Homework 3

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1 Two-photon absorption in a three-level system

In this problem, we use perturbation theory to investigate two-photon absorption within a three-level atom, with states $|a\rangle, |b\rangle$ and $|c\rangle$ with energy eigenvalues $E_a = \hbar\omega_a, E_b = \hbar\omega_b$, and $E_c = \hbar\omega_c$ such that $E_c > E_b > E_a$; here $|a\rangle$ and $|c\rangle$ are assumed to have even parity and $|b\rangle$ has odd parity. In the problem that follows, we drive this three-level atom with a monochromatic field $E(t) = E_o \cos(\omega t)$ producing an interaction of the form $H_{\text{int}} = -\hat{\mu} \cdot E(t)$, and we use time-dependent perturbation theory to find the evolution of our quantum state of the form $|\psi\rangle = \sum_n \gamma_n e^{-i\omega_n t}|n\rangle$.

(a) *Assuming that our atom starts in the ground state (i.e. $\gamma_a^{(0)} = 1$), use second-order perturbation theory to find $\gamma_c^{(2)}(t)$. Through these calculations, we will assume that states $|b\rangle$ and $|c\rangle$ have finite upper state lifetimes. To emulate population decay, be sure to include a phenomenological damping into your susceptibility by making the replacement $\omega_b \to \omega_b - i\Gamma_b$ and $\omega_c \to \omega_c - i\Gamma_c$ where Γ_a and Γ_b are small compared to the transition frequencies.*

The time dependent perturbation theory is summarized as

$$\langle k|\psi(t)\rangle = \sum_{i=0}^{\infty} \gamma_k^{(i)} \mathrm{e}^{-\mathrm{i}\omega_k t}, \tag{1}$$

$$\gamma_k^{(0)} = \text{const.}, \quad \frac{\mathrm{d}\gamma_k^{(i+1)}}{\mathrm{d}t} = \frac{1}{\mathrm{i}\hbar} \sum_n H_{kn}^{(1)} \gamma_n^{(i-1)} \mathrm{e}^{\mathrm{i}(\omega_k - \omega_n)t}. \tag{2}$$

In the current case, due to parity conservation in dipole transition, only transitions $a \to b$ and $b \to c$ are possible. Therefore in the first order perturbation theory, only $\gamma_b^{(1)}$ is non-zero. We have

$$\frac{\mathrm{d}\gamma_b^{(1)}}{\mathrm{d}t} = \frac{1}{\mathrm{i}\hbar} H_{ba}^{\text{dipole}} \gamma_a^{(0)} \mathrm{e}^{\mathrm{i}(\omega_b - \omega_a)t}, \tag{3}$$

$$\begin{aligned} \gamma_b^{(1)} &= -\frac{\boldsymbol{\mu}_{ba} \cdot \boldsymbol{E}_0}{\mathrm{i}\hbar} \cdot \frac{1}{2} \int_{-\infty}^{t} \mathrm{d}t' \left(\mathrm{e}^{\mathrm{i}(\omega + \omega_b - \omega_a)t'} + \mathrm{e}^{\mathrm{i}(-\omega + \omega_b - \omega_a)t'} \right) \\ &= \frac{\boldsymbol{\mu}_{ba} \cdot \boldsymbol{E}_0}{\hbar} \cdot \frac{1}{2} \left(\frac{\mathrm{e}^{\mathrm{i}(\omega + \omega_b - \omega_a)t}}{\omega + \omega_b - \omega_a} + \frac{\mathrm{e}^{\mathrm{i}(-\omega + \omega_b - \omega_a)t}}{-\omega + \omega_b - \omega_a} \right). \end{aligned} \tag{4}$$

Here since we are interested in the response properties of the three-level system under plane waves, not, say, how fast the atom goes away from its initial state, we have pushed the lower bound to $-\infty$, and since each excited state has a finite lifetime, the $-1/(\pm\omega + \omega_b - \omega_a)$ term is simply thrown away, following the practice in the last homework and in the lectures.

