ASEN-6265. Fundamentals of Spectroscopy for Optical Remote Sensing Homework #7 (Radiative Transitions)

- 1. Describe in the quantum mechanics framework: What is transition probability in QM? Please answer the question from the aspects of Schrödinger equation and superposition of states. You are encouraged to consider both semi-classical and full quantum treatments.
- 2. From the semi-classical description and time-dependent perturbation theory, derive the expression of transition probability $P_{if}(t)$ and transition probability per unit time $W_{if}(t)$ for a radiative transition from an initial state $|\Phi_i\rangle$ to a final state $|\Phi_f\rangle$ under the interaction of a radiation field with an atom. The total Hamiltonian operation is

$$\hat{H} = \hat{H}_o + \hat{H}',$$

where $\hat{H}_{o}|\varphi_{n}\rangle = E_{n}|\varphi_{n}\rangle$, $|\Phi_{n}(t)\rangle = |\varphi_{n}\rangle e^{-iE_{n}t/\hbar}$, and $\hat{H}' = \hat{F}(e^{2i\omega t} + e^{-2i\omega t})$. \hat{H}' is regarded as

a perturbation to \hat{H}_o and added to the atom at t = 0. Please show the detailed derivation procedure,

and give the conditions when the first-order perturbation theory is applicable.

3. An optically excited sodium atom Na(3P) with a spontaneous radiative lifetime $\tau(3P) = 16$ ns is placed in a cell filled with 10 mbar nitrogen (N₂) gas at a temperature of T = 400 K.

(1) Calculate the effective lifetime $\tau_{eff}(3P)$ if the quenching cross-section for Na(3P)-N₂ collisions is $\sigma_q = 4 \times 10^{-15} \text{ cm}^2$.

(2) Assume the collision cross-section for Na(3P) with air molecules is the same as Na(3P)-N₂ collisions $\sigma_q = 4 \times 10^{-15} \text{ cm}^2$. In the mesopause region (~ 90 Km), the temperature is T = 200 K, and the atmosphere pressure P = 2 X 10⁻³ mbar. The molecular weight of air molecules is about 28.

Calculate the probability $\frac{dP_{ki}^{collision}}{dt}$ of collision-induced transition and the effective lifetime under

this condition. Can we safely ignore the quenching effect in the mesopause region for the Na fluorescence based on the computation results?

(Please refer to our textbook Section 2.7 (volume I) and Section 6.3 (volume II) for the details of lifetime measurements and related knowledge for this homework problem.)

- 4. A sodium atom is placed in a cavity with walls at the temperature T, producing a thermal radiation field with spectral energy density $\rho(v)$. At what temperature T are the spontaneous and stimulated transition probabilities equal
 - (a) for the transition $3P \rightarrow 3S$ ($\lambda = 589$ nm) with $\tau(3P) = 16$ ns;
 - (b) for the hyperfine transition 3S (F = 3 \rightarrow F = 2) with τ (3F) = 1 s and ν = 1772 MHz?

- 5. Let us consider a real problem in the research of Fe resonance lidar: the radiative lifetime for three excited states of ⁵⁶Fe.
 - (1) For the excited state $z^5 F_5^o$, there are the following allowed transitions with spontaneous transition rates as below:

$$\begin{split} z^{5}F_{5}^{o} &\rightarrow a^{5}D_{4}: \ A_{k1} = 0.162 \times 10^{8} \, s^{-1} \qquad (\lambda = 371.993nm) \\ z^{5}F_{5}^{o} &\rightarrow a^{5}F_{5}: \ A_{k2} = 5.50 \times 10^{-4} \times 10^{8} \, s^{-1} \qquad (\lambda = 501.207nm) \\ z^{5}F_{5}^{o} &\rightarrow a^{5}F_{4}: \ A_{k3} = 1.14 \times 10^{-4} \times 10^{8} \, s^{-1} \qquad (\lambda = 512.736nm) \\ z^{5}F_{5}^{o} &\rightarrow a^{3}F_{4}: \ A_{k4} = 1.8 \times 10^{-6} \times 10^{8} \, s^{-1} \qquad (\lambda = 671.031nm) \end{split}$$

Please calculate the radiative lifetime of the excited state $z^5 F_5^o$.

(2) For the excited state $z^5 F_4^o$, there are the following allowed transitions with spontaneous transition rates as below:

$$z^{5}F_{4}^{o} \rightarrow a^{5}D_{3}: A_{k1} = 0.142 \times 10^{8} s^{-1} \qquad (\lambda = 373.713nm)$$

$$z^{5}F_{4}^{o} \rightarrow a^{5}D_{4}: A_{k2} = 0.0138 \times 10^{8} s^{-1} \qquad (\lambda = 367.991nm)$$

$$z^{5}F_{4}^{o} \rightarrow a^{5}F_{4}: A_{k3} = 4.66 \times 10^{-4} \times 10^{8} s^{-1} \qquad (\lambda = 505.163nm)$$

$$z^{5}F_{4}^{o} \rightarrow a^{5}F_{5}: A_{k4} = 1.39 \times 10^{-4} \times 10^{8} s^{-1} \qquad (\lambda = 493.969nm)$$

$$z^{5}F_{4}^{o} \rightarrow a^{3}F_{4}: A_{k5} = 2.4 \times 10^{-6} \times 10^{8} s^{-1} \qquad (\lambda = 658.122nm)$$

Please calculate the radiative lifetime of the excited state $z^5 F_4^o$.

(3) For the excited state $z^5 D_4^o$, there are the following allowed transitions with spontaneous transition rates as below:

$$\begin{split} z^5 D_4^o &\to a^5 D_4: \ A_{k1} = 0.0970 \times 10^8 \, s^{-1} & (\lambda = 385.991 nm) \\ z^5 D_4^o &\to a^5 D_3: \ A_{k2} = 0.0108 \times 10^8 \, s^{-1} & (\lambda = 392.291 nm) \\ z^5 D_4^o &\to a^5 F_5: \ A_{k3} = 0.0127 \times 10^8 \, s^{-1} & (\lambda = 526.954 nm) \\ z^5 D_4^o &\to a^5 F_4: \ A_{k4} = 0.00259 \times 10^8 \, s^{-1} & (\lambda = 539.713 nm) \end{split}$$

$$z^{5}D_{4}^{o} \rightarrow a^{5}F_{3}: A_{k5} = 2.7 \times 10^{-4} \times 10^{8} s^{-1} \qquad (\lambda = 550.146 nm)$$
$$z^{5}D_{4}^{o} \rightarrow a^{3}F_{4}: A_{k6} = 2.4 \times 10^{-6} \times 10^{8} s^{-1} \qquad (\lambda = 718.002 nm)$$

Please calculate the radiative lifetime of the excited state $z^5 D_4^o$.

(4) In spectroscopy, a term called transition branching ratio (or transition branching fraction) is defined as $R_B = \frac{A_{ki}}{A_k} = \frac{A_{ki}}{1/\tau_k}$ for the transition from $|k\rangle \rightarrow |i\rangle$, where A_{ki} is the spontaneous

transition rate for $|k\rangle \rightarrow |i\rangle$ and A_k is the total spontaneous transition rate associated with the upper level $|k\rangle$. Please calculate the branching ratio R_B for the transitions of $z^5 F_5^o \rightarrow a^5 D_4$ (371.993 nm), $z^5 F_4^o \rightarrow a^5 D_3$ (373.713 nm), and $z^5 D_4^o \rightarrow a^5 D_4$ (385.991 nm).



Partially energy level diagram of ⁵⁶Fe atom.

HW #7 is due on Thursday, March 30th, 2017 in class.