Problem Set 1
Physics498:Theoretical Biophysics /Spring 2001
Professor Klaus Schulten

Problem 1: Spontaneous 2p → 1s emission in hydrogen atom

Determine the rate of spontaneous emission for the 2p → 1s transition in the hydrogen atom.

Problem 2: Optical Transitions in Hexatriene

Hexatriene is a molecule of atomic composition C_6H_8 and a structure as presented in Fig. 1. The relevant electronic degrees of freedom for optical transitions involve the $2p_z$ atomic orbitals of carbon atoms ϕ_j, j=1,2,3,4,5,6 (see Fig. 1). The molecular electronic wave function can be represented as a linear combination

$$\psi_n = \sum_{j=1}^{6} \alpha_j^{(n)} \phi_j. \tag{1}$$

In this case ψ_n are the eigenstates of the following Hamiltonian matrix:

$$-\begin{pmatrix} I & \beta & 0 & 0 & 0 & 0 \\ \beta & I & \beta & 0 & 0 & 0 \\ 0 & \beta & I & \beta & 0 & 0 \\ 0 & 0 & \beta & I & \beta & 0 \\ 0 & 0 & 0 & \beta & I & \beta \\ 0 & 0 & 0 & 0 & \beta & I \end{pmatrix} \begin{pmatrix} \alpha_1^{(n)} \\ \alpha_2^{(n)} \\ \alpha_3^{(n)} \\ \alpha_4^{(n)} \\ \alpha_5^{(n)} \\ \alpha_6^{(n)} \end{pmatrix} = E_n \begin{pmatrix} \alpha_1^{(n)} \\ \alpha_2^{(n)} \\ \alpha_3^{(n)} \\ \alpha_4^{(n)} \\ \alpha_5^{(n)} \\ \alpha_6^{(n)} \end{pmatrix}. \tag{2}$$

(a) Show that a solution of (2) is

$$\alpha_j^{(n)} = N \sin \frac{\pi n j}{7}. \tag{3}$$

where N is the normalizing coefficient defined through $\sum_{j=1}^{6} |\alpha_j^{(n)}|^2 = 1$. Determine the corresponding energy eigenvalues E_n. Plot the energies. Sketch which states ψ_n are occupied and which are unoccupied in the ground state of a molecule (Employ the Pauli exclusion principle). Also sketch the two lowest one-electron electronic excitations. (Notice that there are two different transitions that can bring a system to the second excited state.)
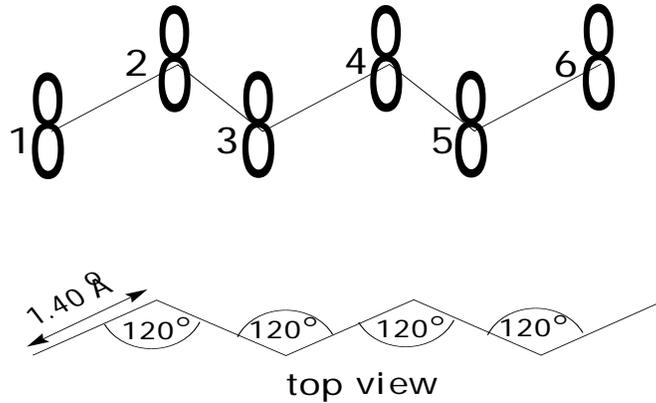
Figure 1: Hexatriene molecule (C_6H_8); approximate structure.

(b) Determine the transition dipole moments $\vec{D}_{nm}$. For this purpose derive first the formula

$$\vec{D}_{nm} = \sum_{j=1}^{6} \alpha_j^{*(n)} \alpha_j^{(m)} \vec{r}_j \ . \tag{4}$$

where $\vec{r}_j$ is the position of the center of the j-th atom. For the evaluation use $\langle \phi_j | \vec{r} | \phi_k \rangle \approx \delta_{jk} \vec{r}_j$. Determine the total rate of absorption for the lowest energy excitation in units N_ω/nanoseconds. [Note: For $n \neq m$ it does not matter where you choose the origin of your coordinate system in which you express $\vec{r}_j$.]

(c) State the selection rules for the optical transitions in hexatriene, i.e., for which type of states ψ_n, ψ_m the transition dipole element $\vec{D}_{nm}$ vanishes. For this purpose consider the symmetry properties of the obtained electronic wavefunctions. In particular, consider the symmetry with respect to 180° rotation around hexatrien's axis of symmetry. Argue that all wavefunctions are either even or odd with respect to this symmetry operation. To get the selection rules consider separately odd-odd, even-even, and odd-even (even-odd) transitions. Explain why the transition to the second one-electron excited state is forbidden, i.e., $\vec{D}_{nm} = \vec{0}$.

