PG SEMESTER-III (PHYSICAL CHEMISTRY SPECIALIZATION)
PROBLEMS ON TIME-DEPENDENT NON-DEGENERATE STATE PERTURBATION THEORY
ASSIGNMENT 4 (23/10/2024)

1. A time-varying Hamiltonian $H(t)$ induces transitions from state $|k\rangle$ at time $t = 0$ to a state $|j\rangle$ at time $t = t'$, with the probability $P_{k\to j}(t')$. Use the first-order time-dependent perturbation theory to show that if $P_{j\to k}(t')$ is the probability that the same Hamiltonian brings about the transition from state $|j\rangle$ to state $|k\rangle$ in the same time interval, then $P_{k\to j}(t') = P_{j\to k}(t')$.

2. A single excited state of an atom decays radiatively to the ground state. Derive the time evolution of radiated power, $P(t)$ for N_0 atoms. Show that, $P(t) = N_0\hbar\omega_0 A\exp(-\gamma t)$, where $\hbar\omega_0$ is the average photon energy and $1/\gamma$ is the radiative lifetime. The electric field is $\vec{\mathcal{E}}(t) = e\mathcal{E}_0\exp(-\gamma t/2)\cos(\omega_0 t)$ for $t \geq 0$ and $\vec{\mathcal{E}}(t) = 0$ for $t < 0$. Derive an expression for the homogeneously broadened spectral intensity, $|S(\omega)|$. In the limit $\gamma \ll \omega_0$, find an expression for $|S(\omega)|$ near $\omega = \omega_0$. If there are different isotopes of the atom in the gas, or Doppler shifts, how do you expect the appearance of the line shape, $|S(\omega)|$, to change?

3. (a) What determines the selection rules for optical transitions at frequency ω between states $|k\rangle$ and $|j\rangle$?
(b) Show that the inverse of the Einstein spontaneous emission coefficient, τ,
$$(A)^{-1} = \frac{3\pi\epsilon_0\hbar c^3}{e^2\omega^3|\langle j|r|k\rangle|^2} = \tau$$
can be rewritten for light emission of wavelength λ from electronic transitions in a harmonic oscillator potential as $(A)^{-1} = 45 \times \lambda^2(\mu\mathrm{m}) = \tau(\mathrm{ns})$, where the wavelength is measured in micrometres and time $\tau$is measured in nanoseconds.
(c) Calculate the spontaneous emission lifetime and spectral line width for an electron making a transition from the first excited state to the ground state of a harmonic oscillator potential characterized by force constant $\kappa = 3.59 \times 10^{-3}\ \mathrm{kg\ s^{-2}}$.

4. A system of atoms can make radiative transitions from an excited state to the ground state. If the probability per unit time of a transition is γ, show that the power spectrum of the radiation is a Lorentzian whose angular frequency width at half-height is equal to γ.

5. A set of identical atoms, which have two states k and j with non-degenerate energies E_k and E_j ($E_k > E_j$), are in a box whose walls are at a constant temperature. By considering the equilibrium numbers of atoms in the two states, show that
$$\frac{A}{B} = \frac{\hbar\omega_{kj}^3}{\pi^2 c^3}$$
where A and B are the Einstein coefficients for spontaneous and stimulated transitions, and $\hbar\omega_{kj} = E_k - E_j$.

6. Starting from the expression for the Einstein coefficient for spontaneous emission, show that, for an atomic electric dipole transition to the ground state in hydrogen, the fractional frequency width is of the order of α^3, where $\alpha = e^2/4\pi\epsilon_0 c\hbar$ is the fine structure constant.

7. A mercury lamp emits radiation of wavelength $254\ \mathrm{nm}$, with a fractional wavelength spread of 10^{-5}. If the output flux is $1\ \mathrm{kWm^{-2}}$, estimate the ratio of stimulated to spontaneous emission processes in the lamp.