PHYS2202 Nonlinear Optics
Problem Set 3 solutions

1. (10 points) **Second order density matrix**
In class, we walked through the calculation of the second order density matrix ($\rho^{(2)}$). However, we made a mistake (OK, I made a mistake) in the moment and got zero, which I said was the wrong result. The error that I made was simply that I didn't look at every density matrix element separately; I basically added them together. Here, you will correct that mistake and find the exact density matrix $\rho^{(2)}(t)$.

As in class, we will make this as simple as possible:

(a) We will consider a two-level system of sub-wavelength spatial extent (so that we can ignore propagation effects).
(b) We will excite the system impulsively (so that our time integrals are as simple as possible).
(c) The excitation will be by a pair of co-linearly propagating pulses. (OK, we could have made this simpler and used only a single pulse, but that would be a little too simple.)
(d) We will also neglect all damping.

In other words, our system has only two eigenstates of the unperturbed Hamiltonian, $\hat{H}_0$, which we will label $|1\rangle$, the ground state, and $|2\rangle$, the excited state. We will call the unperturbed ground state energy E_1, and the excited state energy E_2. The excitation field at the material system is given by $\vec{E}(t) = \hat{z}\mathscr{E}\left[\delta\left(t - \tau_a - \frac{\vec{k}\cdot\vec{x}}{\omega_{21}}\right) + \delta\left(t - \tau_b - \frac{\vec{k}\cdot\vec{x}}{\omega_{21}}\right)\right]$. (This may look like an unusual wave, but while it is somewhat artificial, you should see that it is just a pair of delta function pulses propagating in the same direction.)

Please remember that, unless we specify otherwise, we work in the dipole approximation, and our interaction Hamiltonian has no diagonal elements in the basis of the eigenstates of the unperturbed Hamiltonian.

Assume that initially, the system is in its ground state, i.e., $\rho(t < 0) = |1\rangle\langle 1|$ or

$$\begin{pmatrix} \rho_{11}(t) & \rho_{12}(t) \\ \rho_{21}(t) & \rho_{22}(t) \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}. \tag{1}$$

Your tasks are the following.

(a) Write the density matrix (i.e., write the matrix representation of the density operator in the $(1,0),(0,1)$ basis) for all times $t > \tau$. Just write the part that depends on the time difference $\tau_b - \tau_a$, i.e., the part that depends on interactions with both of the pulses making up the exciting field.

Solution: At second order, the part of the density matrix depending on the time difference $\tau_b - \tau_a$ involves one interaction with each of the two components of the field. The Feynman diagrams describing the contributions to the process look as shown in Fig. 1. In diagram A, for example, the first interaction can only take the system into the ρ_{21} coherence, and the second interaction can only then take it into the ρ_{11} population. The contribution from diagram A is then

$$\rho_A^{(2)}(t) = \rho_{A,11}^{(2)}(t)\,|1\rangle\langle 1| \tag{2}$$

$$= \left(-\frac{i}{\hbar}\right)^2 \int_{-\infty}^{t} d\tau_2 \int_{-\infty}^{\tau_2} d\tau_1 e^{-i\tilde{\Omega}_{11}(t-\tau_2)} \vec{\mu}_{12}\cdot\hat{z}\mathscr{E}\delta\left(\tau_2-\tau_b-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}}\right) \times e^{-i\tilde{\Omega}_{21}(\tau_2-\tau_1)}\vec{\mu}_{21}\cdot\hat{z}\mathscr{E}\delta\left(\tau_1-\tau_a-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}}\right) \tag{3}$$

$$= -\left|\frac{\vec{\mu}_{21}\cdot\hat{z}\mathscr{E}}{\hbar}\right|^2 \exp\left\{-i\left[\tilde{\Omega}_{11}(t-\tau_b)+\tilde{\Omega}_{21}(\tau_b-\tau_a)\right]\right\} \tag{4}$$

$$= -\left|\frac{\vec{\mu}_{21}\cdot\hat{z}\mathscr{E}}{\hbar}\right|^2 \exp\left\{-i\omega_{21}(\tau_b-\tau_a)-\Gamma_{11}(t-\tau_b)-\Gamma_{21}(\tau_b-\tau_a)\right\} \tag{5}$$

