Problem Set 1
Physics 498TBP / Spring 2002
Professor Klaus Schulten

Problem 1: Optical Properties of Ring of Bacteriochlorophylls

Consider a ring of 16 bacteriochlorophyll (BChl) molecules with their centers on a circle of radius 25 Å as shown in Fig. 1. A BChl is excited by light, i.e., it undergoes the transition BChl → BChl*. However, we want to actually describe such transition for the case that the BChls are interacting with each other such that the actual stationary states of the BChl system are linear combinations of states

$$|\alpha\rangle \;=\; |\mathrm{BChl}_1, \mathrm{BChl}_2 \cdots \mathrm{BChl}^*_\alpha \cdots \mathrm{BChl}_{2N}\rangle \;, \alpha \;=\; 1, 2, \ldots\; 2N \qquad (1)$$

where BChl_α is excited and all other BChls are in the ground state.
The transition dipole moments of the excited states for a single BChl, BChl_α, are

$$\vec{d}_\alpha \;=\; d_o \begin{pmatrix} \cos\phi_\alpha \\ \sin\phi_\alpha \\ 0 \end{pmatrix} \quad , \; \phi_\alpha \;=\; \frac{\pi\alpha(N\,+\,1)}{N} \;, \qquad (2)$$

where $d_o \;=\; 10$ Debye (1 Debye = 0.208 electron charge Å).
In constructing the Hamiltonian matrix in the basis of the states $|\alpha\rangle$ assume that the coupling between the BChls is given by

$$\langle\alpha|\hat{H}|\beta\rangle = \left(\frac{\vec{d}_\alpha \cdot \vec{d}_\beta}{{r_{\alpha\beta}}^3} - \frac{3(\vec{r}_{\alpha\beta} \cdot \vec{d}_\alpha)\;(\vec{r}_{\alpha\beta} \cdot \vec{d}_\beta)}{{r_{\alpha\beta}}^5} \right) \quad , \;\; \beta \neq \alpha \qquad (3)$$

and neglect all interactions except those between nearest neighbors. Assume for the excitation energies of individual BChls

$$\langle\alpha|\hat{H}|\alpha\rangle \;=\; 1.6\,\mathrm{eV}\;. \qquad (4)$$

The ground state of the system is defined as

$$|\;0\rangle \;=\; |\mathrm{BChl}_1, \mathrm{BChl}_2 \cdots \mathrm{BChl}_\alpha \cdots \mathrm{BChl}_{2N}\rangle \;, \qquad (5)$$

i.e., that state in which none of the BChls are excited.

(a) Determine the stationary states $|\tilde{n}\rangle$, n= 1, 2, ... 16 of the Hamiltonian H and the corresponding energy ϵ_n. Plot the energies.

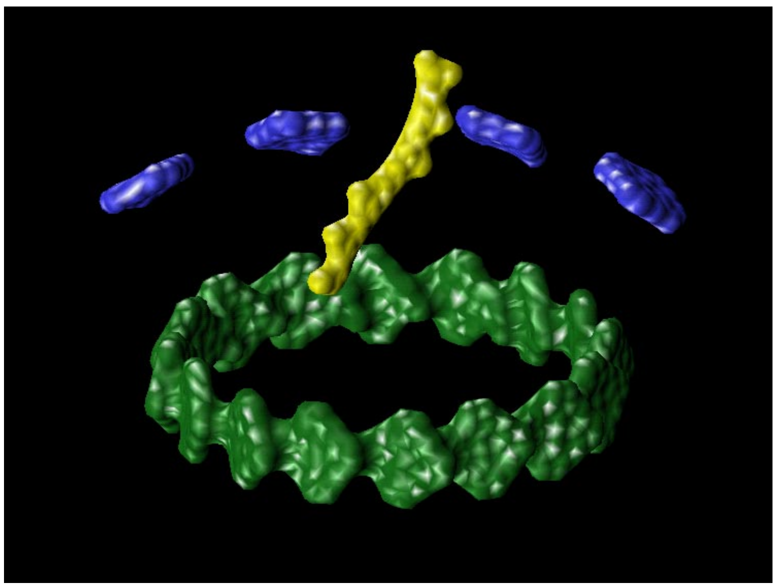

Figure 1: Spatial arrangement of the conjugated π-electron systems of the chromophores within the LH2 complex from *Rs. molischianum.* The conjugated systems are represented in surface representation. For clarity, only four of the eight B800 BChl's (blue) and one of the eight carotenoids (yellow) present in LH2 are shown. The conjugated systems within the ring of sixteen B850 BChl's (green) appear to be connected to each other. This ring of chlorophylls is the subject of the problem set.

(b) Determine the transition dipole moments $\langle 0|\mathbf{r}|\tilde{n}\rangle$ that describe the optical transitions $|0\rangle \rightarrow |\tilde{n}\rangle$. Calculate the respective transition rates and compare with the transition rates for individual BChls.