Similarly, from

$$\frac{\mathrm{d}\gamma_c^{(2)}}{\mathrm{d}t} = \frac{1}{\mathrm{i}\hbar} H_{cb}^{\text{dipole}} \gamma_b^{(1)} \mathrm{e}^{\mathrm{i}(\omega_c - \omega_b)t} = -\frac{1}{\mathrm{i}\hbar} \cdot \frac{1}{2} \boldsymbol{\mu}_{cb} \cdot \boldsymbol{E}_0 (\mathrm{e}^{\mathrm{i}(\omega + \omega_c - \omega_b)t} + \mathrm{e}^{\mathrm{i}(-\omega + \omega_c - \omega_b)t}) \cdot \gamma_b^{(1)}, \tag{5}$$

we get

$$\begin{aligned} \gamma_c^{(2)} = \frac{\boldsymbol{\mu}_{cb} \cdot \boldsymbol{E}_0}{\hbar} \frac{\boldsymbol{\mu}_{ba} \cdot \boldsymbol{E}_0}{\hbar} \cdot \frac{1}{4} \Bigg(& \frac{\mathrm{e}^{\mathrm{i}(2\omega + \omega_c - \omega_a)t}}{(2\omega + \omega_c - \omega_a)(\omega + \omega_b - \omega_a)} + \\ & \frac{\mathrm{e}^{\mathrm{i}(-2\omega + \omega_c - \omega_a)t}}{(-2\omega + \omega_c - \omega_a)(-\omega + \omega_b - \omega_a)} + \frac{\mathrm{e}^{\mathrm{i}(\omega_c - \omega_a)t}}{(\omega_c - \omega_a)(\omega + \omega_b - \omega_a)} + \\ & \frac{\mathrm{e}^{\mathrm{i}(\omega_c - \omega_a)t}}{(\omega_c - \omega_a)(-\omega + \omega_b - \omega_a)} \Bigg). \end{aligned} \tag{6}$$

Since each excited state has finite lifetime, we do the substitution $\omega_{b,c} \to \omega_{b,c} - \mathrm{i}\Gamma_{b,c}$ and get

$$
\begin{aligned}
\gamma_c^{(2)} = \frac{\boldsymbol{\mu}_{cb} \cdot \boldsymbol{E}_0}{\hbar} \frac{\boldsymbol{\mu}_{ba} \cdot \boldsymbol{E}_0}{\hbar} \cdot \frac{1}{4} \Bigg(& \frac{\mathrm{e}^{\mathrm{i}(2\omega + \omega_c - \omega_a)t}}{(2\omega + \omega_c - \omega_a - \mathrm{i}\Gamma_c)(\omega + \omega_b - \omega_a - \mathrm{i}\Gamma_b)} + \\
& \frac{\mathrm{e}^{\mathrm{i}(-2\omega + \omega_c - \omega_a)t}}{(-2\omega + \omega_c - \omega_a - \mathrm{i}\Gamma_c)(-\omega + \omega_b - \omega_a - \mathrm{i}\Gamma_b)} + \\
& \frac{\mathrm{e}^{\mathrm{i}(\omega_c - \omega_a)t}}{(\omega_c - \omega_a - \mathrm{i}\Gamma_c)(\omega + \omega_b - \omega_a - \mathrm{i}\Gamma_b)} + \frac{\mathrm{e}^{\mathrm{i}(\omega_c - \omega_a)t}}{(\omega_c - \omega_a - \mathrm{i}\Gamma_c)(-\omega + \omega_b - \omega_a - \mathrm{i}\Gamma_b)} \Bigg).
\end{aligned}
\tag{7}
$$

Here in principle we should also include the imaginary parts of $\omega_{b,c}$ in the oscillating factors $\mathrm{e}^{\mathrm{i}(\cdots)t}$; if we do so, eventually we should multiply $\mathrm{e}^{\Gamma_c t}$ to the expression above. But similar to the case in the last homework, when evaluating $\langle\psi|$, we should do the substitution $\omega_{b,c} \to \omega_{b,c} + \mathrm{i}\Gamma_{b,c}$, and in the c component of $\langle\psi|$ we get a $\mathrm{e}^{\mathrm{i}(\mathrm{i}\Gamma_c)t}$ factor, which cancels the $\mathrm{e}^{\Gamma_c t}$ factor in $|\psi\rangle$; on the other hand, the imaginary parts in the denominator do not cancel and have real physical consequences when we calculate the expectation values. So we can ignore the $\mathrm{e}^{\Gamma_c t}$ factor in $\gamma_c^{(2)}$ and still get everything right.

