text{field}}^{(1)}(t')\hat{\mu}^{(I)}(t) - \hat{\mu}^{(I)}(t)H_{\text{field}}^{(1)}(t')]\right\} \\ &= \frac{i}{\hbar} \int_{t_0}^t dt' \text{tr}\left\{\hat{W}_{\text{eq}}[U_{\text{mol}}^+(t' - t_0)H_{\text{field}}(t')U_{\text{mol}}^+(t - t')\hat{\mu}U_{\text{mol}}(t - t_0) \right. \\ &\quad \left. - U_{\text{mol}}^+(t - t_0)\hat{\mu}U_{\text{mol}}(t - t')H_{\text{field}}(t')U_{\text{mol}}(t' - t_0)]\right\} \\ &= \frac{i}{\hbar} \int_{t_0}^t dt' \text{tr}\left\{\hat{W}_{\text{eq}}[\hat{\mu}^{(I)}(t - t'), \hat{\mu}^{(I)}(0)]_-\right\} \mathbf{E}(\mathbf{r}; t') \end{aligned}$$

inserting the last expression into the macroscopic polarization, the *linear dielectric susceptibility* is obtained as

$$\chi_{jj'}(t - t') = \frac{i}{\hbar} \Theta(t - t') n_{\text{mol}} C_{jj'}^{(\text{d-d})}(t - t') ;$$

we introduced the *dipole–dipole correlation function*

$$C_{jj'}^{(\text{d-d})}(t) = \text{tr}\left\{\hat{W}_{\text{eq}}\left[\hat{\mu}_j^{(I)}(t), \hat{\mu}_{j'}^{(I)}(0)\right]_-\right\}$$

which represents a second–rank tensor;

before considering the case of randomly oriented molecules we assume for the following that all matrix elements of the dipole operator show in the  $z$ –direction of a coordinate system where the  $z$ –axis is defined by the direction of the electric field–strength; then, the correlation function tensor reduces to a single component identical with

$$C_{\text{d-d}}(t) = \text{tr}\left\{\hat{W}_{\text{eq}}\left[\hat{\mu}^{(I)}(t), \hat{\mu}^{(I)}(0)\right]_-\right\}$$

and the absorption coefficient is obtained as (note  $n = 1$ )

$$\alpha(\omega) = \frac{4\pi\omega}{c} \text{Im} \int dt e^{i\omega t} \frac{i}{\hbar} \Theta(t) n_{\text{mol}} C_{\text{d-d}}(t) = \frac{4\pi\omega n_{\text{mol}}}{\hbar c} \text{Re} \int_0^{\infty} dt e^{i\omega t} C_{\text{d-d}}(t)$$

### 3.5.2 The Absorption Coefficient

we concentrate on a situation where the exciton–vibrational coupling is sufficiently small compared to the Coulomb coupling; if we neglect any contribution of the exciton–vibrational coupling to the absorption spectrum we obtain the absorption as sharp lines at the different exciton energies  $\mathcal{E}_\alpha$ ;

the absorption coefficient can be written as ( $n_{\text{agg}}$  is the volume density of aggregates)

$$\alpha(\omega) = \frac{4\pi\omega n_{\text{agg}}}{3\hbar c} \text{Re} \int_0^\infty dt e^{i\omega t} C_{\text{d-d}}(t)$$

the dipole-dipole correlation function reads

$$C_{jj'}^{(\text{d-d})}(t) = \text{tr} \left\{ \hat{W}_{\text{eq}} \left[ \hat{\mu}_j^{(1)}(t), \hat{\mu}_{j'}^{(1)}(0) \right]_- \right\};$$

in the present case the dipole operator comprises the contributions  $\hat{\mu}_m$  of all molecules in the aggregate according to

$$\hat{\mu} = \sum_m \hat{\mu}_m$$

for the present purposes it is sufficient to restrict the model to transitions into the single exciton state

$$\hat{\mu} = \sum_m \hat{\mu}_m \equiv \sum_m \mathbf{d}_m |m\rangle \langle 0| + \text{h.c.}$$

where  $\mathbf{d}_m$  is the transition matrix element of the two–level model;

let us first study the coherent case where exciton–vibrational coupling is neglected; we introduce the exciton representation of the dipole operator

$$\hat{\mu} = \sum_\alpha \mathbf{d}_\alpha |\alpha\rangle \langle 0| + \text{h.c.}$$

with the transition matrix elements given by

$$\mathbf{d}_\alpha = \langle \alpha | \sum_m \hat{\mu}_m | 0 \rangle = \sum_m c_\alpha^*(m) \mathbf{d}_m$$

the time–dependent dipole operator entering the dipole–dipole correlation function  $C_{\text{d-d}}(t)$  reads

$$\begin{aligned} \hat{\mu}(t) &= \sum_\alpha \mathbf{d}_\alpha e^{iH_{\text{agg}}^{(1)}t/\hbar} |\alpha\rangle \langle 0| e^{-iH_{\text{agg}}^{(0)}t/\hbar} + \text{h.c.} \\ &\approx \sum_\alpha \mathbf{d}_\alpha e^{i\mathcal{E}_\alpha t/\hbar} |\alpha\rangle \langle 0| + \text{h.c.} \end{aligned}$$

