

Problem 1 ((10 points) Second order density matrix) Score: _____. In class, we walk 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 integral are as simple as possible).
- (c) The excitation will be by a pair of co-linearly propagation pulse. (OK, we could have made this simpler and used only a simple pulse, but that would be a little too simple.)
- (d) We will also neglect 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 $\vec{E}(t) = \hat{z}\mathcal{E}[\delta(t - \tau_a - \frac{\vec{k}\cdot\vec{x}}{\omega_{21}}) + \delta(t - \tau_b - \frac{\vec{k}\cdot\vec{x}}{\omega_{21}})]$. (This may look like an unusual wave, but while it is somewhat artificial, you should see that it is just a pair 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.

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

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

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 interaction with both of the pulse making up the exciting field.
- (b) Write the value of the expectation value of the dipole moment operator at $t > \tau$?

Solution: (a) Without loss of generality, we set $\tau_a < \tau_b$. The second-order density matrix for time $t > \tau = \max\{\tau_a + \frac{\vec{k}\cdot\vec{x}}{\omega_{21}}, \tau_b + \frac{\vec{k}\cdot\vec{x}}{\omega_{21}}\}$ is

$$\begin{aligned} \hat{\rho}^{(2)}(t) &= \left(-\frac{i}{\hbar}\right)^2 \hat{U}_0(t) \int_{-\infty}^t d\tau_1 \int_{-\infty}^{\tau_1} d\tau_2 [\hat{H}'_I(\tau_1), [\hat{H}'_I(\tau_2), \hat{\rho}_0]] \hat{U}_0(-t) \\ &= \left(-\frac{i}{\hbar}\right)^2 \hat{U}_0(t) \int_{-\infty}^t d\tau_1 \int_{-\infty}^{\tau_1} d\tau_2 [\hat{H}'_I(\tau_2) \hat{H}'_I(\tau_1) \hat{\rho}_0 - \hat{H}'_I(\tau_2) \hat{\rho}_0 \hat{H}'_I(\tau_1) - \hat{H}'_I(\tau_1) \hat{\rho}_0 \hat{H}'_I(\tau_2) + \hat{\rho}_0 \hat{H}'_I(\tau_1) \hat{H}'_I(\tau_2)] \hat{U}_0(-t) \\ &= \left(-\frac{i}{\hbar}\right)^2 \left[\int_{-\infty}^t d\tau_2 \int_{-\infty}^{\tau_2} d\tau_1 \hat{U}_0(t - \tau_2) \hat{H}_I(\tau_2) \hat{U}_0(\tau_2 - \tau_1) \hat{H}_I(\tau_1) \hat{\rho}_0 \hat{U}_0(-(\tau_2 - \tau_1)) \hat{U}_0(-(t - \tau_2)) \right. \\ &\quad - \int_{-\infty}^t d\tau_2 \int_{-\infty}^{\tau_2} d\tau_1 \hat{U}_0(t - \tau_2) \hat{H}_I(\tau_2) \hat{U}_0(\tau_2 - \tau_1) \hat{\rho}_0 \hat{H}_I(\tau_1) \hat{U}_0(-(\tau_2 - \tau_1)) \hat{U}_0(-(t - \tau_2)) \\ &\quad - \int_{-\infty}^t d\tau_2 \int_{-\infty}^{\tau_2} d\tau_1 \hat{U}_0(t - \tau_2) \hat{U}_0(\tau_2 - \tau_1) \hat{H}_I(\tau_1) \hat{\rho}_0 \hat{U}_0(-(\tau_2 - \tau_1)) \hat{H}_I(\tau_2) \hat{U}_0(-(t - \tau_2)) \\ &\quad \left. + \int_{-\infty}^t d\tau_2 \int_{-\infty}^{\tau_2} d\tau_1 \hat{U}_0(t - \tau_2) \hat{U}_0(\tau_2 - \tau_1) \hat{\rho}_0 \hat{H}_I(\tau_1) \hat{U}_0(-(\tau_2 - \tau_1)) \hat{H}_I(\tau_2) \hat{U}_0(-(t - \tau_2)) \right] \\ &= \left(-\frac{i}{\hbar}\right)^2 \left[\int_{-\infty}^t d\tau_2 \int_{-\infty}^{\tau_2} d\tau_1 \hat{U}_0(t - \tau_2) \hat{H}_I(\tau_2) \hat{U}_0(\tau_2 - \tau_1) [(-\vec{p} \cdot \vec{E}(\tau_1))_{12} |1\rangle\langle 2| + (-\vec{p} \cdot \vec{E}(\tau_1))_{21} |2\rangle\langle 1|] |1\rangle\langle 1| \hat{U}_0(-(\tau_2 - \tau_1)) \hat{U}_0(-(t - \tau_2)) \right. \\ &\quad - \int_{-\infty}^t d\tau_2 \int_{-\infty}^{\tau_2} d\tau_1 \hat{U}_0(t - \tau_2) \hat{H}_I(\tau_2) \hat{U}_0(\tau_2 - \tau_1) |1\rangle\langle 1| [(-\vec{p} \cdot \vec{E}(\tau_1))_{12} |1\rangle\langle 2| + (-\vec{p} \cdot \vec{E}(\tau_1))_{21} |2\rangle\langle 1|] \hat{U}_0(-(\tau_2 - \tau_1)) \hat{U}_0(-(t - \tau_2)) \\ &\quad - \int_{-\infty}^t d\tau_2 \int_{-\infty}^{\tau_2} d\tau_1 \hat{U}_0(t - \tau_2) \hat{U}_0(\tau_2 - \tau_1) [(-\vec{p} \cdot \vec{E}(\tau_1))_{12} |1\rangle\langle 2| + (-\vec{p} \cdot \vec{E}(\tau_1))_{21} |2\rangle\langle 1|] |1\rangle\langle 1| \hat{U}_0(-(\tau_2 - \tau_1)) \hat{H}_I(\tau_2) \hat{U}_0(-(t - \tau_2)) \\ &\quad \left. + \int_{-\infty}^t d\tau_2 \int_{-\infty}^{\tau_2} d\tau_1 \hat{U}_0(t - \tau_2) \hat{U}_0(\tau_2 - \tau_1) |1\rangle\langle 1| [(-\vec{p} \cdot \vec{E}(\tau_1))_{12} |1\rangle\langle 2| + (-\vec{p} \cdot \vec{E}(\tau_1))_{21} |2\rangle\langle 1|] \hat{U}_0(-(\tau_2 - \tau_1)) \hat{H}_I(\tau_2) \hat{U}_0(-(t - \tau_2)) \right] \\ &= \left(-\frac{i}{\hbar}\right)^2 \mathcal{E} \left[\int_{-\infty}^t d\tau_2 \int_{-\infty}^{\tau_2} d\tau_1 \hat{U}_0(t - \tau_2) \hat{H}_I(\tau_2) \hat{U}_0(\tau_2 - \tau_1) [\delta(\tau_1 - \tau_a - \frac{\vec{k}\cdot\vec{x}}{\omega_{21}}) + \delta(\tau_1 - \tau_b - \frac{\vec{k}\cdot\vec{x}}{\omega_{21}})] p_{21} |2\rangle\langle 1| \right] \end{aligned}$$

