Problem Set 5
Physics 483 / Fall 2002
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.

Problem2: Selection Rules for One-Photon Absorption in Hydrogen Atoms

Determine the selection rules for one-photon absorption processes in the hydrogen atom, i.e., for which combination of quantum numbers n, ℓ, m for the initial state and n', ℓ', m' for the final state one can expect non-zero absorption rates. Assume the dipole approximation and linearly polarized radiation. Express the operator $\vec{r}$ in the matrix element $\langle \text{final state}|\, \vec{r}\, |\text{initial state}\rangle$ through linear combinations of $r\, Y_{\ell m}(\theta, \phi)$, where $Y_{\ell m}$ denotes the speherical harmonics, and use the identity

$$\int_0^\pi \int_0^{2\pi} Y_{\ell_1 m_1}(\theta,\phi)\, Y_{\ell_2 m_2}(\theta,\phi)\, Y_{\ell_3 m_3}(\theta,\phi)\, \sin\theta d\theta d\phi \tag{1}$$
$$= \left[\frac{(2\ell_1+1)(2\ell_2+1)(2\ell_3+1)}{4\pi}\right]^{\frac{1}{2}} \begin{pmatrix} \ell_1 & \ell_2 & \ell_3 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell_1 & \ell_2 & \ell_3 \\ m_1 & m_2 & m_3 \end{pmatrix}$$

Problem 3: 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

$$\psi_n = \sum_{j=1}^{n} \alpha_j^{(n)} \phi_j . \tag{2}$$

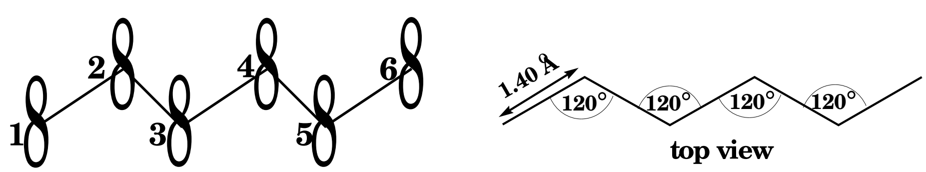

Figure 1: Hexatriene molecule (C_6H_8); approximate structure.

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

$$-\begin{pmatrix} I & \beta & 0 & 0 & 0 & 0 \\ \beta & I & \beta & 0 & 0 & 0 \\ 0 & \beta & I & \beta & 0 & 0 \\ 0 & 0 & \beta & I & \beta & 0 \\ 0 & 0 & 0 & \beta & I & \beta \\ 0 & 0 & 0 & 0 & \beta & I \end{pmatrix} \begin{pmatrix} \alpha_1^{(n)} \\ \alpha_2^{(n)} \\ \alpha_3^{(n)} \\ \alpha_4^{(n)} \\ \alpha_5^{(n)} \\ \alpha_6^{(n)} \end{pmatrix} = E_n \begin{pmatrix} \alpha_1^{(n)} \\ \alpha_2^{(n)} \\ \alpha_3^{(n)} \\ \alpha_4^{(n)} \\ \alpha_5^{(n)} \\ \alpha_6^{(n)} \end{pmatrix} . \tag{3}$$

(a) Show that a solution of (3) is

$$\alpha_j^{(n)} = N\ sin \frac{\pi n j}{7} . \tag{4}$$

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.)

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

$$\vec{D}_{nm} = \sum_{j=1}^{6} \alpha_j^{*(n)} \alpha_j^{(m)} \, \vec{r}_j \ . \tag{5}$$

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^o 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., $\vec{D}_{nm} = \vec{0}$.

Problem 5: The Bee's Compass

Bees and many other animals can perceive the polarization of the sun light scattered in the sky as it appears to an observer on the ground. You are asked to provide an estimate for the pattern of polarization across the whole sky. Assume for this purpose that the ground (earth surface) is a plane P_1, and that all scattering of the sun light in the atmosphere is due to a single elastic (Rayleigh) scattering event in the sky at positions lying in a plane P_2 coplanar to P_1 and, say, 3 km above P_1. In order to describe the scattering asume that the sun's incident radiation is everywhere parallel at points in P_2.
Attach then to each location $(x_o, y_o, 3\text{ km})$ in P_2 a right-handed coordinate system, the orthogonal axes $(\hat{u}_1, \hat{u}_2, \hat{u}_3)$ of which are oriented towards East, North, and"Up", respectively. Denote the wave vector of the sun's radiation by $\vec{k}_s$ and

its polar coordinates in the $(\hat{u}_1, \hat{u}_2, \hat{u}_3)$ coordinate system by (k_s, θ_s, ϕ_s). Define the vector $\vec{r}_{obs}$ which points from $(x_o, y_o, 3 \text{ km})$ to the position $(0, 0, 0)$ of the observer in P_1. The polar coordinates of $\vec{r}_{obs}$ in $(\hat{u}_1, \hat{u}_2, \hat{u}_3)$ are $(r_{obs}, \theta_{obs}, \phi_{obs})$. You are asked to adopt this notation in your solution.

Obviously, according to the suggested model the scattered sun light seen by the observer is due to radiation impinging on points $(x_o, y_o, 3 \text{ km})$ with wave vector (k_s, θ_s, ϕ_s) and elastically scattered into the direction $\vec{r}_{obs}$. Assume for the morning sun $(\theta_s, \phi_s) = (80^o, 0^o)$, for the sun at noon time $(\theta_s, \phi_s) = (10^o, -90^o)$, and for the evening sun $(\theta_s, \phi_s) = (80^o, 180^o)$. Assume that the sun's radiation before scattering is unpolarized.

Defining two suitable directions (see class notes on Thomson scattering) $\hat{u}^{(1)}_{obs}, \hat{u}^{(2)}_{obs}$ of polarization of the radiation scattered towards the observer, determine the scattering cross section $d\sigma_1/d\Omega_{obs}$ and $d\sigma_2/d\Omega_{obs}$ of the scattered radiation with polarization in the directions $\hat{u}^{(1)}_{obs}$ and $\hat{u}^{(2)}_{obs}$, respectively. Plot the projection of the resulting vector

$$\frac{d\sigma_1}{d\Omega_{obs}} \, \hat{u}^{(1)}_{obs} \; + \; \frac{d\sigma_2}{d\Omega_{obs}} \, \hat{u}^{(2)}_{obs} \tag{6}$$

onto the plane P_2 for the morning, noon time and evening sun, each for a representative sample of points in the P_2 plane. Explain how a bee can tell from such polarization pattern geographic North.

For your calculation use the expression for Rayleigh scattering derived in class. Assume that the relevant tensor ($\hat{e}_j, j = 1, 2, 3$ denotes the three directions of the cartesian coordinate system)

$$R_{jk} \;=\; \sum_m \frac{\langle 0|\hat{e}_j \cdot \vec{r}|m\rangle\langle m|\hat{e}_k \cdot \vec{r}|0\rangle}{\epsilon_m \;-\; \epsilon_o} \tag{7}$$

is isotropic, i.e., proportional to the 3×3 uni matrix $\mathbb{1}$.

The problem set needs to be handed in by Thursday, November 21, 2002 into the mail box of Deyu Lu in Loomis.