21 Intermolecular Energy transfer

21.1 incoherent transfer

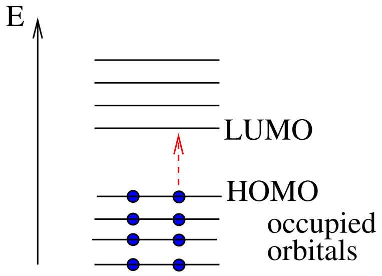
We consider the transfer of energy from an excited donor molecule D* to an acceptor molecule A

$$D^* + A \rightarrow D + A^*$$

We assume that the optical transitions of both molecules can be described by the transition between the highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals. The Hartree-Fock groundstate of one molecule can be written as a Slater determinant of doubly occupied molecular orbitals

$$|HF> = |\phi_{1\uparrow}\phi_{1\downarrow}\cdots\phi_{HO\uparrow}\phi_{HO\downarrow}|$$

Figure 104: HOMO-LUMO transition



Promotion of an electron from the HOMO to the LUMO creates a singlet or a triplet state which both are linear combinations of the four determinants

$$|\uparrow\downarrow> = |\phi_{1\uparrow}\phi_{1\downarrow}\cdots\phi_{HO\uparrow}\phi_{LU\downarrow}|$$

$$| \downarrow\uparrow >= |\phi_{1\uparrow}\phi_{1\downarrow} \cdots \phi_{HO\downarrow}\phi_{LU\uparrow}|$$

$$| \uparrow\uparrow >= |\phi_{1\uparrow}\phi_{1\downarrow} \cdots \phi_{HO\uparrow}\phi_{LU\uparrow}|$$

$$| \downarrow\downarrow >= |\phi_{1\uparrow}\phi_{1\downarrow} \cdots \phi_{HO\downarrow}\phi_{LU\downarrow}|$$

obviously the last two determinants are the components of the triplet state with $S_z = \pm 1$

$$|T, +1 >= | \uparrow\uparrow >$$

$$|T, -1 >= | \downarrow\downarrow >$$

For the first two components consider the square of the total spin (let $\hbar = 1$ for a moment)

$$S^2 = (S_1 + S_2)^2 = S_1^2 + S_2^2 + 2S_{1x}S_{2x} + 2S_{1y}S_{2y} + 2S_{1z}S_{2z}$$

where the components of each spin are described by the matrices

$$S_x = \begin{pmatrix} 0 & 1/2 \\ 1/2 & 0 \end{pmatrix} \quad S_y = \begin{pmatrix} 0 & -i/2 \\ i/2 & 0 \end{pmatrix} \quad S_z = \begin{pmatrix} 1/2 & 0 \\ 0 & -1/2 \end{pmatrix}$$

For the first two determinants

$$S_1^2 + S_2^2 + 2S_{1z}S_{2z}| >= (\frac{3}{4} + \frac{3}{4} - \frac{1}{2})| >= | >$$

and further

$$S^2| \uparrow\downarrow >= | \uparrow\downarrow > +2(\frac{1}{4} - \frac{i^2}{4})| \downarrow\uparrow >= | \uparrow\downarrow > +| \downarrow\uparrow >$$

and similarly with the two determinants exchanged. This shows that the symmetric and antisymmetric combinations are Eigenvectors of the total spin operator

$$S^2 \frac{1}{\sqrt{2}}(| \uparrow\downarrow > +| \downarrow\uparrow >) = 2\frac{1}{\sqrt{2}}(| \uparrow\downarrow > +| \downarrow\uparrow >) \quad \text{triplet}$$

$$S^2 \frac{1}{\sqrt{2}}(| \uparrow\downarrow > -| \downarrow\uparrow >) = 0 \quad \text{singlet}$$

Let us now consider the states of the molecule pair DA. The groundstate is

$$|\phi_{1\uparrow}\phi_{1\downarrow} \cdots \phi_{HO,D,\uparrow}\phi_{HO,D,\downarrow}\phi_{HO,A,\uparrow}\phi_{HO,A,\downarrow}|$$

which will be simply denoted as

$$|DA >= |D_\uparrow D_\downarrow A_\uparrow A_\downarrow|$$

The excited singlet state of the donor is

$$|D^*A>=\frac{1}{\sqrt{2}}(|D^*_\uparrow D_\downarrow A_\uparrow A_\downarrow|-|D^*_\downarrow D_\uparrow A_\uparrow A_\downarrow|)$$

and the excited state of the acceptor is

$$|DA^*>=\frac{1}{\sqrt{2}}(|D_\uparrow D_\downarrow A^*_\uparrow A_\downarrow|-|D_\uparrow D_\downarrow A^*_\downarrow A_\uparrow|)$$

The interaction responsible for energy transfer is the Coulombic electron-electron interaction

$$V(\phi_1\phi_{1'}\phi_2\phi_{2'})=\int d^3r_1d^3r_2\phi^*_{1\sigma}(r_1)\phi^*_{2,\sigma'}(r_2)\frac{e^2}{4\pi\epsilon|r_1-r_2|}\phi_{1'\sigma}(r_1)\phi_{2',\sigma'}(r_2)$$

and the transfer matrix element consists of four summands. The first one is

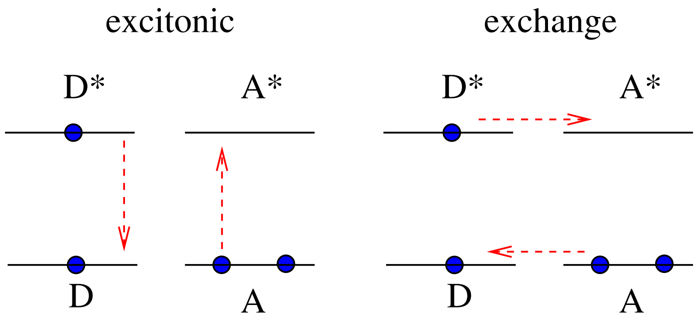
$$\frac{1}{2}<|D^*_\uparrow D_\downarrow A_\uparrow A_\downarrow|V|D_\uparrow D_\downarrow A^*_\uparrow A_\downarrow|>$$

which give the two contributions

$$\frac{1}{2}V(D^*D\,A\,A^*)-\frac{1}{2}V(D^*A^*A\,D)$$

where the first part is the excitonic interaction and the second part is the exchange interaction

Figure 105: excitonic and exchange interactions



The second summand

$$-\frac{1}{2}<|D^*_\uparrow D_\downarrow A_\uparrow A_\downarrow|V|D_\uparrow D_\downarrow A^*_\downarrow A_\uparrow|>=\frac{1}{2}V(D^*D\,A\,A^*)$$

has now exchange contribution due to the spin orientations. Also we note that for the triplet combination its sign changes. The two remaining summands are just mirror images of the first two. Alltogether the interaction is

$$2V(D^*DAA^*)-V(D^*A^*AD)\quad\text{singlet}$$

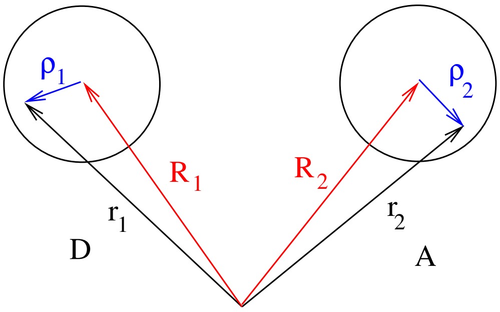
$$-V(D^*A^*AD)\quad\text{triplet}$$

In the triplet case energy can be transferred only by the exchange coupling (Dexter mechanism). Since this involves the overlap of electronic wavefunctions ie will be important at small distances. In the singlet state the excitonic interaction allows for energy transfer also at larger distances.

