# 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 ($N_2$) gas at a temperature of T = 400 K.
(1) Calculate the effective lifetime $\tau_{eff}$(3P) if the quenching cross-section for Na(3P)-$N_2$ collisions is $\sigma_q = 4 \times 10^{-15}$ cm$^2$.
(2) Assume the collision cross-section for Na(3P) with air molecules is the same as Na(3P)-$N_2$ collisions $\sigma_q = 4 \times 10^{-15}$ 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 $\rho(\nu)$. At what temperature T are the spontaneous and stimulated transition probabilities equal
(a) for the transition 3P → 3S ($\lambda$ = 589 nm) with $\tau$(3P) = 16 ns;
(b) for the hyperfine transition 3S (F = 3 → F = 2) with $\tau$(3F) = 1 s and $\nu$ = 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:

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

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

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

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

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:

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

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

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

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

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

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:

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

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

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

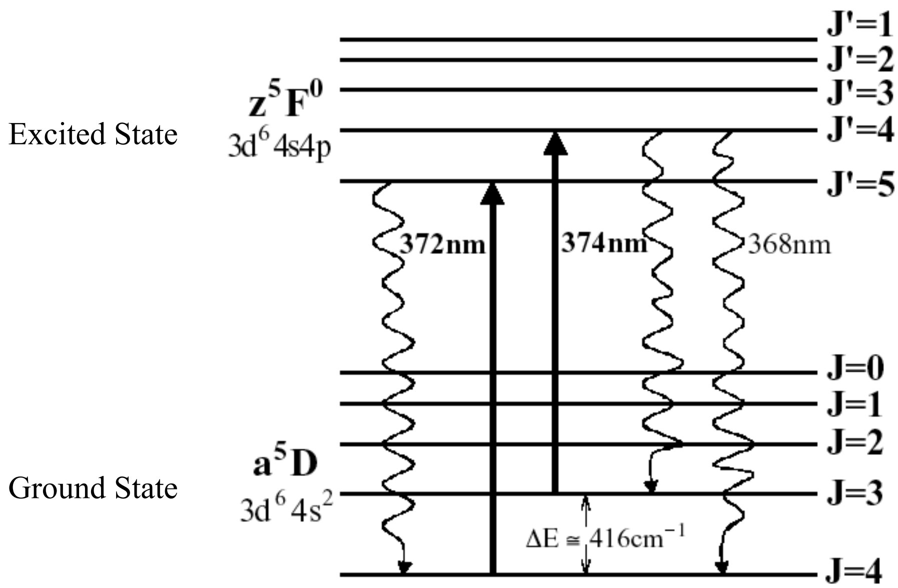
$z^5D_4^o \rightarrow a^5F_4$: $A_{k4} = 0.00259 \times 10^8 s^{-1}$ $(\lambda = 539.713 nm)$

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

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

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 $|k\rangle \rightarrow |i\rangle$, 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 $z^5F_5^o \rightarrow a^5D_4$ (371.993 nm), $z^5F_4^o \rightarrow a^5D_3$ (373.713 nm), and $z^5D_4^o \rightarrow a^5D_4$ (385.991 nm).




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

**HW #7 is due on Wednesday, October 30th, 2013 in class.**