the trace in  $C_{\text{d-d}}(t)$  is a trace with respect to the electronic states  $|0\rangle$  and  $|m\rangle$ ; the equilibrium statistical operator gives a projection onto the electronic ground state of the aggregate,  $\hat{W}_{\text{eq}} = |0\rangle \langle 0|$ ; neglecting antiresonant contributions results in (the prefactor 1/3 follows from the orientational averaging)

$$\alpha(\omega) = \frac{4\pi^2\omega n_{\text{agg}}}{3c} \sum_\alpha |\mathbf{d}_\alpha|^2 \delta(\mathcal{E}_\alpha - \hbar\omega)$$



the strength for transitions from the ground state into the single–exciton state  $|\alpha\rangle$  is determined by the respective transition dipole moment, where the expansion coefficients  $c_\alpha(m)$  give the contribution of the  $m$ th molecule to the single–exciton eigenstate  $|\alpha\rangle$ ; to characterize this quantity we compute the oscillator strength; for a collection of molecules with identical transition dipole moments (same magnitude and same spatial orientation),  $\mathbf{d}_m = \mathbf{d}$ , it reads

$$O_\alpha = \frac{|\mathbf{d}_\alpha|^2}{|\mathbf{d}|^2} = \left| \sum_m c_\alpha(m) \right|^2 .$$

in the limit of weak exciton–vibrational coupling the absorption reads

$$\alpha(\omega) = \frac{4\pi\omega n_{\text{agg}}}{3\hbar c} \sum_\alpha |\mathbf{d}_\alpha|^2 \frac{\gamma_\alpha}{(\omega - \mathcal{E}_\alpha/\hbar)^2 + \gamma_\alpha^2}$$

the quantity  $\gamma_\alpha$  is the homogeneous broadening;

### Static Disorder

an important factor determining the width of absorption lines of artificially prepared or naturally occurring aggregates is static disorder; a change of the energy level structure, for example, from aggregate to aggregate leads to an additional broadening of the absorption which is measured on a sample containing a large number of aggregates; one can characterize such a behavior by a set of parameters  $y \equiv \{y_j\}$  which enter the Hamiltonian and describe a specific energetic and structural situation in the aggregate; the parameters  $y$  will be additionally labelled by  $A$ , which counts all aggregates contained in the sample volume  $V$ ; this should indicate that set  $y$  varies from aggregate to aggregate; accordingly, every aggregate will have its own absorption cross section

$$\sigma = \sigma(\omega; y_A)$$

the cross section follows from the absorption coefficient as

$$\sigma = \alpha/n_{\text{agg}}$$

and we may write:

$$\alpha_{\text{inh}}(\omega) = \frac{1}{V} \sum_{A \in V} \sigma(\omega; y_A)$$

the inhomogeneous broadening can be described as an averaging with respect to different realizations of the aggregate’s structure and energy spectrum; this is called a configurational average;

if there exist a large number of different realizations one can change from the summation to the integration with respect to the different parameters  $y_j$

$$\alpha_{\text{inh}}(\omega) = \int dy \mathcal{F}(y) \sigma(\omega; y)$$

the integration extends over the whole set of parameters; the appropriate normalized distribution function  $\mathcal{F}(y)$  can formally be introduced as

$$\mathcal{F}(y) = \frac{1}{V} \sum_{A \in V} \prod_j \delta(y_j - y_{Aj})$$

for specific applications  $\mathcal{F}(y)$  is taken to be a continuous function of the parameters  $y_j$ ; we consider the simple case, where disorder can be described by Gaussian distributions of the various exciton levels around certain mean values  $\bar{\mathcal{E}}_\alpha$ .

$$\mathcal{F}(y) \rightarrow \mathcal{F}(y \equiv \{\mathcal{E}_\alpha\}) = n_{\text{agg}} \prod_{\alpha} \mathcal{F}_\alpha(\mathcal{E}_\alpha - \bar{\mathcal{E}}_\alpha)$$

with

$$\mathcal{F}_\alpha(E) = \frac{1}{\sqrt{2\pi}\Delta_\alpha} \exp\left\{-\frac{E^2}{2\Delta_\alpha^2}\right\}$$

here  $\Delta_\alpha$  is the width of the Gaussian distribution for the state  $|\alpha\rangle$ ; taking the cross section the inhomogeneously broadened absorption spectrum is obtained as

$$\alpha_{\text{inh}}(\omega) = \int d\mathcal{E} \mathcal{F}(\mathcal{E}) \sigma(\omega; \mathcal{E}) = \frac{4\pi^2 \omega n_{\text{agg}}}{3c} \sum_{\alpha} |\mathbf{d}_\alpha|^2 \mathcal{F}_\alpha(\hbar\omega - \bar{\mathcal{E}}_\alpha)$$

in this simple case the distribution of microscopic parameters directly determines the lineshape of the inhomogeneously broadened spectrum;