Problem Set 8
Physics 480 / Fall 1999
Professor Klaus Schulten

Problem 1: Two-State System

A particle can exist in two states described by the vectors $|1\rangle = \binom{1}{0}$ and $|2\rangle = \binom{0}{1}$ and is described by the Schrödinger equation

$$i\hbar \frac{d}{dt} \begin{pmatrix} \alpha(t) \\ \beta(t) \end{pmatrix} = \begin{pmatrix} E_o & U \\ U & E_o \end{pmatrix} \begin{pmatrix} \alpha(t) \\ \beta(t) \end{pmatrix} . \tag{1}$$

(a) Determine the wave function $\binom{\alpha(t)}{\beta(t)}$ of the system at all times $t > t_o$ in case that the system is initially, i.e., at $t = t_o$, in state $|1\rangle$. For this purpose expand the wave function in terms of eigenvectors of the Hamiltonian matrix.
(b) Evaluate the probability that the system is found in state $|2\rangle$ at time t.
(c) Using `mathematica` repeat (a) and (b) for the case of the Hamiltonian matrix

$$\hat{H} = \begin{pmatrix} 0 & 1 \\ 1 & \delta \end{pmatrix} . \tag{2}$$

for δ values $\delta = 0$, 0.1, 1, 2, 10.

Problem 2: Displaced Harmonic Oscillator in Matrix Representation

(a) Determine by means of the operators $\hat{a}^+$ and $\hat{a}^-$ introduced in class the matrix representation of the Hamiltonian $H_a = H_o - m\omega^2 a x$ in the basis of eigenstates $|n\rangle_o$ of the undisplaced oscillator $H_o = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2$, i.e., $H_o|n\rangle_o = \hbar\omega(n + \frac{1}{2})|n\rangle_o$.

(b) Provide a simple argument why the energy of the ground state $|0\rangle_a$ is $E_{oa} = \hbar\omega(\frac{1}{2} - \frac{m\omega}{2\hbar}a^2)$.

(c) Expand the state $|0\rangle_a$ in terms of eigenstates of the undisplaced oscillator

$$|0\rangle_a = \sum_{n=0}^{\infty} c_n |n\rangle_o \tag{3}$$

and show that the coefficients c_n obey the eigenvalue problem

$$\sum_{n=0}^{\infty} (H_{mn} - E_{oa}\,\delta_{mn})\, c_n = 0 , \tag{4}$$

where

$$H_{mn} = {}_o\langle m|H_a|n\rangle_o \tag{5}$$

and E_{oa} has been determined in (a) and (b).

(d) Express c_m in terms of c_0 and determine c_o through the normalization condition ${}_a\langle 0|0\rangle_a = 1$. Sketch c_n^2 as a function of n for various a values.

Problem 3: Benzene

(a) Determine the stationary states of a quantum mechanical system described by the 6×6 Hamiltonian matrix

$$\hat{H} \;=\; \begin{pmatrix} E_o & -t & 0 & 0 & 0 & -t \\ -t & E_o & -t & 0 & 0 & 0 \\ 0 & -t & E_0 & -t & 0 & 0 \\ 0 & 0 & -t & E_o & -t & 0 \\ 0 & 0 & 0 & -t & E_o & -t \\ -t & 0 & 0 & 0 & -t & E_o \end{pmatrix} . \tag{6}$$

In this representation the basis vectors

$$\begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{pmatrix} , \begin{pmatrix} 0 \\ 1 \\ 0 \\ 0 \\ 0 \\ 0 \end{pmatrix} , \begin{pmatrix} 0 \\ 0 \\ 1 \\ 0 \\ 0 \\ 0 \end{pmatrix} , \begin{pmatrix} 0 \\ 0 \\ 0 \\ 1 \\ 0 \\ 0 \end{pmatrix} , \begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 1 \\ 0 \end{pmatrix} , \begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 1 \end{pmatrix} , \tag{7}$$

correspond to $2p$ atomic orbitals centered at the site of carbon atoms 1, 2, ..., 6 of benzene. Employ stationary states

$$\psi_n \;=\; \begin{pmatrix} \psi_{n1} \\ \psi_{n2} \\ \psi_{n3} \\ \psi_{n4} \\ \psi_{n5} \\ \psi_{n6} \end{pmatrix} \tag{8}$$

where

$$\psi_{nm} \;=\; N_n \, \exp(i \, 2 \, m \, n\pi/6) \tag{9}$$

where m, n are appropriately chosen integers. Plot the energies of the stationary state for $E_0 \;=\; 0$ and $t \;=\; 2.6$ eV.