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$$\begin{aligned}
& -\exp\left[-\frac{i}{\hbar}\hat{H}_0(t-\tau_b-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})\right]p_{21}p_{12}\exp\left[-\frac{i}{\hbar}(E_1-E_2)(\tau_b-\tau_a)\right]|2\rangle\langle 2|\exp\left[\frac{i}{\hbar}\hat{H}_0(t-\tau_b-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})\right] \\
& -\exp\left[-\frac{i}{\hbar}\hat{H}_0(t-\tau_b-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})\right]p_{21}p_{12}\exp\left[-\frac{i}{\hbar}(E_2-E_1)(\tau_b-\tau_a)\right]|2\rangle\langle 2|\exp\left[\frac{i}{\hbar}\hat{H}_0(t-\tau_b-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})\right] \\
& +\exp\left[-\frac{i}{\hbar}\hat{H}_0(t-\tau_b-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})\right]p_{12}p_{21}\exp\left[-\frac{i}{\hbar}(E_1-E_2)(\tau_b-\tau_a)\right]|1\rangle\langle 1|\exp\left[\frac{i}{\hbar}\hat{H}_0(t-\tau_b-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})\right] \\
& =\left(-\frac{i}{\hbar}\right)^2\mathcal{E}^2\left[p_{12}p_{21}\exp\left[-\frac{i}{\hbar}(E_2-E_1)(\tau_b-\tau_a)\right]|1\rangle\langle 1| \right. \\
& \quad -p_{21}p_{12}\exp\left[-\frac{i}{\hbar}(E_1-E_2)(\tau_b-\tau_a)\right]|2\rangle\langle 2| \\
& \quad -p_{21}p_{12}\exp\left[-\frac{i}{\hbar}(E_2-E_1)(\tau_b-\tau_a)\right]|2\rangle\langle 2| \\
& \quad \left.+p_{12}p_{21}\exp\left[-\frac{i}{\hbar}(E_1-E_2)(\tau_b-\tau_a)\right]|1\rangle\langle 1|\right] \\
& =2\left(-\frac{i}{\hbar}\right)^2\mathcal{E}^2p_{12}p_{21}\begin{pmatrix}1 & 0 \\ 0 & -1\end{pmatrix}\cos\left[\frac{(E_2-E_1)(\tau_b-\tau_a)}{\hbar}\right]. \tag{2}
\end{aligned}$$