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Problem 3: Optical Properties of Bacteriochlorophyll Ring

Consider a ring of 16 bacteriochlorophyll (BChl) molecules with their centers on a circle of radius 25 Å as shown in Fig. 2. Assume that the circle lies in the (x, y)-plane. A BChl is excited by light, i.e., it undergoes the transition BChl $\rightarrow$ 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

$$|\alpha\rangle \;=\; |\text{BChl}_1, \text{BChl}_2 \cdots \text{BChl}^*_\alpha \cdots \text{BChl}_{2N}\rangle \,, \alpha \;=\; 1, 2, \ldots 2N \qquad (5)$$

where BChl$_\alpha$ is excited and all other BChls are in the ground state.

The transition dipole moments of the excited states for a single BChl, BChl$_\alpha$, are

$$\vec{d}_\alpha \;=\; d_o \begin{pmatrix} \cos\phi_\alpha \\ \sin\phi_\alpha \\ 0 \end{pmatrix} \quad, \; \phi_\alpha \;=\; \frac{\pi\alpha(N + 1)}{N} \,, \qquad (6)$$

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

$$\langle\alpha|\hat{H}|\beta\rangle = \left(\frac{\vec{d}_\alpha \cdot \vec{d}_\beta}{r_{\alpha\beta}{}^3} - \frac{3(\vec{r}_{\alpha\beta} \cdot \vec{d}_\alpha)\,(\vec{r}_{\alpha\beta} \cdot \vec{d}_\beta)}{r_{\alpha\beta}{}^5} \right) \quad, \; \beta \neq \alpha \qquad (7)$$

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

$$\langle\alpha|\hat{H}|\alpha\rangle \;=\; 1.6\,\text{eV} \,. \qquad (8)$$

The ground state of the system is defined as

$$|\,0\rangle \;=\; |\text{BChl}_1, \text{BChl}_2 \cdots \text{BChl}_\alpha \cdots \text{BChl}_{2N}\rangle \,, \qquad (9)$$

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.

(b) Determine the transition dipole moments $\langle 0|H|\tilde{n}\rangle$ 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.
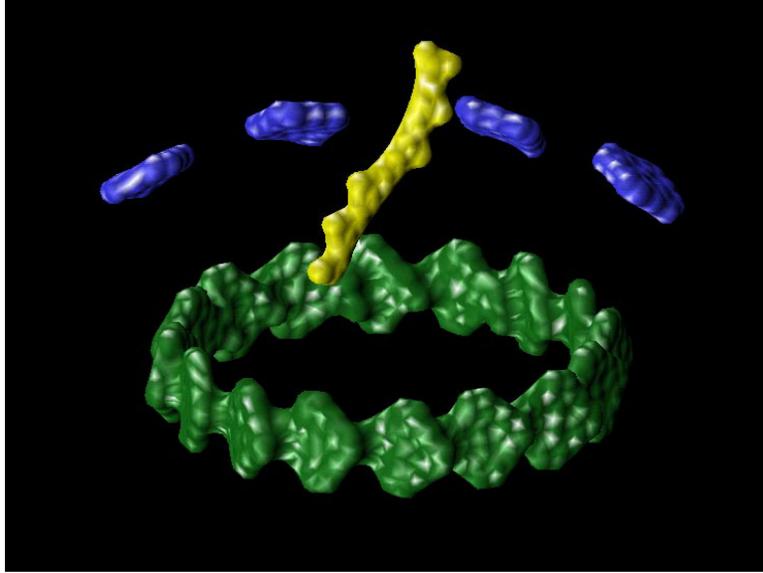
Figure 2: Spatial arrangement of the conjugated π-electron systems of the chromophores within the LH2 complex from *Rs. molischianum*. The conjugated systems are represented in surface representation. For clarity, only four of the eight B800 BChl's (blue) and one of the eight carotenoids (yellow) present 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.

(c) Assume now that the system of BChls is dimerized, i.e., the positions of BChls on the circular periphery is defined through angles

$$
\begin{aligned}
\gamma_\alpha &= \frac{\pi\alpha}{N} + \delta \, , \alpha = 1, 3, 5, \ldots \\
\gamma_\alpha &= \frac{\pi\alpha}{N} - \delta \, , \alpha = 2, 4, 6, \ldots
\end{aligned}
\tag{10}
$$

where $\delta = \pi/100$. Determine the eigenstates and energies as requested in (a).

(d) Determine the transition dipole moments for the dimerized BChl ring.

Due Tuesday, February 13th in class.