Similarly, the diagram B makes a contribution

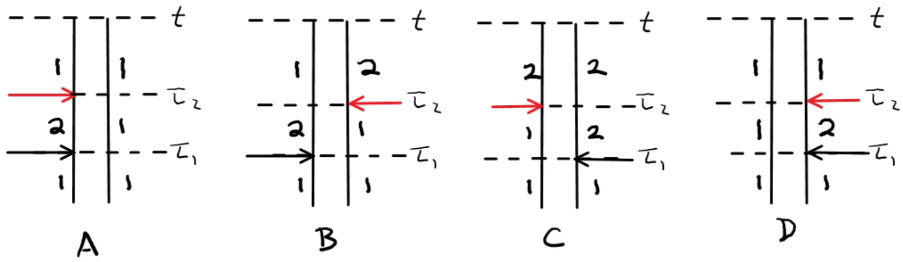

Figure 1: Time-domain double-sided Feynman diagrams for the second-order density matrix. (Error: The upper left number in diagram B should be 2.)

$$\rho_B^{(2)}(t) = \rho_{B,22}^{(2)}(t)\,|2\rangle\langle 2| \tag{6}$$

$$\rho_{B,22}^{(2)}(t) = (-1)\left(-\frac{i}{\hbar}\right)^2 \int_{-\infty}^{t} d\tau_2 \int_{-\infty}^{\tau_2} d\tau_1 e^{-i\tilde{\Omega}_{22}(t-\tau_2)} \vec{\mu}_{12}\cdot\hat{z}\mathscr{E}\delta\left(\tau_2-\tau_b-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}}\right) \times e^{-i\tilde{\Omega}_{21}(\tau_2-\tau_1)}\vec{\mu}_{21}\cdot\hat{z}\mathscr{E}\delta\left(\tau_1-\tau_a-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}}\right) \tag{7}$$

$$= \left|\frac{\vec{\mu}_{21}\cdot\hat{z}\mathscr{E}}{\hbar}\right|^2 \exp\left\{-i\left[\tilde{\Omega}_{22}(t-\tau_b)+\tilde{\Omega}_{21}(\tau_b-\tau_a)\right]\right\} \tag{8}$$

$$= \left|\frac{\vec{\mu}_{21}\cdot\hat{z}\mathscr{E}}{\hbar}\right|^2 \exp\left\{-i\omega_{21}(\tau_b-\tau_a)-\Gamma_{22}(t-\tau_b)-\Gamma_{21}(\tau_b-\tau_a)\right\}. \tag{9}$$

Diagram C is just the complex conjugate of diagram B, but if that is not obvious, we can calculate it explicitly:

$$\rho_C^{(2)}(t) = \rho_{C,22}^{(2)}(t)|2\rangle\langle 2| \tag{10}$$

$$\rho_{C,22}^{(2)}(t) = (-1)\left(-\frac{i}{\hbar}\right)^2 \int_{-\infty}^{t} d\tau_2 \int_{-\infty}^{\tau_2} d\tau_1 e^{-i\tilde{\Omega}_{22}(t-\tau_2)}\vec{\mu}_{21}\cdot\hat{z}\mathscr{E}\delta\left(\tau_2-\tau_b-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}}\right)$$
$$\times e^{-i\tilde{\Omega}_{12}(\tau_2-\tau_1)}\vec{\mu}_{12}\cdot\hat{z}\mathscr{E}\delta\left(\tau_1-\tau_a-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}}\right) \tag{11}$$

$$= \left|\frac{\vec{\mu}_{21}\cdot\hat{z}\mathscr{E}}{\hbar}\right|^2 \exp\left\{-i\left[\tilde{\Omega}_{22}(t-\tau_b)-\tilde{\Omega}_{21}(\tau_b-\tau_a)\right]\right\} \tag{12}$$

$$= \left|\frac{\vec{\mu}_{21}\cdot\hat{z}\mathscr{E}}{\hbar}\right|^2 \exp\left\{i\omega_{21}(\tau_b-\tau_a)-\Gamma_{22}(t-\tau_b)-\Gamma_{21}(\tau_b-\tau_a)\right\}. \tag{13}$$