We will now apply a multipole expansion to the excitonic matrix element

$$V(D*DAA*) = \int d^3r_1 d^3r_2 \phi^*_{D*}(r_1)\phi^*_{A'}(r_2)\frac{e^2}{4\pi\epsilon|r_1-r_2|}\phi_D(r_1)\phi_{A*}(r_2)$$

Figure 106: multipole expansion



We take the position of the electrons relative to the centers of the molecules

$$r_{1,2} = R_{1,2} + \rho_{1,2}$$

and expand the Coulombic interaction

$$\frac{1}{|r_1-r_2|} = \frac{1}{|R_1-R_2+\rho_1-\rho_2|}$$

using the Taylor series

$$\frac{1}{|R+\rho|} = \frac{1}{|R|} - \frac{1}{|R|^2}\frac{\rho R}{|R|} + \frac{1}{2}\frac{3|R|(R\rho)^2-|R|^3\rho^2}{|R|^6} + \cdots$$

for

$$R = R_1 - R_2 \quad \rho = \rho_1 - \rho_2$$

The zeroth order term vanishes due to the orthogonality of the orbitals. The first order term gives

$$-\frac{e^2}{4\pi\epsilon|R|^3}R\int d^3\rho_1 d^3\rho_2 \phi^*_{D*}(r_1)\phi_D(r_1)(\rho_1-\rho_2)\phi^*_A(r_2)\phi_{A*}(r_2)$$

and also vanishes due to the orthogonality. The second order term gives the leading contribution

$$\frac{e^2}{4\pi\epsilon|R|^6}\frac{1}{2}\int d^3\rho_1 d^3\rho_2 \phi^*_{D*}(r_1)\phi_D(r_1)(3|R|(R\rho_1-R\rho_2)^2-|R|^3(\rho_1-\rho_2)^2)\phi^*_A(r_2)\phi_{A*}(r_2)$$

Only the integrals over mixed products of ρ_1 and ρ_2 are not zero. They can be expressed with the help of the transition dipoles

$$\mu_1 = \int d^3\rho_1 \phi^*_{D*}(\rho_1) e\rho_1 \phi_D(\rho_1)$$

$$\mu_2 = \int d^3\rho_2 \phi^*_{A}(\rho_2) e\rho_2 \phi_{A*}(\rho_2)$$

as

$$V = \frac{e^2}{4\pi\epsilon|R|^5}\left(|R|^2\mu_1\mu_2 - 3(R\mu_1)(R\mu_2)\right)$$

This is often written with an orientation dependent factor K

$$V = \frac{K}{|R|^3}|\mu_1||\mu_2|$$

Now consider once more Fermi's golden rule for the transition between vibronic states $|i> \rightarrow |f>$

$$k = \frac{2\pi}{\hbar^2}\sum_{i,f} P_i| < i|V|f > |^2\delta(\omega_i - \omega_f)$$

$$= \frac{1}{\hbar^2}\int \sum_{if} P_i < i|e^{-i\omega_i t}V|f > e^{i\omega_f t} < f|V|i > dt$$

$$= \frac{1}{\hbar^2}\int \sum_{i} P_i < i|e^{-\frac{it}{\hbar}H_0}Ve^{\frac{it}{\hbar}H_0}V|i > dt$$

$$= \frac{1}{\hbar^2}\int dt \ < V(t)V(0) >$$

The Hamiltonian is partitioned as

$$\begin{pmatrix} H_{D*} + H_A & V_{D*A*} \\ V^\dagger_{D*A*} & H_D + H_{A*} \end{pmatrix} = H_0 + V$$

and initially only the donor is excited. Then the average is over the vibrational states of $D*A$

$$k = \frac{1}{\hbar^2}\frac{K^2}{|R|^6}\int dt < D*A|\mu_1(t)\mu_2(t)\mu_1(0)\mu_2(0)|D*A >$$

Here we assumed that the orientation does not change on the relevant time scale ($K^2 = (2/3)(e^2/4\pi\epsilon)^2$) . Since each of the dipole operators acts only on one of the molecules we have

$$k = \frac{1}{\hbar^2}\frac{K^2}{|R|^6}\int dt \ < D*|\mu_1(t)\mu_1(0)|D* >< A|\mu_2(t)\mu_2(0)|A >$$

The two factors are related to the acceptor absorption and donor fluorescence spectra. Consider the optical transition $A \to A*$. The absorption coefficient is proportional to the Einstein coefficient times the photon energy

$$B\,\hbar\omega = \frac{\mu^2}{3\epsilon_0\hbar^2}\hbar\omega$$

where the so called line strength of the singlet -singlet transition is given by

$$\mu =< A_\uparrow A_\downarrow|er|\frac{1}{\sqrt{2}}\left(|A*_\uparrow A_\downarrow> - |A*_\downarrow A_\uparrow>\right)$$

$$= \sqrt{2}\int d^3r\,\phi_A(er)\phi_{A*}$$

Hence apart from some factors the absorption spectrum is given by

$$\alpha(\hbar\omega) = \sum_{i,f} P_i| < i|\mu^2|f > |^2\delta(\hbar\omega + \hbar\omega_i - \hbar\omega_f)$$

$$= \frac{1}{2\pi\hbar}\sum P_i \int dt\, e^{-i\omega t} < i|e^{-i\omega_i t}\mu|f > e^{i\omega_f t} < f|\mu|i >$$

$$= \frac{1}{2\pi\hbar}\int dt\, e^{-i\omega t} < A|e^{-\frac{it}{\hbar}H_0}\mu e^{\frac{it}{\hbar}H_0}\mu|A >$$

$$= \frac{1}{2\pi\hbar}\int dt\, e^{-i\omega t} < A|\mu(t)\mu(0)|A >$$

Similarly the fluorescence intensity of the Donor is proportional to

$$A = \frac{8\pi h\nu^3}{c^3}B$$

and the properly normalized fluorescence is

$$\sigma(\hbar\omega) = \frac{1}{2\pi\hbar}\int dt\, e^{-i\omega t} < D * |\mu(-t)\mu(0)|D* >$$

$$= \frac{1}{2\pi\hbar}\int dt\, e^{i\omega t} < D * |\mu(t)\mu(0)|D* >$$

Let us now make use of the Condon approximation again. Then the dipole moment does not depend on the nuclear coordinates and can be written as

$$\mu = |A > \mu_{AA*} < A * | + \text{h.c.}$$

The propagator can be written as

$$e^{-\frac{it}{\hbar}H_0} = |A > e^{-\frac{it}{\hbar}(E_A + H_A)} < A| + |A* > e^{-\frac{it}{\hbar}(E_{A*} + H_{A*})} < A * |$$

and the dipole correlation function becomes

$$< An|e^{-\frac{it}{\hbar}H_0}\mu e^{\frac{it}{\hbar}H_0}\mu|An >=$$

$$=< An|e^{-\frac{it}{\hbar}H_0}\mu e^{\frac{it}{\hbar}H_0}\mu_{AA*}|A*n>$$

$$=\mu_{AA*}< An|e^{-\frac{it}{\hbar}H_0}|A>< A|\mu|A*>< A*|e^{\frac{it}{\hbar}H_0}|A*n>$$

$$=|\mu_{AA*}|^2 e^{\frac{it}{\hbar}(E_{A*}-E_A)}< n|e^{-\frac{it}{\hbar}H_A}e^{\frac{it}{\hbar}H_{A*}}|n>$$