(b) Do the same for the case of a $2N$-dimensional Hamiltonian of the same type describing electrons hopping between $2N$ sites on a ring. For $N \;\rightarrow\; \infty$ the Hamiltonian describes electrons moving in a one-dimensional crystal. Plot the energies of the stationary states for $2N \;=\; 16$.

Problem 4: Hexatriene and Carotenoids

(a) Determine the stationary states of a quantum mechanical system described by the Hamiltonian

$$\hat{H} \;=\; \begin{pmatrix} E_o & -t & 0 & 0 & 0 & 0 \\ -t & E_o & -t & 0 & 0 & 0 \\ 0 & -t & E_0 & -t & 0 & 0 \\ 0 & 0 & -t & E_o & -t & 0 \\ 0 & 0 & 0 & -t & E_o & -t \\ 0 & 0 & 0 & 0 & -t & E_o \end{pmatrix} . \tag{10}$$

Employ stationary states in the form as stated in Eq. (8) where

$$\psi_{nm} \;=\; N_n \,\sin\frac{2\,m\,n\,\pi}{7} \tag{11}$$

where m, n are appropriately chosen integers. Assume $E_0 \;=\; 0$ and $t \;=\; 2.6$ eV.

(b) Do the same for the case of a 2N-dimensional Hamiltonian of the same type that describe the electronic excitations in carotenoids.

(c) Plot the eigenvalues for N=3, 11, the latter corresponding to the carotenoid shown in Fig. 1. Plot all eigenstates for N=3.

Problem 5: Physics of Light Harvesting

An introduction to the material covered in this problem set can be found at `http://www.ks.uiuc.edu/Research/psu/psu.html`. Also note that a color version of the problem set can be found at the class web site given below.

(a) Chlorophyll molecules absorb light energy in photosynthetic life forms, e.g., in green plants, convert the absorbed radiation into electromic excitation that is transfered through a hierarchical aggregate of these molecules held in place by proteins. The excitation reaches a centrally located protein that utilizes the electromic excitation to conduct an electron across a membrane charging the respective biological cells and fueling thereby the cells' metabolism. We consider here this process in a particular photosynethtic system, that of so-called purple bacteria.
In purple bacteria the chlorophylls and other chromophores are held in place by the protein shown in Fig. 1, top. We want to describe here the ring of sixteen chlorophylls presented without the remaining part of the protein on the bottom of Fig. 1. The electronic excitations of the sixteen chlorophylls are coupled and are described approximately by a 16 $\times$16 Hamiltonian of the type (6) where the basis states of the type (7) correspond to electronic excitations of the individual chlorophylls. Assume in this case $E_0 \;=\; 1.5$ eV. Actually, the chlorophylls shown in Fig. 1, bottom, are located with their central magnesium atoms on a ring of radius 46 Å, all in the same orientation with the main molecular plane orthogonal to the ring plane and in a tangential orientation as discernable in the figure. The overall system of sixteen chlorophylls has a sixteen-fold symmetry axes, i.e., rotation by 22.5^o leaves the chlorophyll aggregate unchanged. The electronically excited chlorophylls interact with each other through van der Waals (induced dipole–induced dipole) interaction according to the expression

$$W_{jk} \;=\; C\left(\frac{\vec{d}_j\cdot\vec{d}_k}{{r_{jk}}^3} - \frac{3(\vec{r}_{jk}\cdot\vec{d}_j)\;(\vec{r}_{jk}\cdot\vec{d}_k)}{{r_{jk}}^5}\right)\,, \tag{12}$$

where $\vec{d}_j$ are unit vectors describing the direction of the j-th chlorophyl (i.e.,

tangential to the ring) and $\vec{r}_{jk}$ is the vector connecting the Mg centers of chlorophyl j with chlorophyl k. The value of C is 100 Å^3 eV.
Evaluate the respective Hamiltonian. Verify that the Hamiltonian exhibits the sixteen-fold symmetry axis before you proceed.

