CEM 882, Problem Set 4 – Due Tuesday, April 1 – Please email a pdf to weliky@chemistry.msu.edu

Please show all units in calculations. Please make clear with arrows and carats which quantities are vectors.

1. We will do a quantum mechanical calculation of the transition rate induced by radiation between the k_1 and k_2 states of the radial atom in the xy plane with radius a_0. The calculation will be done in a "rotating frame" in which the electric field of the radiation $\boldsymbol{\varepsilon}_{rad} = \varepsilon_{rad}\, \boldsymbol{x}$. The transition rate is $|\langle \varphi_{k2} \,|\, -\boldsymbol{\mu} \,.\, \boldsymbol{\varepsilon}_{rad}\, |\varphi_{k1}\rangle|/\hbar$ where φ_{k1} is the initial eigenstate of the atom, φ_{k2} is final eigenstate of the atom, and $\boldsymbol{\mu}$ is the dipole moment operator. You can understand the plausibility of this expression by considering the time-dependent Schrodinger Equation.

a. (15 points) Derive an expression for $\boldsymbol{\mu}$ as a linear combination of $\boldsymbol{x}$ and $\boldsymbol{y}$ components and in terms of e, a_0, and ϕ.

b. (15 points) Derive an expression for $-\boldsymbol{\mu} \,.\, \boldsymbol{\varepsilon}_{rad}$ in terms of ε_{rad}, e, a_0, and ϕ. Your expression should have complex exponentials rather than sines and cosines.

c. (20 points) Derive the "selection rules", ie. the equation(s) which relate k_1 and k_2 for transitions with non-zero rates.

d. (10 points) Consider that radiative intensity = radiative power/area and consider a 1 W radiation source focused to a square with 1 mm edge length. The magnitude of the radiative electric field can be calculated using the formula that radiative electric field in V/cm ≈ square root of radiative intensity in mW/cm^2. Calculate the radiative electric field in units of V/cm and to two significant figures.

e. (15 points) Calculate the transition time for an allowed transition in units of s and to two significant figures.

f. (10 points) Is your **e** result qualitatively reasonable or is it not qualitatively reasonable? Provide a reasoned explanation for your choice.

2. Consider all π electrons of benzene as electrons of a radial atom. The 260 nm transition of benzene is interpreted to be the lowest energy transition of a π electron of this atom.

a. (30 points) Draw an energy level diagram with states and their k values of the ground state configuration of the π electrons of benzene. Because of the two spin states of an electron, there can be two electrons in each k state. Add the state(s) for the excited configuration and make sure that your energy spacings are quantitative. Use your results from problem 1 to draw arrows for the allowed radiative transition(s).

b. (20 points) Use the radiative transition wavelength to calculate the radius of benzene in units of Å and to three significant figures.

c. (10 points) Use the C–C bond length of benzene to calculate the radius of benzene in units of Å and to three significant figures.

d. (15 points) Your **b** and **c** results should be in good agreement. What is the major contributor to the energies of the π electrons? Provide a reasoned explanation for your choice.

e. (15 points) Explain the most important contribution to the π electron energies which is neglected in the **a**/**b** calculation of the benzene radius. Explain why inclusion of this contribution could lead to a different calculated radius.