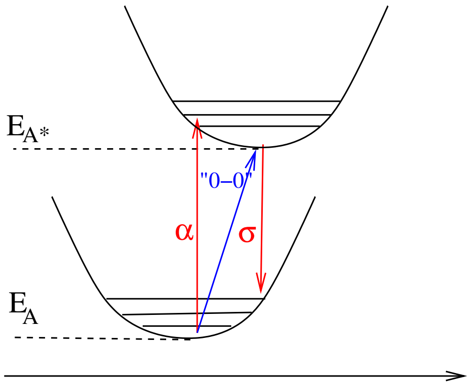
But this now involves the correlation function for the nuclear motion and the absorption spectrum becomes

$$\alpha=\frac{1}{2\pi\hbar}\int dt\, e^{i(\omega_{A*A}-\omega)t}F_A(t)$$

similarly the fluorescence spectrum

$$\sigma=\frac{1}{2\pi\hbar}\int dt\, e^{i(\omega-\omega_{D*D})t}F_{D*}(t)$$

Figure 107: absorption and emission



Finally the energy transfer rate becomes

$$k=\frac{1}{\hbar^2}\frac{K^2}{|R|^6}|\mu_{DD*}|^2|\mu_{AA*}|^2\int dt\, e^{i(\omega_{A*A}-\omega_{D*D})t}F_A(t)F_{D*}(t)$$

In the frequency domain this will lead to a convolution of the two spectra. The inverse Fourier transformations are

$$F_A(t)=\hbar\int d\omega e^{i\omega t}\alpha(\omega+\omega_{A*A})$$

$$F_{D*}(t)=\hbar\int d\omega e^{i\omega t}\sigma(\omega_{D*D}-\omega)$$

and we find

$$\int dt\, e^{i(\omega_{A*A}-\omega_{D*D})t}F_A(t)F_{D*}(t)$$

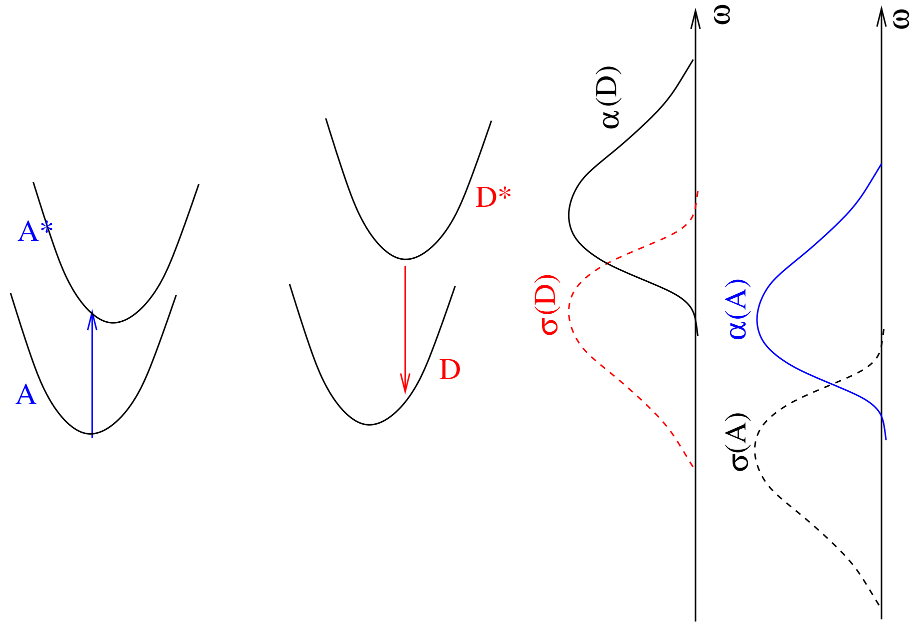
$$= \hbar^2 \int dt\, e^{i(\omega_{A*A}-\omega_{D*D})t} \int\int d\omega d\omega'\, e^{i(\omega+\omega')t} \alpha(\omega+\omega)\sigma(\omega_{D*D}-\omega')$$

$$= 2\pi\hbar^2 \int\int d\omega d\omega' \delta(\omega+\omega'+\omega_{A*A}-\omega_{D*D})\alpha(\omega-\omega_{A*A})\sigma(\omega'-\omega_{DD*})$$

$$= 2\pi\hbar^2 \int d\omega\, \alpha(\omega)\sigma(\omega)$$

For optimum efficiency of energy transfer the maximum of the absorption of the acceptor should be at longer wavelength.

Figure 108: Energy transfer



Consider now energy transfer in the triplet state. Here the transitions are optically not allowed and the rate is

$$k = \frac{1}{\hbar^2} \int dt\, < V(t)V(0) >$$

The interaction operator now changes the electronic state of both molecules simultaneously and can be written as[58]

$$V = |D* > |A > V_{exc} < A*| < D| + h.c.$$

and the rate becomes in the static case ($V_{exc} = const$)

$$k = \frac{1}{\hbar^2} \int dt < D*; n_{D*}| < A; n_A| e^{-\frac{it}{\hbar}H_0} V e^{\frac{it}{\hbar}H_0} V|A; n_A > |D*; n_{D*} >$$

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[58] we assume that the wavefunction of the pair can be factorized approximately

$$\frac{V_{exc}^2}{\hbar^2}\int dt < n_{D*}| < n_A|e^{-\frac{it}{\hbar}(E(D*A)+H_{D*}+H_A)}e^{\frac{it}{\hbar}(E(DA*)+H_D+H_{A*})}|n_A > |n_{D*} >$$

$$= \frac{V_{exc}^2}{\hbar^2}\int dt\, e^{-\frac{it}{\hbar}(E(D*A)-E(DA*))} < n_{D*}|e^{-\frac{it}{\hbar}H_{D*}}e^{\frac{it}{\hbar}H_D}|n_{D*} >< n_A|e^{-\frac{it}{\hbar}H_A}e^{\frac{it}{\hbar}H_{A*}}|n_A >$$

$$= \frac{V_{exc}^2}{\hbar^2}\int dt\, e^{-it(\omega_{D*D}-\omega_{A*A})}F_{D*}(t)F_A(t)$$

which is very similar to the Förster expression. The excitonic interaction is replaced by the exchange coupling matrix element and the Convolution of the optical spectra is replaced by the convolution of the Franck-Condon weighted densities of states.

21.2 coherent energy transfer

If the excitonic coupling is large compared to fluctuations of the excitation energies, a coherent excitation of two or more molecules can be generated.

