Fundamentals of Spectroscopy for Optical Remote Sensing
Homework #5 (Radiative Transitions)

1. 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 (for time t → large enough). 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.

2. Derive the relationship between Einstein A and B coefficients from the semi-classical theory and from the full quantum treatment.

3. An optically excited sodium atom Na(3P) with a spontaneous radiative lifetime τ(3P) = 16 ns is placed in a cell filled with 10 mbar nitrogen (N_2) gas at a temperature of T = 400 K.
(1) Calculate the effective lifetime τ_{eff}(3P) if the quenching cross-section for Na(3P)-N_2 collisions is $\sigma_q = 4 \text{ X } 10^{-15}$ cm^2.
(2) Assume the collision cross-section for Na(3P) with air molecules is the same as Na(3P)-N_2 collisions $\sigma_q = 4 \text{ X } 10^{-15}$ 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 and Section 11.3 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 ρ(ν). At what temperature T are the spontaneous and stimulated transition probabilities equal
(a) for the transition 3P → 3S (λ = 589 nm) with τ(3P) = 16 ns;
(b) for the hyperfine transition 3S (F = 3 → 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 ^{56}Fe.

(1) For the excited state $z^5F_5^o$, there are the following allowed transitions with spontaneous transition rates as below:

$$z^5F_5^o \to a^5D_4: \; A_{k1} = 0.162 \times 10^8 s^{-1} \quad (\lambda = 371.993nm)$$

$$z^5F_5^o \to a^5F_5: \; A_{k2} = 5.50 \times 10^{-4} \times 10^8 s^{-1} \quad (\lambda = 501.207nm)$$

$$z^5F_5^o \to a^5F_4: \; A_{k3} = 1.14 \times 10^{-4} \times 10^8 s^{-1} \quad (\lambda = 512.736nm)$$

$$z^5F_5^o \to a^3F_4: \; A_{k4} = 1.8 \times 10^{-6} \times 10^8 s^{-1} \quad (\lambda = 671.031nm)$$

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

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

$$z^5F_4^o \to a^5D_3: \; A_{k1} = 0.142 \times 10^8 s^{-1} \quad (\lambda = 373.713nm)$$

$$z^5F_4^o \to a^5D_4: \; A_{k2} = 0.0138 \times 10^8 s^{-1} \quad (\lambda = 367.991nm)$$

$$z^5F_4^o \to a^5F_4: \; A_{k3} = 4.66 \times 10^{-4} \times 10^8 s^{-1} \quad (\lambda = 505.163nm)$$

$$z^5F_4^o \to a^5F_5: \; A_{k4} = 1.39 \times 10^{-4} \times 10^8 s^{-1} \quad (\lambda = 493.969nm)$$

$$z^5F_4^o \to a^3F_4: \; A_{k5} = 2.4 \times 10^{-6} \times 10^8 s^{-1} \quad (\lambda = 658.122nm)$$

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

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

$$z^5D_4^o \to a^5D_4: \; A_{k1} = 0.0970 \times 10^8 s^{-1} \quad (\lambda = 385.991nm)$$

$$z^5D_4^o \to a^5D_3: \; A_{k2} = 0.0108 \times 10^8 s^{-1} \quad (\lambda = 392.291nm)$$

$$z^5D_4^o \to a^5F_5: \; A_{k3} = 0.0127 \times 10^8 s^{-1} \quad (\lambda = 526.954nm)$$

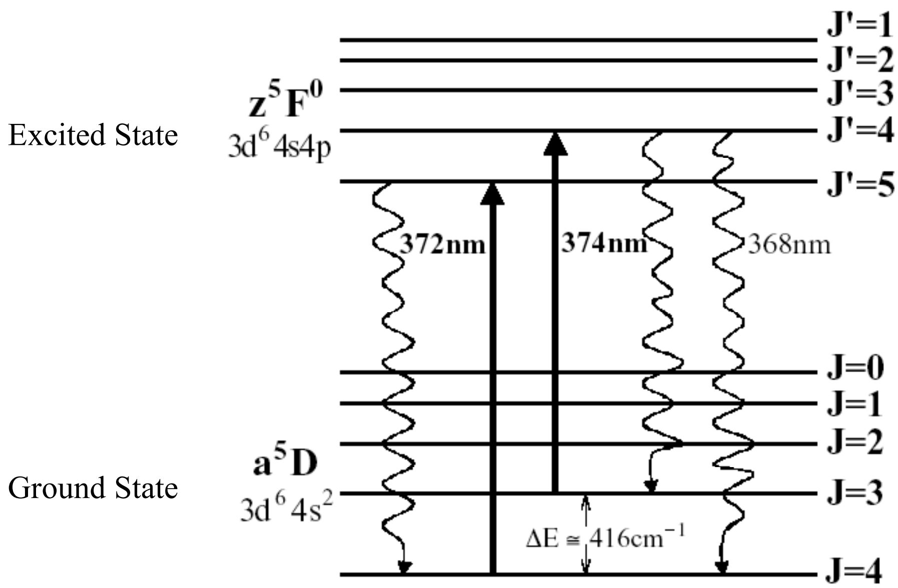
$$z^5D_4^o \to a^5F_4: \; A_{k4} = 0.00259 \times 10^8 s^{-1} \quad (\lambda = 539.713nm)$$

$$z^5D_4^o \to a^5F_3: \; A_{k5} = 2.7 \times 10^{-4} \times 10^8 s^{-1} \quad (\lambda = 550.146nm)$$

$z^5D_4^o \to a^3F_4$: $A_{k6} = 2.4 \times 10^{-6} \times 10^8 s^{-1}$ $(\lambda = 718.002 nm)$

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

(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 $|k\rangle \to |i\rangle$, where A_{ki} is the spontaneous transition rate for $|k\rangle \to |i\rangle$ 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 $z^5F_5^o \to a^5D_4$ (371.993 nm), $z^5F_4^o \to a^5D_3$ (373.713 nm), and $z^5D_4^o \to a^5D_4$ (385.991 nm).



Partially energy level diagram of ^{56}Fe atom.