Finally, diagram D is just the complex conjugate of diagram A. In total, then, we find that

$$\rho^{(2)}(t,\tau_b,\tau_a) = 2\left|\frac{\vec{\mu}_{21}\cdot\hat{z}\mathscr{E}}{\hbar}\right|^2 e^{-\Gamma_{21}(\tau_b-\tau_a)}\cos\left[\omega_{21}(\tau_b-\tau_a)\right]$$
$$\times\left[-e^{-\Gamma_{11}(t-\tau_b)}|1\rangle\langle 1| + e^{-\Gamma_{22}(t-\tau_b)}|2\rangle\langle 2|\right] \tag{14}$$

Note that at $t=\tau_b=\tau_a$, the trace of $\rho^{(2)}$ is zero. This makes sense insofar as the net change in population produced by excitation should be zero; only the individual populations should change but in such a way that the total sum of populations remains 1.

(b) Write the value of the expectation value of the dipole moment operator at $t>\tau$?

Solution: $<\hat{\mathbf{d}}>= \mathrm{Tr}\left(\hat{\mathbf{d}}\hat{\rho}\right)$. We will just focus on the second-order contribution. Since there are no coherences, the expectation value of the dipole moment operator is zero. If that is not clear, we can explicitly calculate the expectation value:

$$<\hat{\mathbf{d}}> = \langle 1|\hat{\mathbf{d}}\hat{\rho}^{(2)}|1\rangle + \langle 2|\hat{\mathbf{d}}\hat{\rho}^{(2)}|2\rangle \tag{15}$$
$$= \langle 1|\hat{\mathbf{d}}\hat{\mathbf{1}}\hat{\rho}^{(2)}|1\rangle + \langle 2|\hat{\mathbf{d}}\hat{\mathbf{1}}\hat{\rho}^{(2)}|2\rangle \tag{16}$$
$$= \langle 1|\hat{\mathbf{d}}\left(|1\rangle\langle 1|+|2\rangle\langle 2|\right)\hat{\rho}^{(2)}|1\rangle + \langle 2|\hat{\mathbf{d}}\left(|1\rangle\langle 1|+|2\rangle\langle 2|\right)\hat{\rho}^{(2)}|2\rangle \tag{17}$$

Recall that we define the interaction Hamiltonian as having to matrix elements between the same eigenstate of the Hamiltonian $\hat{H}_0$, so $\hat{\mathbf{d}} = d_{21}|2\rangle\langle 1| + d_{12}|1\rangle\langle 2|$. Therefore,

$$<\hat{\mathbf{d}}>= d_{12}\rho_{21}^{(2)} + d_{21}\rho_{12}^{(2)}. \tag{18}$$

We now see explicitly that if there are no coherences, $<\mathbf{d}>=0$.

2. (20 points) **The third-order density matrix** We now go two steps further than in the previous problem. We will consider the next order in the density matrix, and we will excite the system with three electromagnetic pulses that are traveling in different directions:

$$\vec{E}(t) = \hat{z}\mathscr{E}_0\left[\delta\left(t-\tau_a-\frac{\vec{k}_a\cdot\vec{x}}{\omega_{21}}\right)+\delta\left(t-\tau_b-\frac{\vec{k}_b\cdot\vec{x}}{\omega_{21}}\right)+\delta\left(t-\tau_c-\frac{\vec{k}_c\cdot\vec{x}}{\omega_{21}}\right)\right].$$

We are interested in the third-order contribution to the optical response. This will require that we calculate the third-order density matrix. As we saw in our treatment of a classical oscillator, when we have more than just a single monochromatic wave, the number of new frequencies can rapidly expand. If we include pulses in different directions, the same happens: we get new pulses characterized with wave vectors in different directions than any that were present in the input pulses. However, different frequencies and wave vectors are easy to distinguish. To separate frequencies we can use spectrometers. To separate wave vectors characterized by different directions, we can just place our detector in the path of the direction of propagation that interests us. Here, we will focus on a single direction, that given by $\vec{k}_c + \vec{k}_b - \vec{k}_a$. This will dramatically reduce the number of processes that we have to consider, since combined with the impulsive nature of our excitation it automatically chooses a small subset of interactions with the various delta function pulses.