21.2.1 strongly coupled dimers

Let us consider a dimer consisting of two strongly coupled molecules A and B as in the reaction center of photosynthesis. The two excited states

$$|A * B >, |AB* >$$

are mixed due to the excitonic interaction. The eigenstates are given by the eigenvectors of the matrix

$$\begin{pmatrix} E_{A*B} & V \\ V & E_{AB*} \end{pmatrix}$$

For a symmetric dimer the diagonal energies have the same value and the eigenvectors can be characterized as symmetric or antisymmetric

$$\begin{pmatrix} \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \end{pmatrix}\begin{pmatrix} E_{A*B} & V \\ V & E_{A*B} \end{pmatrix}\begin{pmatrix} \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \end{pmatrix} = \begin{pmatrix} E_{A*B}-V & \\ & E_{A*B}+V \end{pmatrix}$$

The two excitonic states are split by $2V$ [59]. The transition dipoles of the two dimer bands are given by

$$\mu_\pm = \frac{1}{\sqrt{2}}(\mu_A \pm \mu_B)$$

and the intensities by

$$|\mu_\pm|^2 = \frac{1}{2}(\mu_A^2 + \mu_B^2 \pm 2\mu_A\mu_B)$$

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[59] also known as Davidoff splitting

For a symmetric dimer $\mu_A^2 = \mu_B^2 = \mu^2$ and

$$|\mu_\pm|^2 = \mu^2(1 \pm \cos\alpha)$$

where α denotes the angle between μ_A and μ_B . In case of an approximately C_2 symmetric structure the components of μ_A and μ_B are furthermore related by symmetry operations. If we choose the C_2 axis along the z-axis we have

$$\begin{pmatrix} \mu_{Bx} \\ \mu_{By} \\ \mu_{Bz} \end{pmatrix} = \begin{pmatrix} -\mu_{Ax} \\ -\mu_{Ay} \\ \mu_{Az} \end{pmatrix}$$

and therefore

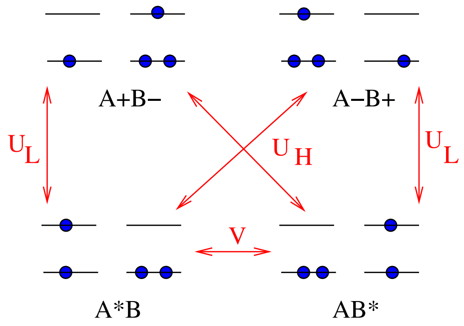
$$\frac{1}{\sqrt{2}}(\mu_A + \mu_B) = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 \\ 0 \\ 2\mu_{Az} \end{pmatrix}$$

$$\frac{1}{\sqrt{2}}(\mu_A - \mu_B) = \frac{1}{\sqrt{2}} \begin{pmatrix} 2\mu_{Ax} \\ 2\mu_{Ay} \\ 0 \end{pmatrix}$$

which shows that the transition to the state $|+>$ is polarized along the symmetry axis whereas the transition to $|->$ is polarized perpendicularly.

For the special pair dimer interaction with internal charge transfer states $|A+B->$ and $|A-B+>$ has to be considered. In the simplest model the following interaction matrix elements are important.

Figure 110: extended dimer model

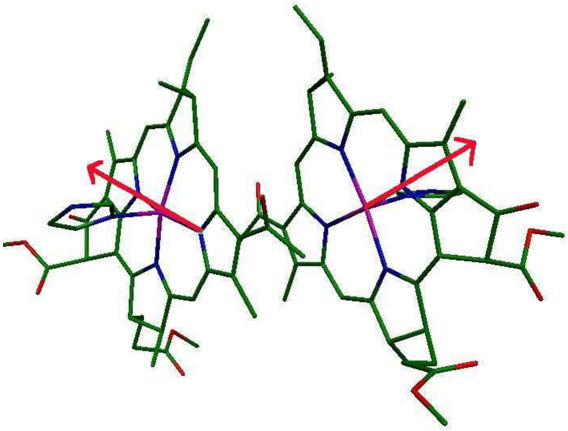


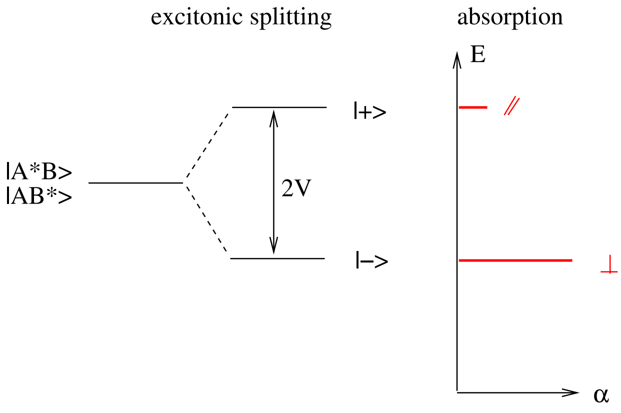
The local excitation $A*B$ is coupled to the CT state $A+B-$ by transferring an electron between the two LUMOS

$$< A{*}B|H|A{+}B{-} >= \frac{1}{2} < (A{*}_\uparrow A_\downarrow - A{*}_\downarrow A_\uparrow)B_\uparrow B_\downarrow H(B{*}_\uparrow A_\downarrow - B{*}_\downarrow A_\uparrow)B_\uparrow B_\downarrow >$$

$$= H_{A*,B*} = U_L$$

Figure 109: special pair dimer





and to the CT state $A-B+$ by transferring an electron between the HOMOs

$$< A{*}B|H|A{-}B{+} >= \frac{1}{2} < (A{*}_\uparrow A_\downarrow - A{*}_\downarrow A_\uparrow)B_\uparrow B_\downarrow H(A{*}_\uparrow B_\downarrow - A{*}_\downarrow B_\uparrow)A_\uparrow A_\downarrow >$$

$$= -H_{A,B} = U_H$$

Similarly the second local excitation couples to the CT states by

$$< AB{*}|H|A{+}B{-} >= \frac{1}{2} < (B{*}_\uparrow B_\downarrow - B{*}_\downarrow B_\uparrow)A_\uparrow A_\downarrow H(B{*}_\uparrow A_\downarrow - B{*}_\downarrow A_\uparrow)B_\uparrow B_\downarrow >$$

$$= -H_{A,B} = U_H$$

$$< AB{*}|H|A{-}B{+} >= \frac{1}{2} < (B{*}_\uparrow B_\downarrow - B{*}_\downarrow B_\uparrow)A_\uparrow A_\downarrow H(A{*}_\uparrow B_\downarrow - A{*}_\downarrow B_\uparrow)A_\uparrow A_\downarrow >$$

$$= H_{A*,B*} = U_L$$

The interaction of the four states is summarozed by the matrix

$$H = \begin{pmatrix} E_{A*B} & V & U_L & U_H \\ V & E_{B*A} & U_H & U_L \\ U_L & U_H & E_{A+B-} & \\ U_H & U_L & & E_{A-B+} \end{pmatrix}$$

Again for a symmetric dimer $E_{B*A} = E_{AB*}$ and $E_{A+B-} = E_{A-B+}$ and the interaction matrix can be simplified by transforming to symmetrized basis functions with the transformation matrix

$$S = \begin{pmatrix} \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} & & \\ -\frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} & & \\ & & \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \\ & & -\frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \end{pmatrix}$$