Problem 2: Semiclassical Theory of Electron Transfer

Consider electron transfer described in terms of a system coupled to a classical degree of freedom q (vibration). In the reactant state it has the energy

$$V_{\mathrm{r}}(q) = \frac{1}{2} f q^2 \tag{6}$$

whereas in the product state the energy is

$$V_{\mathrm{p}}(q) = \frac{1}{2} f (q - q_0)^2 + E_{\mathrm{red}} \quad . \tag{7}$$

The rate for the transition r $\rightarrow$ p is described by the formula

$$k_{\mathrm{cl}} = \frac{2\pi}{\hbar} |U|^2 S_{\mathrm{cl}}(0) \tag{8}$$

where U is a coupling constant not considered here. $S_{\mathrm{cl}}(E)$ is given by

$$S_{\mathrm{cl}}(E) = p_0[q(E)] \left| \frac{dq}{dE} \right| \tag{9}$$

where $p_0(q)$ is the classical Boltzmann distribution corresponding to $V_{\mathrm{r}}(q)$ and $q(E)$ is given by inverting

$$E(q) = V_{\mathrm{p}}(q) - V_{\mathrm{r}}(q) \quad . \tag{10}$$

a) Show ($\sigma_{\mathrm{cl}} = k_{\mathrm{B}} T / f$)

$$S_{\mathrm{cl}}(E) = \frac{1}{\sqrt{2\pi \sigma_{\mathrm{cl}} f^2 q_0^2}} \exp\left[- \frac{(E_0 - E + \frac{1}{2} f q_0^2)^2}{2 f^2 q_0^2 \sigma_{\mathrm{cl}}} \right] \tag{11}$$

b) Plot k_{cl} as a function of T for values of your choice.
Describe now the initial distribution quantum mechanically. For this purpose define

$$k_{\mathrm{qm}} = \frac{2\pi}{\hbar} |U|^2 S_{\mathrm{qm}}(0) \tag{12}$$

where

$$S_{\rm qm}(E) = p_{\rm qm}[q(E)]\left|\frac{dq}{dE}\right| \quad . \tag{13}$$

Here the distribution $p_{\rm qm}(q)$ is given by

$$p_{\rm qm}(q') = {\rm tr}\rho_0\delta(q-q') \tag{14}$$

and $q(E)$ is as defined above. In this expression ρ_0 is the density matrix of the oscillator described by $V_{\rm r}(q)$ and is defined in the basis of eigenstates

$$H_{\rm r}|\tilde{n}\rangle = \hbar\omega(n+\frac{1}{2})|\tilde{n}\rangle \tag{15}$$

where

$$H_{\rm r} = \frac{\hat{p}^2}{2m} + \frac{1}{2}f\hat{q}^2 \tag{16}$$

and ω is the associated frequency $\sqrt{f/m}$.

(c) Show

$$[\rho_0]_{nm} = \delta_{nm}(1-e^{-\frac{\hbar\omega}{k_BT}})e^{\frac{\hbar\omega}{2k_BT}}e^{-\frac{\hbar\omega(n+\frac{1}{2})}{k_BT}} \tag{17}$$

(d) (difficult, extra credit)
To determine $p_{\rm qm}(q)$ use

$$\delta(q-q') = \frac{1}{2\pi}\int_{-\infty}^{\infty} dx e^{ix(q-q')} \tag{18}$$

an then evaluate $\Phi(x)$ defined through

$$\begin{aligned} p_{\rm qm}(q') &= \frac{1}{2\pi}\int_{-\infty}^{\infty} dx e^{-ixq'}\Phi(x) \\ \Phi(x) &= {\rm tr}\rho_0 e^{ixq} \end{aligned} \tag{19}$$

Show

$$\Phi(x) = e^{-\frac{1}{2}\sigma_{\rm qm}x^2} \tag{20}$$

where

$$\sigma_{\rm qm} = \frac{\hbar}{2m\omega}\coth\frac{\hbar\omega}{2k_BT} \tag{21}$$

(e) Show that $S_{\rm qm}(E)$ is given by eq. 11 where $\sigma_{\rm cl}$ is replaced by $\sigma_{\rm qm}$ as defined above.

(f) Plot $k_{\rm qm}$ as a function of T. Explain why the value does not vanish for $T \to 0$ by inspecting $p_{\rm qm}(q')$ for $T \to 0$. What is $p_{\rm qm}(q')$ at $T = 0$?

Problem 3: End-End-Reaction of One-Dimensional Polymer

A one-dimensional model polymer consists of $2N$ segments $j = 1, 2, \ldots 2N$ of unit length with adjacent segments j and $j+1$ connected through joints. Each segment can have two possible orientations, one in the positive and one in the negative direction of a fixed axis. Thus, the polymer can assume 2^{2N} different conformations; each conformation is characterized by a well defined end-to-end distance x of the polymer.
(a) Show that for long polymers (N large) the equilibrium distribution of x is Gaussian and given by

$$p_0(x) \;=\; \left(4\pi b^2 N\right)^{-1/2} \exp\left(-x^2/4b^2N\right) \;, \tag{22}$$

where b is the bond length of the polymer.
(b) Demonstrate that the solution of the Smoluchowski equation

$$\tau_R\, \partial_t p(x,t) \;=\; \left(4Nb^2\partial_x^2 + 2\partial_x x\right) p(x,t) \;, \tag{23}$$

where τ_R is a characteristic relaxation time, relaxes toward the equilibrium distribution (22). Hint: Show that $p_0(x)$ as defined in (a) is a stationary solution.
(c) Show that

$$p(x,t|x_0,t_0) \;=\; \frac{1}{\sqrt{4b^2N\pi\, S(t,t_0)}} \exp\left[-\frac{\left(x \,-\, x_0\, e^{-2(t-t_0)/\tau}\right)^2}{4b^2NS(t,t_0)}\right] \tag{24}$$

$$S(t,t_0) \;=\; 1 \,-\, e^{-(t-t_0)/\tau} \tag{25}$$

is a solution of (23) for the initial condition $p(x,t_0|x_0,t_0) \;=\; \delta(x \,-\, x_0)$.

The problem set needs to be handed in by Thursday, March 7 in class.