Your tasks are the following:

(a) Calculate the entire density matrix (but only that part characterized by the wave vector specified above) at times $t > \tau_c + \frac{\vec{k}_c \cdot \vec{x}}{\omega_{21}}$.

Solution: Since we have specified the wave vector of the third-order response (at least the part of the response of interest to us here), let us start by identifying what processes could yield such a wave vector. In the following, we assume that the time ordering at position $\vec{x} = 0$ is $t > \tau_c > \tau_b > \tau_a$.

The wave vector is determined by the propagation periods, since it is during those periods that the system evolves, and the wave vector is the direction and magnitude of the fastest phase evolution as time changes. In this problem, we will have evolution periods between each interaction as well as between the final interaction and the eventual time at which we want to know the density matrix. During each evolution period, the system is evolving either in a coherence ρ_{21} or ρ_{12} or in a population ρ_{11} or ρ_{22}. To realize a density matrix that evolves as $e^{i\left(\vec{k}^{(3)} \cdot \vec{x} - \omega_{21} t\right)}$ with $\vec{k}^{(3)} = \vec{k}_c + \vec{k}_b - \vec{k}_a$, we need evolutions that look like $\exp\left\{-i\omega_{21}\left[t - (\tau_c + \frac{\vec{k}_c \cdot \vec{x}}{\omega_{21}})\right]\right\}$ and $\exp\left\{+i\omega_{21}\left[(\tau_b + \frac{\vec{k}_b \cdot \vec{x}}{\omega_{21}}) - (\tau_a + \frac{\vec{k}_a \cdot \vec{x}}{\omega_{21}})\right]\right\}$. In other words, given a time ordering $t > \tau_c > \tau_b > \tau_a$ (take $\vec{x} = 0$), the system needs to evolve in the $|1\rangle\langle 2|$ coherence between the interaction with pulses a and b and in the $|2\rangle\langle 1|$ coherence between the interaction with pulse c and the time at which we want to know the density matrix.

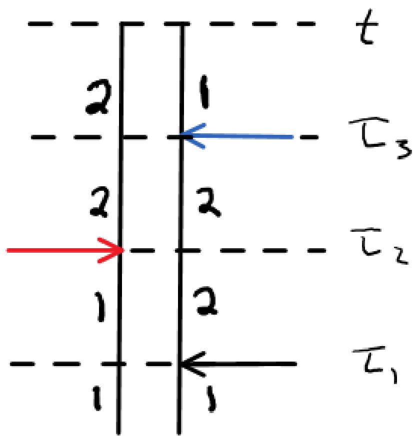

Figure 2: Double-sided Feynman diagram for component of the density matrix with wave vector $\vec{k}_c + \vec{k}_b - \vec{k}_a$

Since each interaction must change the state on the left or right side of the diagram, the relevant double-sided Feynman diagram is shown in Fig. 2. The process described by this diagram yields a third-order density matrix at time t given by $\hat{\rho}^{(3)}(t) = \rho_{21}^{(3)}(t)\,|2\rangle\,\langle 1|$, where