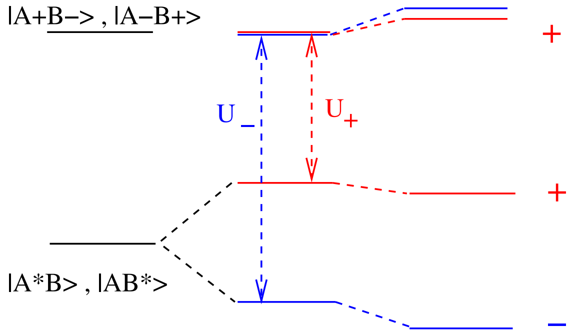
The transformation gives

$$S^{-1} H\, S = \begin{pmatrix} E_* - V & & U_L - U_H & \\ & E_* + V & & U_L + U_H \\ U_L - U_H & & E_{CT} & \\ & U_L + U_H & & E_{CT} \end{pmatrix}$$

where the states of different symmetry are decoupled

$$H_+ = \begin{pmatrix} E_* + V & U_L + U_H \\ U_L + U_H & E_{CT} \end{pmatrix} \quad H_- = \begin{pmatrix} E_* - V & U_L - U_H \\ U_L - U_H & E_{CT} \end{pmatrix}$$

Figure 111: dimer states



21.2.2 circular molecular aggregates

We consider now a circular aggregate of N chromophores as it is found in the light harvesting complexes of photosynthesis.[60] We align the C_N symmetry axis along the z-axis. The position of the n-th molecule is

$$\vec{R}_n = R \begin{pmatrix} \cos(2\pi\, n/N) \\ \sin(2\pi\, n/N) \\ 0 \end{pmatrix} \qquad n = 0, 1 \cdots N-1$$

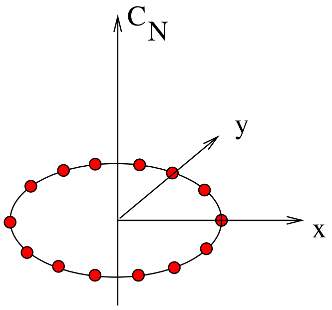
which can also be written with the help of a rotation matrix

$$S_N = \begin{pmatrix} \cos(2\pi/N) & -\sin(2\pi/N) & \\ \sin(2\pi/N) & \cos(2\pi/N) & \\ & & 1 \end{pmatrix}$$

as

$$\vec{R}_n = S_N^n \vec{R}_0 \quad \vec{R}_0 = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}$$

Figure 112: circular aggregate



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[60] R.J.Cogdell,A.Gall,J.Köhler, Quart.Rev.Biophys. 39,3(2006) pp227-324
M.Ketelaars et al, Biophys. J. 80 (2001) 1591-1603
M.Matsushita et al, Biophys.J. 80 (2001) 1604-1614

similarly the transition dipoles are given by

$$\vec{\mu}_n = S_N^n \vec{\mu}_0$$

the component parallel to the symmetry axis is the same for all monomers

$$\mu_{n,z} = \mu_{0,z}$$

whereas for the component in the pependicular plane

$$\begin{pmatrix} \mu_{n,x} \\ \mu_{n,y} \end{pmatrix} = \begin{pmatrix} \cos(n2\pi/N) & -\sin(n2\pi/N) \\ \sin(n2\pi/N) & \cos(n2\pi/N) \end{pmatrix} \begin{pmatrix} \mu_{0,x} \\ \mu_{0,y} \end{pmatrix}$$

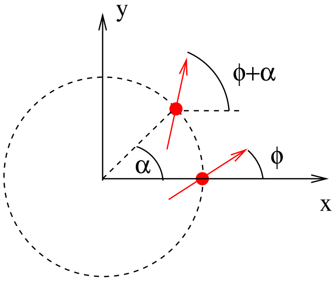
We describe the orientation of $\vec{\mu}_0$ in the x-y plane by an angle ϕ_0:

$$\begin{pmatrix} \mu_{0,x} \\ \mu_{0,y} \end{pmatrix} = \mu_\perp \begin{pmatrix} \cos(\phi) \\ \sin(\phi) \end{pmatrix}$$

Then we have

$$\begin{pmatrix} \mu_{n,x} \\ \mu_{n,y} \end{pmatrix} = \mu_{bot} \begin{pmatrix} \cos(\phi + n2\pi/N) \\ \sin(\phi + n2\pi/N) \end{pmatrix}$$

Figure 113: orientation of the transition dipoles



We denote the local excitation of the n-th molecule by

$$|n> = |A_0 A_2 \cdots A_n^* \cdots A_{N-1}>$$

Due to the symmetry of the system the excitonic interaction is invariant against the S_N rotation and therefore

$$< m|V|n > = < m-n|V|0 > = < 0|V|n-m >$$

Without an magnetic field the coupling matrix elements can be choosen real and depend only on $|m-n|$. Within the dipole-dipole approximation we have furthermore

$$V_{|m-n|} = < m|V|n > =$$

$$= \frac{e^2}{4\pi\epsilon |R_{mn}|^5} \left(|R_{mn}|^2 \vec{\mu}_m \vec{\mu}_n - 3(\vec{R}_{mn}\vec{\mu}_m)(\vec{R}_{mn}\vec{\mu}_n) \right)$$

Now we find

$$\vec{R}_{mn} = \vec{R}_m - \vec{R}_n = (S_N^m - S_N^n)\vec{R}_0 = S_N^n(S_N^{m-n} - 1)\vec{R}_0$$

$$|R_{mn}| = R\left|\begin{pmatrix} \cos((m-n)2\pi/N) - 1 & \sin((m-n)2\pi/N) & \\ -\sin((m-n)2\pi/N) & \cos((m-n)2\pi/N) - 1 & \\ & & 0 \end{pmatrix}\begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}\right|$$

$$= R|\cos((m-n)2\pi/N) - 1|$$

and

$$\vec{\mu}_m\vec{\mu}_n = (S_N^m\vec{\mu}_0)(S_N^n\vec{\mu}_0) = \mu_0^T S_N^{n-m}\mu_0$$

$$= \begin{pmatrix} \mu_x & \mu_y & \mu_z \end{pmatrix}\begin{pmatrix} \cos(2\pi(n-m)/N) & \sin(2\pi(n-m)/N) & \\ -\sin(2\pi(n-m)/N) & \cos(2\pi(n-m)/N) & \\ & & 1 \end{pmatrix}\begin{pmatrix} \mu_x \\ \mu_y \\ \mu_z \end{pmatrix}$$

$$= \mu_z^2 + (\mu_x^2 + \mu_y^2)\cos(2\pi(n-m)/N)$$

and finally

$$\vec{R}_{mn}\vec{\mu}_m = \Big((S_N^m - S_N^n)\vec{R}_0\Big)\, S_N^m\vec{\mu}_0$$

$$= R_0^T(S_N^{-m} - S_N^{-n})S_N^m\mu_0 = R_0^T(1 - S_N^{m-n})\mu_0$$

$$= \mu_x(1 - \cos(2\pi(m-n)/N)) - \mu_y\sin(2\pi(m-n)/N))$$

$$\vec{R}_{mn}\vec{\mu}_n = \Big((S_N^m - S_N^n)\vec{R}_0\Big)\, S_N^n\vec{\mu}_0$$

$$= R_0^T(S_N^{-m} - S_N^{-n})S_N^n\mu_0 = R_0^T(S_N^{n-m} - 1)\mu_0$$

$$= \mu_x(\cos(2\pi(m-n)/N) - 1) - \mu_y\sin(2\pi(m-n)/N))$$

and the product is

$$(\vec{R}_{mn}\vec{\mu}_m)(\vec{R}_{mn}\vec{\mu}_n) = (\mu_x(1-\cos) - \mu_y\sin)(-\mu_x(1-\cos) - \mu_y\sin)$$

$$= \mu_y^2\sin(2\pi(m-n)/N)^2 - \mu_x^2(1 - \cos(2\pi(m-n)/N))^2$$

The interaction matrix has the form

$$H = \begin{pmatrix} E_0 & V_1 & V_2 & \cdots & V_2 & V_1 \\ V_1 & E_1 & V_1 & \cdots & V_3 & V_2 \\ V_2 & V_1 & \ddots & & & \vdots \\ \vdots & \vdots & & & & V_2 \\ V_2 & V_3 & & & & V_1 \\ V_1 & V_2 & \cdots & V_2 & V_1 & E_{N-1} \end{pmatrix}$$