(b) *Assuming that our energy spacing meets the condition for resonant twophoton absorption (i.e., $\omega_c - \omega_a \cong 2\omega$), perform the rotating wave approximation to simplify your result from part (a). [Hint: all of the terms with fast-oscillating phases should vanish] Use this result find the probability, P_c, that the atom occupies state $|c\rangle$. Since this probability, P_c, is independent of time it can also be viewed as the steady-state population of state $|c\rangle$.*

Since $\omega_c - \omega_a \simeq 2\omega$, only the $-2\omega + \omega_c - \omega_a$ term is the slowly-oscillating term, and by rotating wave approximation

$$
\gamma_c^{(2)} \approx \frac{\boldsymbol{\mu}_{cb} \cdot \boldsymbol{E}_0}{\hbar} \frac{\boldsymbol{\mu}_{ba} \cdot \boldsymbol{E}_0}{\hbar} \cdot \frac{1}{4} \frac{\mathrm{e}^{\mathrm{i}(-2\omega + \omega_c - \omega_a)t}}{(-2\omega + \omega_c - \omega_a - \mathrm{i}\Gamma_c)(-\omega + \omega_b - \omega_a - \mathrm{i}\Gamma_b)}. \tag{8}
$$

Thus the steady-state population on state c is

$$
P_c = |\psi_c^{(2)}| = \frac{|\boldsymbol{\mu}_{cb} \cdot \boldsymbol{E}_0|^2 |\boldsymbol{\mu}_{ba} \cdot \boldsymbol{E}_0|^2}{16\hbar^4} \frac{1}{((\omega_c - \omega_a - 2\omega)^2 + \Gamma_c^2)((\omega_b - \omega_a - \omega)^2 + \Gamma_b^2)}. \tag{9}
$$

(c) *Notice that the excited state population satisfies the following rate equation $dP_c/dt = -2\Gamma_c P_c + R_c$, where R_c is the two-photon absorption rate for the atom. Use this expression to find R_c and the two-photon absorption crosssection, $\sigma_{TPA}(I)$, at steady state; here, I is the intensity of light. For the purposes of this calcluation, assume the atom lives in a material with refractive index n. [Hint: $R_c = I\sigma_{TPA}(I)/\hbar\omega$]*

When equilibrium hasn't be achieved, since $\psi_c^{(2)} \sim \mathrm{e}^{-\Gamma_c t} \Rightarrow P_c \sim \mathrm{e}^{-2\Gamma_c t}$, the rate equation for P_c is

$$
\frac{\mathrm{d}P_c}{\mathrm{d}t} = -2\Gamma_c P_c + R_c, \tag{10}
$$

where R_c is the two-photon absorption rate for the atom. Now since the system is already in equilibrium, we have

$$
R_c = 2\Gamma_c P_c = \frac{|\boldsymbol{\mu}_{cb} \cdot \boldsymbol{E}_0|^2 |\boldsymbol{\mu}_{ba} \cdot \boldsymbol{E}_0|^2}{8\hbar^4} \frac{\Gamma_c}{((\omega_c - \omega_a - 2\omega)^2 + \Gamma_c^2)((\omega_b - \omega_a - \omega)^2 + \Gamma_b^2)}. \tag{11}
$$

The two-photon absorption (TPA) cross section can be determined by

$$
R_c \cdot \hbar\omega = I\sigma_{\mathrm{TPA}} = \text{energy absorbed per second}. \tag{12}
$$

The intensity is the time average of Poynting vector,

$$
I = \frac{1}{2} \frac{\epsilon_0 c}{n} |\boldsymbol{E}_0|^2, \tag{13}
$$

and therefore by replacing E_0^2 by I, we get

$$
\sigma_{\mathrm{TPA}} = \frac{n^2 \omega I}{2\epsilon_0 c \hbar^3} |\boldsymbol{\mu}_{cb} \cdot \hat{\boldsymbol{\epsilon}}|^2 |\boldsymbol{\mu}_{ba} \cdot \hat{\boldsymbol{\epsilon}}|^2 \frac{\Gamma_c}{((\omega_c - \omega_a - 2\omega)^2 + \Gamma_c^2)((\omega_b - \omega_a - \omega)^2 + \Gamma_b^2)}. \tag{14}
$$

Here $\hat{\boldsymbol{\epsilon}}$ is the polarization direction of the incident beam.