(b) Prove that the vectors of the type (8, 9) are eigenstates of the present Hamiltonian. Evaluate the five lowest eigenvalues and compare with the result in problem 3b.

(c) Extend now your treatment to two of the small ring proteins shown in Fig. 2. For this purpose assume two ring-like chlorophyll aggregates as in (a,b), separated by a center-to-center distance of 110 Å. Calculate the associated 32×32 Hamiltonian employing Eq. (12) and determine the 32 32-dimensional vectors that are its stationary states using Mathematica's eigenvalue and eigenvector routines. Assume an initial ($t = 0$) state in which ring 1 is in its electronic ground state as described in (a, b). Expand this state in terms of stationary states of the whole system to solve the time-dependent Schrödinger equation posed by the 32×32 Hamiltonian. Define the probability to find the electronic excitation in ring 2 at time t and plot the result. If you are unable to do the numerical calculations, describe in detail how you would do the calculations in principle, providing all needed formulas.

The problem set needs to be handed in by Tuesday,November 16.
The web page of Physics 480 is at
`http://www.ks.uiuc.edu/Services/Class/PHYS480/`

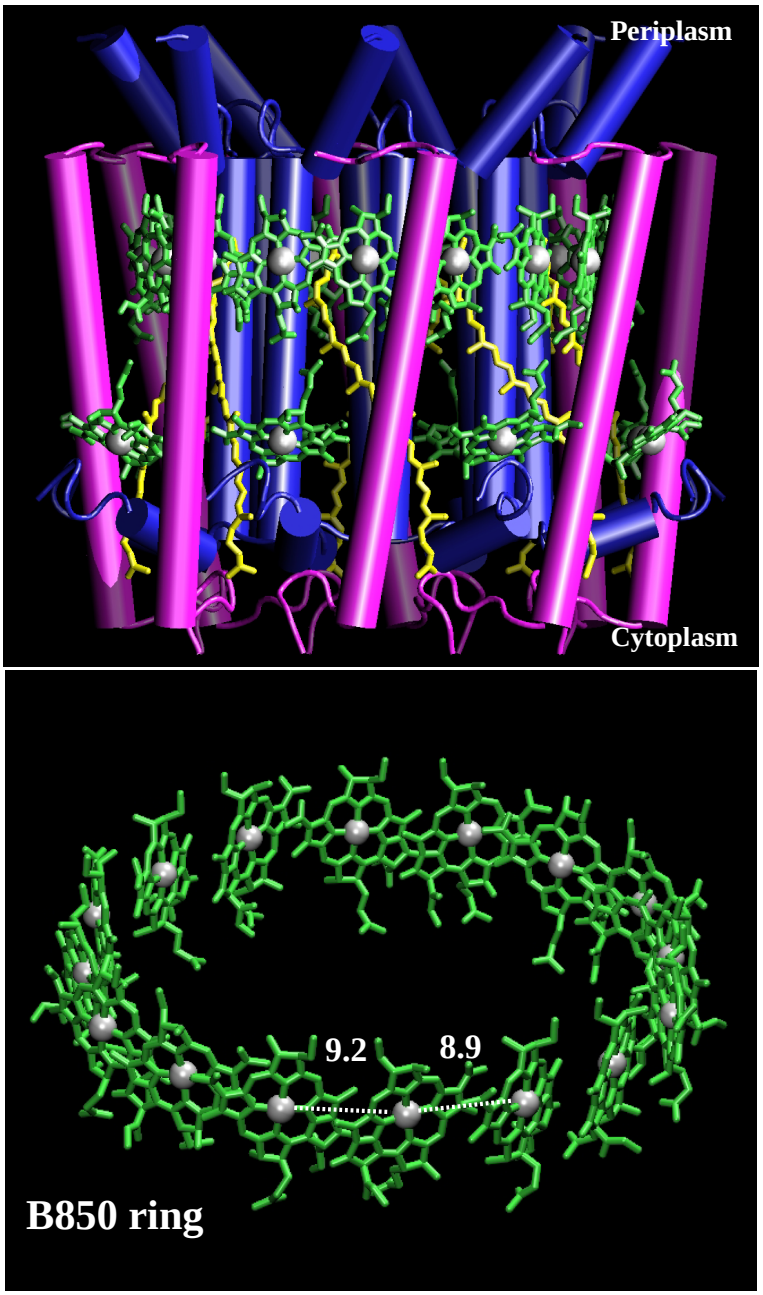

Figure 1: Light harvesting protein in a purple bacterium (see text). Top: the protei contains socalled α-helical segments that are shown as cylinders. The chlorophyll molecules are shown in green and the carotenoids are in shown yellow; Bottom: arrangement of a ring-like aggregate of sixteen chlorophyll molecules contained in the protein. Distances between central Mg atoms of two neighboring BChls are given in Å. In the present treatment we assume that the Mg atomns are all equidistant.

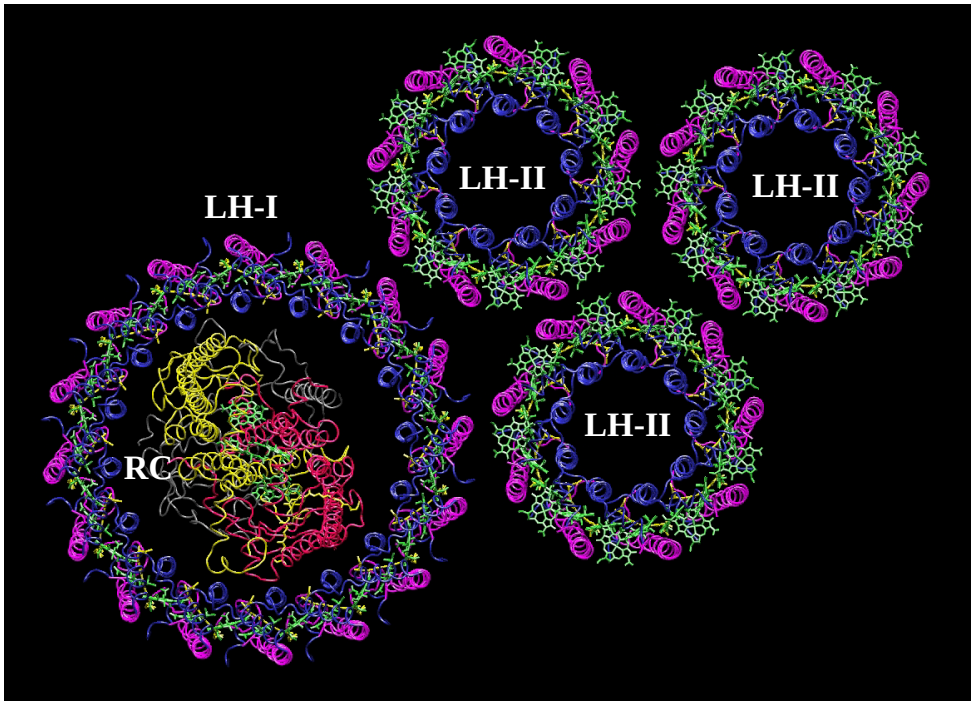

Figure 2: Arrangement of light harvesting proteins and the photosynthetic reaction center in a purple bacterium. A large ring-like protein containing an aggregate of 32 chlorophylls and sixteen carotenoids surrounds the photosynthetic reaction center that consumes electronic excitation and uses it to generate a potential energy gradient across the membrane (in the plane of the figure). The smaller proteins are of the type shown in Fig. 1. They surround the large ring protein, only three proteins being shown here. You are asked to describe electronic excittaion transfer between two of the small ring proteins.