Problem 3: Light harvesting complex

The circular light harvesting complex of the bacterium *Rhodopseudomonas acidophila* consists of 9 Bacteriochlorophyll dimers in a C_9-symmetric arrangement. The two subunits of a dimer are denoted as α and β . The exciton Hamiltonian with nearest neighbour interactions only is (with the index n taken as modulo 9)

$$\mathcal{H} = \sum_{n=1}^{9} \{E_\alpha |n;\alpha >< n;\alpha| + E_\beta |n;\beta >< n;\beta| + V_{dim}(|n;\alpha >< n;\beta| + h.c.) +$$

$$+V_{\beta\alpha,1}(|n-1;\alpha >< n;\beta| + |n;\beta >< n+1;\alpha|)\}$$

Transform the Hamiltonian to delocalized states

$$|k;\alpha >= \frac{1}{3}\sum_{n=1}^{9} e^{ikn\phi}|n;\alpha > \qquad |k;\beta >= \frac{1}{3}\sum_{n=1}^{9} e^{ikn\phi}|n;\beta >$$

$$k = 0, \pm 1, \pm 2, \pm 3, \pm 4 \quad \phi = 2\pi/9$$

(a) Show that states with different k-values do not interact

$$< k', \alpha(\beta)|\mathcal{H}|k, \alpha(\beta) >= 0 \quad \text{if } k \neq k'$$

(b) Find the matrix elements

$$H_{\alpha\alpha}(k) =< k;\alpha|\mathcal{H}|k;\alpha > \quad H_{\beta\beta}(k) =< k;\beta|\mathcal{H}|k;\beta > \quad H_{\alpha\beta}(k) =< k;\alpha|\mathcal{H}|k;\beta >$$

(c) Solve the Eigenvalue problem

$$\begin{pmatrix} H_{\alpha\alpha}(k) & H_{\alpha\beta}(k) \\ H^*_{\alpha\beta}(k) & H_{\beta\beta}(k) \end{pmatrix} \begin{pmatrix} C_\alpha \\ C_\beta \end{pmatrix} = E_{1,2}(k) \begin{pmatrix} C_\alpha \\ C_\beta \end{pmatrix}$$

(d) The transition dipole moments are given by

$$\vec{\mu}_{n,\alpha} = \mu \left| \begin{pmatrix} \sin\theta \, \cos(\phi_\alpha - \nu + n\phi) \\ \sin\theta \, \sin(\phi_\alpha - \nu + n\phi) \\ \cos\theta \end{pmatrix} \right| \qquad \vec{\mu}_{n,\beta} = \mu \left| \begin{pmatrix} \sin\theta \, \cos(\phi_\beta + \nu + n\phi) \\ \sin\theta \, \sin(\phi_\beta + \nu + n\phi) \\ \cos\theta \end{pmatrix} \right|$$

$$\nu = 10.3^o, \phi_\alpha = -112.5^o, \ \phi_\beta = 63.2^o, \theta = 84.9^o.$$

Determine the optically allowed transitions from the groundstate and calculate the relative intensities

Problem 1: Absorption spectrum

Within the Born-Oppenheimer approximation the rate for optical transitions of a molecule from its ground state to an electronically excited state is proportional to

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

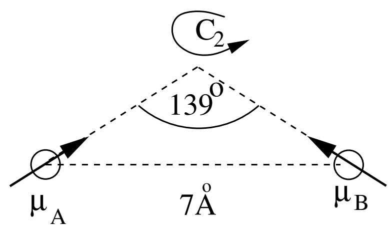
Show that this Golden rule expression can be formulated as the Fourier integral of the dipole moment correlation function

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

and that within the Condon approximation this reduces to the correlation function of the nuclear motion.

Problem 2: Photosynthetic Reaction Center

The "special pair" in the photosynthetic reaction center of Rps.viridis is a dimer of two bacteriochlorophyll molecules whose centers of mass have a distance of 7Å. The transition dipoles of the two molecules include an angle of 139^o.



Calculate energies and intensities of the two dimer bands from a simple exciton model

$$\mathcal{H} = \begin{pmatrix} -\Delta/2 & V \\ V & \Delta/2 \end{pmatrix}$$

as a function of the energy difference Δ and the interaction V. The Hamiltonian is pepresented here in a basis spanned by the two localized excited states $|A * B >$ and $|B * A >$.