$$\begin{aligned}\rho_{21}^{(3)}(t) = (-1)^2\left(-\frac{i}{\hbar}\right)^3 \int_{-\infty}^{t} d\tau_3 \int_{-\infty}^{\tau_3} d\tau_2 \int_{-\infty}^{\tau_2} d\tau_1 \Bigg\{\left[-\frac{\vec{d}_{12}\cdot\hat{z}\mathscr{E}_0}{\hbar}\delta\left(\tau_1-\tau_a-\frac{\vec{k}_a\cdot\vec{x}}{\omega_{21}}\right)\right]\\ \times\left[-\frac{\vec{d}_{21}\cdot\hat{z}\mathscr{E}_0}{\hbar}\delta\left(\tau_2-\tau_b-\frac{\vec{k}_b\cdot\vec{x}}{\omega_{21}}\right)\right]\left[-\frac{\vec{d}_{21}\cdot\hat{z}\mathscr{E}_0}{\hbar}\delta\left(\tau_3-\tau_c-\frac{\vec{k}_c\cdot\vec{x}}{\omega_{21}}\right)\right]\\ \times\exp\left[-i\tilde{\Omega}_{21}\left(t-\tau_3\right)\right]\exp\left[-i\tilde{\Omega}_{22}\left(\tau_3-\tau_2\right)\right]\exp\left[-i\tilde{\Omega}_{12}\left(\tau_2-\tau_1\right)\right]\Bigg\}. \qquad (19)\end{aligned}$$

Thanks to the delta functions, integration is straightforward

$$\begin{aligned}\rho_{21}^{(3)}(t) &= -i\frac{\left|\vec{d}_{21}\cdot\hat{z}\right|^2\vec{d}_{21}\cdot\hat{z}\mathscr{E}_0^3}{\hbar^3}\exp\Bigg\{-i\tilde{\Omega}_{21}\left[t-\left(\tau_c+\frac{\vec{k}_c\cdot\vec{x}}{\omega_{21}}\right)\right] \qquad (20)\\ &-\Gamma_{22}\left[\left(\tau_c+\frac{\vec{k}_c\cdot\vec{x}}{\omega_{21}}\right)-\left(\tau_b+\frac{\vec{k}_b\cdot\vec{x}}{\omega_{21}}\right)\right]-i\tilde{\Omega}_{12}\left[\left(\tau_b+\frac{\vec{k}_b\cdot\vec{x}}{\omega_{21}}\right)-\left(\tau_a+\frac{\vec{k}_a\cdot\vec{x}}{\omega_{21}}\right)\right]\Bigg\}\\ &= -i\frac{\left|\vec{d}_{21}\cdot\hat{z}\right|^2\vec{d}_{21}\cdot\hat{z}\mathscr{E}_0^3}{\hbar^3}\exp\left\{i\left[\left(\vec{k}_c+\vec{k}_b-\vec{k}_a\right)\cdot\vec{x}-\omega_{21}(t-\tau_c-(\tau_b-\tau_a))\right]\right\} \qquad (21)\\ &\times\exp\left\{-\Gamma_{21}\left[(t-\tau_c+\tau_b-\tau_a)-\frac{\left(\vec{k}_c-\vec{k}_b+\vec{k}_a\right)\cdot\vec{x}}{\omega_{21}}\right]\right\}\\ &\times\exp\left\{-\Gamma_{22}\left[\tau_c-\tau_b+\frac{\left(\vec{k}_c-\vec{k}_b\right)\cdot\vec{x}}{\omega_{21}}\right]\right\}. \qquad (22)\end{aligned}$$

Note that in the case that $\vec{x}=0$ this is simply

$$\begin{aligned}\rho_{21}^{(3)}(t) &= -i\frac{\left|\vec{d}_{21}\cdot\hat{z}\right|^2\vec{d}_{21}\cdot\hat{z}\mathscr{E}_0^3}{\hbar^3}\exp\left\{-i\left[\omega_{21}(t-\tau_c-(\tau_b-\tau_a))\right]\right\} \qquad (23)\\ &\times\exp\left\{-\Gamma_{21}\left(t-\tau_c+\tau_b-\tau_a\right)-\Gamma_{22}\left(\tau_c-\tau_b\right)\right\}. \qquad (24)\end{aligned}$$

