1) Selection rules for optical absorption. In class, we derived the following formulas for the electric dipole (ED), electric quadrupole (EQ), and magnetic dipole (MD) absorption cross sections for an atom in an EM wave that is propagating in the $\hat{x}$ direction with $\mathbf{E} \parallel \hat{y}$ and $\mathbf{B} \parallel \hat{z}$:

$$
\sigma_{ED}(\omega) = \frac{4\pi^2\omega}{\hbar c}|\langle n|d_y|s\rangle|^2\delta(\omega - \omega_{ns})
$$

$$
\sigma_{EQ}(\omega) = \frac{\pi^2\omega^3}{\hbar c^3}|\langle n|Q_{xy}|s\rangle|^2\delta(\omega - \omega_{ns})
$$

$$
\sigma_{MD}(\omega) = \frac{\pi^2\omega e^2}{\hbar c^3 m^2}|\langle n|L_z + 2S_z|s\rangle|^2\delta(\omega - \omega_{ns})
$$

(1)

where the operators appearing in the matrix elements are $d_y = -ey$ and $Q_{xy} = -exy$. Similar formulas apply to waves with $\mathbf{E}$ or $\mathbf{B}$ in other Cartesian directions. If necessary, remind yourself about the Wigner-Eckart Theorem.

a) Show that if $L$ and $S$ are conserved separately, the MD transitions are forbidden, and the ED transitions obey the selection rules

$$
\Delta L = 0, \pm 1, \quad \Delta M_L = 0, \pm 1, \quad \Delta S = 0, \quad \Delta M_S = 0
$$

(2)

What are the corresponding selection rules for EQ transitions?

b) If $L$ and $S$ are conserved separately, it also follows that transitions with $\Delta L = 0$ are ED allowed for multielectron atoms but not for one-electron atoms. Explain. (Hint: If you add $L_1 + L_2$ to get a total orbital $L \in |L_1 - L_2|, ..., L_1 + L_2$, the resulting parity is $(-)^{L_1}(-)^{L_2}$, not $(-)^{L}$.)

c) In light atoms, where spin-orbit is weak, $[H, L]$ and $[H, S]$ are approximately but not exactly zero. Transitions that violate the selection rules derived in Part (a) are said to be weakly forbidden. (Weakly allowed would be an equally good term, but weakly forbidden is conventional.) Consider the three lowest energy states of the oxygen atom: $^3P$, $^1D$, and $^1S$. The $^3P$ is the ground state (it breaks up under spin-orbit interaction into closely-spaced $^3P_2$, $^3P_1$, and $^3P_0$ levels) followed by $^1D$ and $^1S$ states at about 1 eV and 2 eV above $^3P$. (All of these states are built from the $1s^22s^22p^4$ orbital configuration. The spectroscopic notation is $^{2S+1}L_J$.) Of the transitions $^1S \rightarrow ^1D$, $^1S \rightarrow ^3P_0$, $^3P_1$, $^3P_2$, and $^1D \rightarrow ^3P_0$, $^3P_1$, $^3P_2$, classify each according to whether it is absolutely forbidden (don’t forget parity!), weakly forbidden, or allowed.
(Cultural note: When weakly forbidden transitions were first observed in the suns corona and in some nebulae, it was thought that these lines corresponded to a new element, “nebulium”. Bowen, in 1928, finally showed them to be weakly forbidden transitions of familiar atoms.)

2) a) The “diamagnetic interaction” is the name for the “$A^2$ term”

\[ V^{(2)}(t) = \frac{e^2}{2mc^2} \sum_j A(r_j, t)^2 \] (3)

in the coupling between an atom and an incident EM wave which, as in Problem 1, we take to be $A(r, t) = A_0 \hat{y}e^{ikx}e^{-i\omega_0 t}$. Expanding the $e^{ikx}$ factor and keeping the first non-vanishing term, show that this interaction causes transitions from state $|s\rangle$ to state $|n\rangle$ of the atom to occur at a rate

\[ \Gamma(s \rightarrow n) = \frac{2\pi e^2 \omega_0^2 A_0^4}{\hbar^2 m^2 c^6} |d_{ns}|^2 \delta(\omega_{ns} - 2\omega_0) \] (4)

where $d_{ns}$ is the dipole matrix element between the states. (Note that the selection rules are the same as for electric dipole absorption, but the absorption occurs at frequency $2\omega_0$ instead of $\omega_0$.)

b) For visible wavelengths, what incident power (order of magnitude, in watts/cm$^2$) is necessary to make these transitions comparable in intensity to simple electric dipole transitions at $\omega_{ns} = \omega_0$?

3) This is Einstein’s “detailed balance” derivation of the spontaneous emission rate based on thermodynamic principles. Consider a cavity in which atoms are continually making transitions between ground state $|s\rangle$ and an excited state $|n\rangle$. The atoms interact with a black-body radiation field with energy density

\[ \rho_{rad}(\omega) = \frac{\hbar \omega^3}{\pi^2 c^3} \frac{1}{e^{\frac{\hbar \omega}{kT}} - 1} \] (5)

In the steady state there are on average $N_s$ atoms in the state $|s\rangle$ and $N_n$ atoms in state $|n\rangle$, in equilibrium at temperature $T$,

\[ \frac{N_s}{N_n} = e^{E_{ns}/kT}. \] (6)
Thus, everything (atoms and radiation field) is in equilibrium at temperature $T$.

a) By requiring that the rate $N_s\Gamma_{abs}$ at which atoms go from $|s\rangle \rightarrow |n\rangle$ is equal to the rate $N_n(\Gamma_{spont} + \Gamma_{stim})$ at which atoms go from $|n\rangle \rightarrow |s\rangle$, show

$$\Gamma_{spont} = \frac{\Gamma_{stim} \hbar \omega_{ns}^3}{\rho_{rad}(\omega_{ns}) \pi^2 c^3}$$  \hspace{1cm} (7)

b) Assuming that the semiclassical result

$$\sigma_{stim}(\omega) = \frac{4\pi^2\omega}{\hbar c} \sum_n |\hat{e} \cdot d_{ns}|^2 \delta(\omega - \omega_{ns})$$  \hspace{1cm} (8)

derived in class (here $\hat{e}$ is the direction of the electric field) is correct even for the fully quantum case, use this to determine $\Gamma_{stim}/\rho_{rad}$ and thus to show that (in the electric dipole approximation)

$$\Gamma_{spont} = \frac{4\omega_{ns}^3}{3\hbar c^3} |d_{ns}|^2.$$  \hspace{1cm} (9)

(In class we will later compare this with the result of a fully quantum-mechanical treatment of the radiation field.)