Due to the symmetry the excitonic wavefunctions are easily constructed as

$$|k> = \frac{1}{\sqrt{N}}\sum_{n=0}^{N-1} e^{ikn}|n>$$

with

$$k = \frac{2\pi}{N} l \qquad l = 0, 1, \cdots N-1$$

$$< k'|H|k > = \frac{1}{N} \sum_{n'=0}^{N-1} \sum_{n=0}^{N-1} e^{ikn} e^{-ik'n'} < n'|H|n >$$

$$= \frac{1}{N} \sum_{n'=0}^{N-1} \sum_{n=0}^{N-1} e^{ikn} e^{-ik'n'} H_{|n-n'|}$$

substitute

$$m = n - n'$$

to get

$$< k'|H|k > = \frac{1}{N} \sum_{n=0}^{N-1} \sum_{m=n}^{n-N+1} e^{i(k-k')n + ik'm} H_{|m|}$$

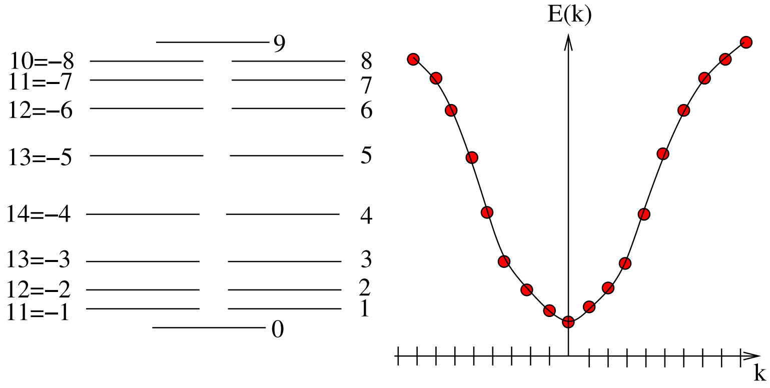
$$= \delta_{k,k'} \sum_{m=0}^{N-1} e^{ik'm} H_{|m|}$$

$$= \delta_{k,k'} \left(E_0 + 2V_1 \cos k + 2V_2 \cos 2k + \cdots\right)$$

For even N the lowest and highest state are not degenerate whereas for all of the other states

$$E_k = E_{N-k} = E_{-k}$$

Figure 114: exciton dispersion relation



The transition dipoles of the k-states are given by

$$\vec{\mu}_k = \frac{1}{\sqrt{N}} \sum_{n=0}^{N-1} e^{ikn} \vec{\mu}_n = \frac{1}{\sqrt{N}} \sum_{n=0}^{N-1} e^{ikn} S_N^n \vec{\mu}_0$$

$$= \frac{1}{\sqrt{N}} \sum_{n=0}^{N-1} e^{ikn} \begin{pmatrix} \mu_x \cos(2\pi\, n/N) + \mu_y \sin(2\pi\, n/N) \\ \mu_y \cos(2\pi\, n/N) - \mu_x \sin(2\pi\, n/N) \\ \mu_z \end{pmatrix}$$

For the z-component we have

$$\frac{1}{\sqrt{N}} \mu_z \sum_{n=0}^{N-1} e^{ikn} = \sqrt{N} \mu_z \delta_{k,0}$$

For the x,y-component we introduce complex variables

$$\mu_{k,\pm} = \frac{1}{\sqrt{2}} (\mu_{k,x} \pm i\mu_{k,y}) =$$

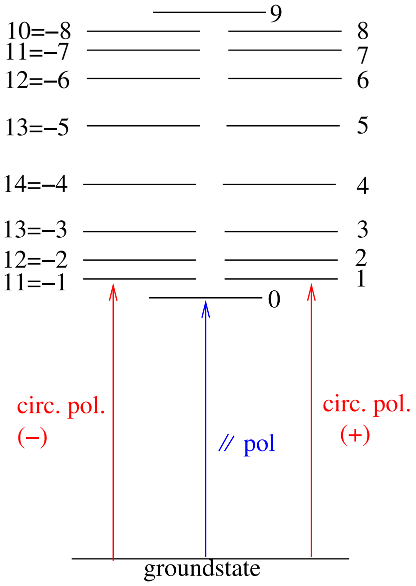
$$= \frac{1}{\sqrt{N}} \sum_{n=0}^{N-1} e^{ikn} \begin{pmatrix} \frac{1}{\sqrt{2}} & \pm\frac{i}{\sqrt{2}} & 0 \end{pmatrix} \begin{pmatrix} \cos(\frac{2\pi n}{N}) & -\sin(\frac{2\pi n}{N}) & \\ \sin(\frac{2\pi n}{N}) & \cos(\frac{2\pi n}{N}) & \\ & & 1 \end{pmatrix} \begin{pmatrix} \mu_x \\ \mu_y \\ \mu_z \end{pmatrix}$$

$$= \frac{1}{\sqrt{N}} \sum_{n=0}^{N-1} e^{ikn} \begin{pmatrix} \frac{1}{\sqrt{2}} e^{\pm i2n\pi/N} & \pm\frac{i}{\sqrt{2}} e^{\pm i2n\pi/N} & 0 \end{pmatrix} \begin{pmatrix} \mu_x \\ \mu_y \\ \mu_z \end{pmatrix}$$

$$= \frac{1}{\sqrt{N}} \sum_{n=0}^{N-1} e^{i(k \pm 2\pi/N)} \begin{pmatrix} \frac{1}{\sqrt{2}} & \frac{\pm i}{\sqrt{2}} \end{pmatrix} \begin{pmatrix} \mu_x \\ \mu_y \end{pmatrix}$$

$$= \sqrt{N} \delta_{k,\pm 2\pi/N} \mu_\pm \qquad \text{with } \mu_\pm = \frac{1}{\sqrt{2}} (\mu_x \pm i\mu_y)$$

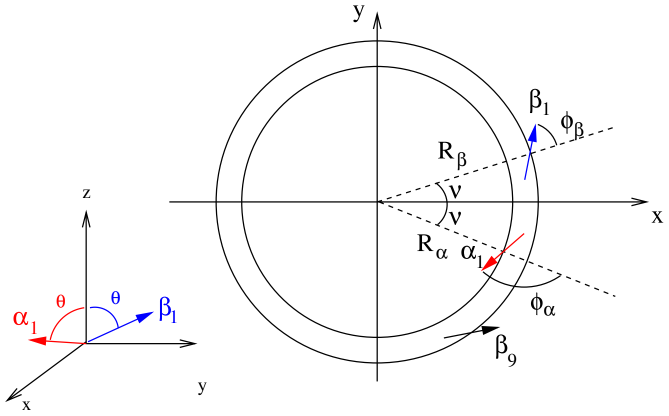
Figure 115: allowed optical transitions



21.2.3 dimerized systems of LHII

The light harvesting complex LHII contains a ring of nine weakly coupled chlorophylls and another ring of nine stronger coupled chlorophyll dimers. The two units forming a dimer will be denoted as α, β.