(d)

How to get $\frac{\mathrm{d}I}{\mathrm{d}z}$

2 Quantum treatment of nonlinear susceptibility

(a) In this section we generalize the procedure in the first problem. The external electric field now is

$$\boldsymbol{E}(t) = \sum_p \boldsymbol{E}_p \mathrm{e}^{-\mathrm{i}\omega_p t} + \text{c.c.}. \tag{15}$$

Here to simply the derivation, we follow the convention in Boyd and slightly misuse the notation in the following way:

- $\sum_p$ means to sum over all optical modes p, *and* the positive- and negative-frequencies.
- $\boldsymbol{E}(\omega_p)$, likewise, means E_p when $\omega_p > 0$, and E_p^* when $\omega_p < 0$.

In this way $\sum_p F(E(\omega_p)^*, -\omega_p)\mathrm{e}^{\mathrm{i}\omega_p t}$ can be replaced by $\sum_p F(E(\omega_p), \omega_p) \times \mathrm{e}^{-\mathrm{i}\omega_p t}$.

The zeroth order state is

$$\gamma_n^{(0)} = \delta_{n,\mathrm{g}}. \tag{16}$$

Therefore the first order perturbation is determined by

$$\frac{\mathrm{d}\gamma_m^{(1)}}{\mathrm{d}t} = \frac{1}{\mathrm{i}\hbar} \underbrace{(-\boldsymbol{\mu}_{m\mathrm{g}} \cdot \sum_p \boldsymbol{E}(\omega_p)\mathrm{e}^{-\mathrm{i}\omega_p t})}_{H_{\text{int}}} \mathrm{e}^{\mathrm{i}(\omega_m - \omega_\mathrm{g})t}, \tag{17}$$

and therefore after integration we get

$$\gamma_m^{(1)}(t) = \frac{1}{\hbar} \sum_p \frac{\boldsymbol{\mu}_{m\mathrm{g}} \cdot \boldsymbol{E}(\omega_p)}{(\omega_m - \omega_\mathrm{g} - \omega_p)} \mathrm{e}^{\mathrm{i}(\omega_m - \omega_\mathrm{g} - \omega_p)t}. \tag{18}$$

The second order perturbation is determined by

$$\frac{\mathrm{d}\gamma_m^{(2)}}{\mathrm{d}t} = \frac{1}{\mathrm{i}\hbar} \sum_n \underbrace{(-\boldsymbol{\mu}_{mn} \cdot \sum_q \boldsymbol{E}(\omega_q)\mathrm{e}^{-\mathrm{i}\omega_q t})}_{H_{\text{int}}} \mathrm{e}^{\mathrm{i}(\omega_m - \omega_n)t} \cdot \underbrace{\frac{1}{\hbar} \sum_p \frac{\boldsymbol{\mu}_{n\mathrm{g}} \cdot \boldsymbol{E}(\omega_p)}{(\omega_n - \omega_\mathrm{g} - \omega_p)} \mathrm{e}^{\mathrm{i}(\omega_n - \omega_\mathrm{g} - \omega_p)t}}_{\gamma_n^{(1)}}, \tag{19}$$

and after integration we get

$$\gamma_m^{(2)}(t) = \frac{1}{\hbar^2} \sum_{p,q} \sum_n \frac{(\boldsymbol{\mu}_{mn} \cdot \boldsymbol{E}(\omega_q))(\boldsymbol{\mu}_{n\mathrm{g}} \cdot \boldsymbol{E}(\omega_p))}{(\omega_m - \omega_\mathrm{g} - \omega_p - \omega_q)(\omega_n - \omega_\mathrm{g} - \omega_p)} \mathrm{e}^{\mathrm{i}(\omega_m - \omega_\mathrm{g} - \omega_p - \omega_q)t}. \tag{20}$$

(b) The second order polarization is given by

$$\langle \boldsymbol{\mu} \rangle = \langle \psi^{(2)} | \boldsymbol{\mu} | \psi^{(0)} \rangle + \langle \psi^{(1)} | \boldsymbol{\mu} | \psi^{(1)} \rangle + \langle \psi^{(0)} | \boldsymbol{\mu} | \psi^{(2)} \rangle \,, \tag{21}$$

and therefore