Problem Set 2
Physics 481 / Spring 2000
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: Preparing a Polarized 2p state in Hydrogen Atoms

Assume that planar electromagnetic radiation polarized in an arbitrary direction $\hat{u}$ excites a hydrogen atom from the 1s ground state to a 2p excited state. Determine which linear combination of 2p states will be prepared through absorption. For this purpose note that the three 2p states of the hydrogen atom are degenerate such that the derivation of the absorption rate provided in the class notes needs to be modified: choose the states $|n\rangle$ reached in the perturbation as linear combinations of three degenerate states $|n_j\rangle$, $j = 1, 2, 3$ such that the transition matrix element for one of the linear combinations

$$|\tilde{n}_k\rangle \;=\; \sum_{j=1}^{3} U_{kj}\,|n_j\rangle \quad , \; k = 1,2,3 \quad , \;\; U_{kj} \text{ unitary} \tag{1}$$

is non-zero only for one of the states $|\tilde{n}_k\rangle$, say for $k = 1$. A suitable strategy for this purpose is to assume first that the radiation is polarized into the x_3-direction, determine the proper state $|\tilde{n}_1\rangle$ (trivial!) and then rotate the coordinate system such that the x_3-axis points in the direction of $\hat{u}$.

Problem 3: 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. Express for this purpose the operator $\vec{r}$ in the transition dipole moment $\langle \text{final state}|\,\vec{r}\,|\text{initial state}\rangle$ through spherical tensor operators.

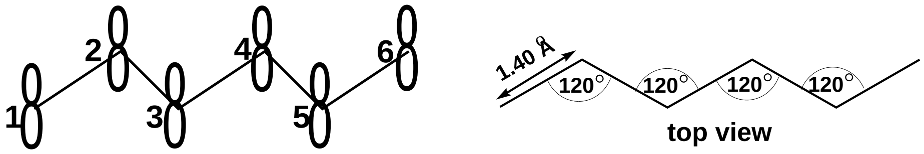

Figure 1: Hexatriene molecule (C_6H_8); approximate structure.

Problem 4: 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

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

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 Nort.
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 $\mathbb{1}$.

Problem 6: Raman scattering - voluntary, no credit

The Raman effect (see class notes) describes the occurrence of weak lines in the spectrum of the light scattered by a gas, liquid, or solid, the energy of which is displaced with respect to the energy of the incoming light. The intensity of the lines and their displacements are characteristic of the substance considered. We will consider the simplest case of the vibrational Raman spectrum for a diatomic molecule. In principle, one discerns two different cases of the Raman effect:

(a) non-resonance (usual) and
(b) resonance (enhanced) scattering.

The states of the system will be described by so-called vibronic wave functions which are products of electronic state and vibrational state wavefunctions, e.g.,

$$\Psi(\vec{r},\vec{R}) = \psi_n^{(el)}(\vec{r},\vec{R})\;\phi_m^{(vib)}(\vec{R}). \tag{8}$$

(a) At room temperature the low resolution non-resonant Raman spectrum of diatomic molecules usually consists of a single line. The frequency of the scattered light is simply shifted from that of the incident light by $\hbar\omega$ to the long-wavelength side, where ω is the vibrational frequency in the elctronic ground state. This implies, in particular, that in the case of non-resonant Raman scattering the only possible transitions in diatomic molecules are those between the two adjacent vibrational states ($\Delta n = \pm 1$, n=vibrational quantum number).

Justify this experimental observation by making use of the Kramers-Heisenberg formula for the scattering cross section of photons. (Consider only those terms in the formula which are responsible for the Raman scattering.) Derive the expression for the intensity of Raman scattering in terms of the electronic transition dipole moments between the ground and (all) excited electronic states, i.e., $\langle$gound state$|\,\vec{r}\,|$excited state$\rangle$ and their first derivatives with respect to the interatomic distance. Show that if one disregards all but the first excited electronic state, the intensity of Raman scattering is directly proportional both to the square of the electronic transition dipole moment between the ground and the first excited state and to the square of the first derivative of the electronic transition dipole moment. The energy difference between different vibrational substates of the same electronic state is assumed to be much less than the energy separation between different electronic states and, therefore, should be disregarded in the derivation.

(b) If the frequency of the incident light is close to that of one of the electronic (electronic-vibrational) transitions in a molecule then resonant Raman scattering occurs. In this case the largest contribution to the Raman part of the Kramers-Heisenberg formula comes from the summation over the vibrational substates of the resonant excited electronic state, since for these ‘resonant terms’ the denominator in the expression becomes very small. The laws valid for non-resonant scattering do not hold for resonant scattering, since in this case the contribution from different vibrational substates of the resonant electronic state varies considerably from one vibrational state to the other. In this case the energy difference between different vibrational substates of the resonant electronic state can not be disregarded any more.

Imagine a gas of molecular hydrogen under low temperature and pressure being illuminated with a laser beam. Assume that initially all the molecules are in the ground vibrational state of the electronic ground state ($^1\Sigma_g^+$). Also assume that the frequency of the incident photons is 'almost in resonance' with that of the transition from the ground state to the ground vibrational state of the first electronic excited state ($^1\Sigma_u^+$). This implies that the dominant term in the Kramers-Heisenberg formula is the one that includes the ground vibrational state of the first electronic excited state, since this is the only term that has a vanishing (very small) denominator. All other terms can be disregarded.

Show that the intensity of Raman scattering in this case is proportional to the forth power of the electronic transition dipole moment between the ground and the first excited electronic states. You are also asked to estimate the relative probabilities of finding a molecule in different final vibrational states (of the electronic ground state) after the scattering of a photon. First show that the probability of finding a molecule in a particular final vibrational state is proportional to the square of the Frank-Condon factor, i.e. of the overlap integral, between the final vibrational state and the 'intermediate' ground vibrational state of the first excited electronic state. Then, using Mathematica, evaluate these Frank-Condon factors numerically for different final vibrational states. Plot the relative probability of finding a molecule in a particular final vibrational state versus quantum number n of the final vibrational state ($n = 1 - 10$). For the hydrogen molecule the vibrational frequencies and interatomic distances are $\omega_0 = 4395$ cm^{-1} and $r_0 = 0.74$ Å in the ground state and $\omega_1 = 1357$ cm^{-1} and $r_1 = 1.30$ Å in the first excited electronic state. Note that the vibrational states for hydrogen in the electronic states $^1\Sigma_g^+$ an d$^1\Sigma_u^+$ differ in the position of the potential minimum as well as in the vibrational frequencies. In evaluating the Frank-Condon factors use the wave functions

$$\phi_n(r) \;=\; \frac{1}{\sqrt{2^n\,n!}}\left[\frac{m\omega}{\pi\hbar}\right]^{\frac{1}{4}} e^{-\frac{m\omega r^2}{2\hbar}}\, H_n\Big(\sqrt{\frac{m\omega}{\hbar}}(r-r_o)\Big) \qquad (9)$$

where $H_n(x)$ denotes the Hermite polynomial given by the `mathematica` function `HermiteH[n,x]`.

Due Tuesday, February 15 in mail box of Gheorghe-Sorin Paraoanu.