Figure 116: Model of the arrangement of BCHls for the LH2 of *Rps.Acidophila*



The arrows represent the transition dipole moments of the BChl molecules. R_α=26.0Å, R_β=27.2Å,$\nu = 10.3^o$,$\phi_\alpha = -112.5^o$, $\phi_\beta = 63.2^o$,$\theta = 84.9^o$.

The transition dipole moments are

$$\vec{\mu}_{n,\alpha} = \mu \begin{pmatrix} \sin\theta\cos(n\frac{2\pi}{N} - \nu + \phi_\alpha) \\ \sin\theta\sin(n\frac{2\pi}{N} - \nu + \phi_\alpha) \\ \cos\theta \end{pmatrix} = \mu S_N^n R_z(-\nu + \phi_\alpha) \begin{pmatrix} \sin\theta \\ 0 \\ \cos\theta \end{pmatrix}$$

$$\vec{\mu}_{n,\beta} = \mu \begin{pmatrix} \sin\theta\cos(n\frac{2\pi}{N} + \nu + \phi_\beta) \\ \sin\theta\sin(n\frac{2\pi}{N} + \nu + \phi_\beta) \\ \cos\theta \end{pmatrix} = \mu S_N^n R_z(+\nu + \phi_\beta) \begin{pmatrix} \sin\theta \\ 0 \\ \cos\theta \end{pmatrix}$$

from which we also find the relation

$$\vec{\mu}_{n,\beta} = R_z(2\nu + \phi_\beta - \phi_\alpha)\vec{\mu}_{n,\alpha}$$

with the experimental value

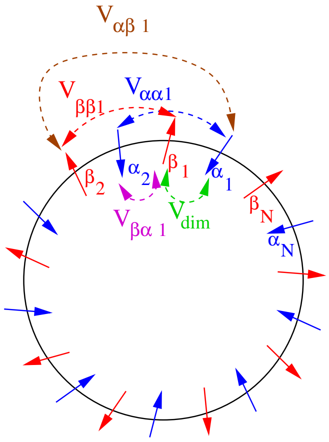
$$2\nu + \phi_\beta - \phi_\alpha = 196.3^o$$

which is very close to the value of $180^o + 20^o$ which we would expect for a circle with C_{18}-symmetrical positions but alternating transition dipole directions.

We have to distinguish the following interaction matrix elements between two monomers in different unit cells:

$$V_{\alpha,\alpha,|m|}, V_{\alpha,\beta,m} = V_{\beta,\alpha,-m}, V_{\alpha,\beta,-m} = V_{\beta,\alpha,m} V_{\beta,\beta,|m|}$$

Figure 117: dimerized ring



The interaction matrix of one dimer is

$$\begin{pmatrix} E_\alpha & V_{dim} \\ V_{dim} & E_\beta \end{pmatrix}$$

The wavefunction has to be generalized as

$$|k,s>=\frac{1}{\sqrt{N}}\sum_{n=0}^{N-1} e^{ikn}(C_{s\alpha}|n\alpha>+C_{s\beta}|n\beta>)$$

$$<k's'|H|ks>=$$

$$=\frac{1}{N}\sum_{n=0}^{N-1}\sum_{n'=0}^{N-1} e^{i(kn-k'n')}\left(C_{s'\alpha}C_{s\alpha}H_{\alpha\alpha|n-n'|}+C_{s'\beta}C_{s\beta}H_{\beta\beta|n-n'|}+C_{s'\alpha}C_{s\beta}H_{\alpha\beta(n-n')}+C_{s'\beta}C_{s\alpha}H_{\beta\alpha(n-n')}\right)$$

$$=\frac{1}{N}\begin{pmatrix} C_{s'\alpha} & C_{s'\beta} \end{pmatrix}\sum_{n=0}^{N-1}\sum_{m=0}^{N-1} e^{i(k-k')n+ik'm}\begin{pmatrix} H_{\alpha\alpha|m|} & H_{\alpha\beta m} \\ H_{\beta\alpha m} & H_{\beta\beta|m|} \end{pmatrix}\begin{pmatrix} C_{s\alpha} \\ C_{s\beta} \end{pmatrix}$$

$$=\delta_{k,k'}\begin{pmatrix} C_{s'\alpha} & C_{s'\beta} \end{pmatrix}\begin{pmatrix} \sum_{m=0}^{N-1} e^{ikm}H_{\alpha\alpha|m|} & \sum_{m=0}^{N-1} e^{ikm}H_{\alpha\beta m} \\ \sum_{m=0}^{N-1} e^{ikm}H_{\beta\alpha m} & \sum_{m=0}^{N-1} e^{ikm}H_{\beta\beta m} \end{pmatrix}\begin{pmatrix} C_{s\alpha} \\ C_{s\beta} \end{pmatrix}$$

The coefficients $C_{s\alpha}$and $C_{s\beta}$ are determined by diagonalization of the matrix

$$H_k=\begin{pmatrix} E_\alpha+2V_{\alpha\alpha,1}\cos k+\cdots & V_{dim}+e^{ik}V_{\alpha\beta,1}+e^{-ik}V_{\alpha\beta,-1}+\cdots \\ V_{dim}+e^{-ik}V_{\alpha\beta,1}+e^{ik}V_{\alpha\beta,-1}+\cdots & E_\alpha+2V_{\beta\beta,1}\cos k+\cdots \end{pmatrix}$$

If we consider only interactions between nearest neighbours this simplifies to

$$H_k=\begin{pmatrix} E_\alpha & V_{dim}+e^{-ik}W \\ V_{dim}+e^{ik}W & E_\beta \end{pmatrix} \quad \text{with } W=V_{\alpha\beta,-1}$$

with the Eigenvalues

$$E_{k,\pm} = \frac{E_\alpha + E_\beta}{2} \pm \sqrt{\frac{(E_\alpha - E_\beta)^2}{4} + V_{dim}^2 + W^2 + 2V_{dim} W \cos k}$$

which in the limit of zero energy splitting $E_\alpha = E_\beta$ becomes

$$E_{k,\pm} = E_a \pm \sqrt{V_{dim}^2 + W^2 + 2V_{dim} W \cos k}$$

and the Eigenvectors are in this limit

$$\frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ \pm e^{-i\chi} \end{pmatrix}, \quad V + e^{-ik} W = |V + e^{-ik} W| e^{i\chi}$$