(b) Write down the density matrix at time t given by $t-\tau_c=\tau_b-\tau_a$.
At this time, the last equation becomes simply

$$\begin{aligned}\rho_{21}^{(3)}(t) &= -i\frac{\left|\vec{d}_{21}\cdot\hat{z}\right|^2\vec{d}_{21}\cdot\hat{z}\mathscr{E}_0^3}{\hbar^3}\exp\left\{i\left[\left(\vec{k}_c+\vec{k}_b-\vec{k}_a\right)\cdot\vec{x}\right]\right\} \qquad (25)\\ &\times\exp\left\{-\Gamma_{21}\left[2\left(\tau_b-\tau_a\right)-\frac{\left(\vec{k}_c-\vec{k}_b+\vec{k}_a\right)\cdot\vec{x}}{\omega_{21}}\right]\right\}\\ &\times\exp\left\{-\Gamma_{22}\left[\tau_c-\tau_b+\frac{\left(\vec{k}_c-\vec{k}_b\right)\cdot\vec{x}}{\omega_{21}}\right]\right\}. \qquad (26)\end{aligned}$$

Note that in the case that $\vec{x} = 0$, this is simply

$$\rho_{21}^{(3)}(t) = -i\frac{\left|\vec{d}_{21} \cdot \hat{z}\right|^2 \vec{d}_{21} \cdot \hat{z}\mathscr{E}_0^3}{\hbar^3} \exp\left\{-\Gamma_{21}\left[2\left(\tau_b - \tau_a\right)\right] - \Gamma_{22}\left[\tau_c - \tau_b\right]\right\}. \tag{27}$$

(c) Suppose now that we have an ensemble of almost (but not quite) identical oscillators characterized by a continuous distribution, $g(\omega_{21})$, of resonant frequencies ω_{21}, where the width of the distribution $g(\omega_{21})$ is $\Delta\omega_{21}$. The density matrix must now be determined by averaging over all the frequencies.

i. Write down the density matrix at time $(t - \tau_c) - (\tau_b - \tau_a) >> \frac{1}{\Delta\omega_{21}}$.

ii. Write the density matrix at time $t - \tau_c = \tau_b - \tau_a$.

Note that you do not need to know the exact distribution $g(\omega_{21})$. We are not looking for a precise answer, just a reasonable estimate. If you really want a distribution, you can assume a Gaussian distribution.

Solution: It is easiest to see what happens if we let $\vec{x} = 0$. In this case, when we integrate over the distribution of ω_{21}, we can pull everything out of the integral in Eq. 23 that is independent of ω_{21}:

$$\rho_{\text{total},21}^{(3)}(t) = \int d\omega_{21}'\, g(\omega_{21}')\rho_{21}^{(3)}(\omega_{21}', t) \tag{28}$$

$$= -i\frac{\left|\vec{d}_{21} \cdot \hat{z}\right|^2 \vec{d}_{21} \cdot \hat{z}\mathscr{E}_0^3}{\hbar^3} \exp\left\{-\Gamma_{21}\left(t - \tau_c + \tau_b - \tau_a\right) - \Gamma_{22}\left(\tau_c - \tau_b\right)\right\}$$
$$\times \int d\omega_{21}'\, g(\omega_{21}') \exp\left\{-i\left[\omega_{21}'(t - \tau_c - (\tau_b - \tau_a))\right]\right\}. \tag{29}$$

The key point here is that the integrand here is oscillatory; for a given set of times, the integrand oscillates as ω_{21}' varies *unless* $t - \tau_c = \tau_b - \tau_a$. In the latter case, the integrand is just the distribution function $g(\omega_{21}'$, which statistically should integrate to 1. In short, we get 0 for the density matrix unless $t - \tau_c = \tau_b - \tau_a$, in which case we get a finite value:

$$\rho_{\text{total},21}^{(3)}(t) = -i\frac{\left|\vec{d}_{21} \cdot \hat{z}\right|^2 \vec{d}_{21} \cdot \hat{z}\mathscr{E}_0^3}{\hbar^3} \exp\left\{-\Gamma_{21}\left(t - \tau_c + \tau_b - \tau_a\right) - \Gamma_{22}\left(\tau_c - \tau_b\right)\right\} \tag{30}$$