The transition dipoles follow from

$$\vec{\mu}_{k,\pm} = \frac{1}{\sqrt{2N}} \sum_{n=0}^{N-1} e^{ikn} (\vec{\mu}_{n,\alpha} \pm e^{-i\chi} R_z(2\nu + \phi_\beta - \phi_\alpha) \vec{\mu}_{n,\alpha})$$

$$= \frac{1}{\sqrt{2N}} (1 \pm e^{-i\chi} R_z(2\nu + \phi_\beta - \phi_\alpha)) \sum_{n=0}^{N-1} e^{ikn} S_N^n \vec{\mu}_{0,\alpha}$$

and similar selection rules as for the simple ring system follow for the second factor

$$\frac{1}{\sqrt{N}} \sum_{n=0}^{N-1} e^{ikn} \mu_{0,z} = \sqrt{N} \delta_{k,0} \mu \cos\theta$$

$$\begin{pmatrix} \frac{1}{\sqrt{2}} & \frac{\pm i}{\sqrt{2}} \end{pmatrix} \frac{1}{\sqrt{N}} \sum_{n=0}^{N-1} e^{ikn} S_N^n \vec{\mu}_{0,\alpha} = \sqrt{N} \delta_{k,\pm 2\pi/N} \mu \sin\theta e^{\pm i(\phi_\alpha - \nu)}$$

The first factor determines the distribution of intensity among the + and - states. In the limit $V = W$ we have

$$V + e^{-ik} W = (1 + e^{-ik}) V = e^{-ik/2} (e^{ik/2} + e^{-ik/2}) V = e^{ik/2} 2V \cos k/2$$

and hence

$$\chi = k/2$$

and the first factor becomes

$$\frac{1}{\sqrt{2}} \pm \frac{1}{\sqrt{2}} e^{-ik/2} \begin{pmatrix} \cos(\pi + 2\pi/2N) & -\sin(\pi + 2\pi/2N) & \\ \sin(\pi + 2\pi/2N) & \cos(\pi + 2\pi/2N) & \\ & & 1 \end{pmatrix}$$

$$= \frac{1}{\sqrt{2}} \mp \frac{1}{\sqrt{2}} e^{-ik/2} \begin{pmatrix} \cos(2\pi/2N) & -\sin(2\pi/2N) & \\ \sin(2\pi/2N) & \cos(2\pi/2N) & \\ & & 1 \end{pmatrix}$$

For the z-component the selection rule of k=0 implies

$$\mu_{z,+} = \sqrt{2N}\delta_{k,0}\mu\cos\theta, \quad \mu_{z,-} = 0$$

and for the perpendicular components we consider

$$\frac{1}{\sqrt{2}}(\mu_{k,x}+i\mu_{k,y}) = \left(\begin{array}{ccc} \frac{1}{\sqrt{2}} & \frac{i}{\sqrt{2}} & ,0 \end{array}\right)\left(\frac{1}{\sqrt{2N}}(1 \pm e^{-ik/2}R_z(2\nu+\phi_\beta-\phi_\alpha))\sum_{n=0}^{N-1} e^{ikn}S_N^n\vec{\mu}_{0,\alpha}\right)$$

The first part

$$\left(\begin{array}{ccc} \frac{1}{\sqrt{2}} & \frac{i}{\sqrt{2}} & ,0 \end{array}\right)\left(\frac{1}{\sqrt{2N}}(1 \pm e^{-ik/2}R_z(2\nu+\phi_\beta-\phi_\alpha))\right)$$

gives

$$\left(\begin{array}{ccc} \frac{1}{\sqrt{2}} & \frac{i}{\sqrt{2}} & ,0 \end{array}\right)\left(\frac{1}{\sqrt{2}} \mp \frac{1}{\sqrt{2}}e^{-ik/2}\left(\begin{array}{ccc} \cos(\pi/N) & -\sin(\pi/N) & \\ \sin(\pi/N) & \cos(\pi/N) & \\ & & 1 \end{array}\right)\right)$$

$$= \frac{1}{2}(1 \mp e^{i\pi/N-ik/2})\left(\begin{array}{ccc} 1 & i & 0 \end{array}\right)$$

and hence

$$\frac{1}{\sqrt{2}}(\mu_{k,x}+i\mu_{k,y}) = \frac{1}{2}(1 \mp e^{i\pi/N-ik/2})\left(\begin{array}{ccc} 1 & i & 0 \end{array}\right)\sum_{n=0}^{N-1} e^{ikn}S_N^n\vec{\mu}_{0,\alpha}$$

$$= \frac{1}{2}(1 \mp e^{i\pi/N-ik/2})\sqrt{2N}\delta_{k,2\pi/N}\mu\sin\theta e^{i(\phi_\alpha-\nu)}$$

which is zero for the upper case (+ states) and

$$\frac{1}{\sqrt{2}}(\mu_{k,x}+i\mu_{k,y})\sqrt{2N}\delta_{k,2\pi/N}\mu\sin\theta e^{i(\phi_\alpha-\nu)}$$

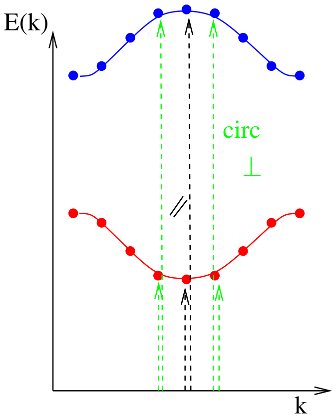
for the lower case (- states)

Similarly we find

$$\frac{1}{\sqrt{2}}(\mu_{k,x}-i\mu_{k,y})\sqrt{2N}\delta_{k,2\pi/N}\mu\sin\theta e^{-i(\phi_\alpha-\nu)}$$

for the (- states)

Figure 118: dispersion relation of the dimer ring



In the LHC the transition dipoles of the two dimer halves are antiparallel. The oscillator strengths of the N molecules are concentrated in the three lowest transitions. This means that the lifetime of the optically allowed states will be reduced compared to the radiative lifetime of a monomer. In the LHC the transition dipoles have only a very small z-component. Therefore in a perfectly symmetric structure the lowest (k=0) state is almost forbidden and has a longer lifetime than the optically allowed $k = \pm 1$ states. Due to the degeneracy of the $k = \pm 1$ states the absorption of photons coming along the symmetry axis does not depend on the polarization.

21.3 Influence of disorder

So far we considered a perfectly symmetrical arrrangement of the chromophores. In reality there exist deviations due to the protein environment and to low frequency nuclear motion which leads to variations of the site energies, the coupling matrix elements and the transition dipoles.

21.3.1 Diagonal disorder

Let us first consider a static distribution of site energies for a ring of N chromophores[61]. The Hamiltonian

$$H = \sum_{n=0}^{N-1} |n>(E_0 + \delta E_n) < n| + \sum_{n=0}^{N-1} \sum_{n'=0, n' \neq n}^{N-1} |n > V_{nn'} < n'|$$

contains energy shifts δE_n which are assumed to have a Gaussian distribution function.

$$P(\delta E_n) = \frac{1}{\Delta\sqrt{\pi}} \exp(-\delta E_n^2/\Delta^2)$$

Transforming to the delocalized states the Hamiltonian becomes

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[61] S.E.Dempster,S.Jang,R.J.Silbey, J.Chem.Phys. 114(2001)10015, S.Jang,R.J.Silbey, J.Chem.Phys. 118 (2003) 9324