(In calculation, we used Heaviside step function: $\theta(x) = \begin{cases} 0, & x \leq 0, \\ 1, & x > 0. \end{cases}$.)

The first-order density matrix is

$$\begin{aligned}
\hat{\rho}^{(1)}(t) & =\left(-\frac{i}{\hbar}\right)\hat{U}_0(t)\int_{-\infty}^td\tau[\hat{H}_0,\rho]\hat{U}_0(-t) \\
& =\left(-\frac{i}{\hbar}\right)\left[\int_{-\infty}^td\tau\hat{U}_0(t-\tau)\hat{H}_I(\tau)\hat{\rho}_0\hat{U}_0(-(t-\tau))-\int_{-\infty}^t\hat{U}_0(t-\tau)\rho_0\hat{H}_I\hat{U}_0(-(t-\tau))\right] \\
& =\left(-\frac{i}{\hbar}\right)\left[\int_{-\infty}^td\tau\hat{U}_0(t-\tau)[(-\vec{p}\cdot\vec{E}(\tau))_{12}|1\rangle\langle 2|+(-\vec{p}\cdot\vec{E}(\tau))_{21}|2\rangle\langle 1|]|1\rangle\langle 1| \right. \\
& \quad \left.-\int_{-\infty}^td\tau\hat{U}_0(t-\tau)|1\rangle\langle 1|[(\vec{p}\cdot\vec{E}(\tau))_{12}|1\rangle\langle 2|+(\vec{p}\cdot\vec{E}(\tau))_{21}|2\rangle\langle 1|]\hat{U}_0(-(t-\tau))\right] \\
& =-\left(-\frac{i}{\hbar}\right)\mathcal{E}\left[\int_{-\infty}^td\tau\hat{U}_0(t-\tau)[\delta(\tau-\tau_a-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})+\delta(\tau-\tau_b-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})]p_{21}|2\rangle\langle 1|\hat{U}_0(-(t-\tau)) \right. \\
& \quad \left.-\int_{-\infty}^td\tau\hat{U}_0(t-\tau)[\delta(\tau-\tau_a-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})+\delta(\tau-\tau_b-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})]p_{12}|1\rangle\langle 2|\hat{U}_0(-(t-\tau))\right] \\
& =-\left(-\frac{i}{\hbar}\right)\mathcal{E}\left[\exp\left[-\frac{i}{\hbar}\hat{H}_0(t-\tau_a-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})\right]p_{21}|2\rangle\langle 1|\exp\left[\frac{i}{\hbar}\hat{H}_0(t-\tau_a-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})\right] \right. \\
& \quad \left. +\exp\left[-\frac{i}{\hbar}\hat{H}_0(t-\tau_b-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})\right]p_{21}|2\rangle\langle 1|\exp\left[\frac{i}{\hbar}\hat{H}_0(t-\tau_b-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})\right] \right. \\
& \quad \left. -\exp\left[-\frac{i}{\hbar}\hat{H}_0(t-\tau_a-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})\right]p_{12}|1\rangle\langle 2|\exp\left[\frac{i}{\hbar}\hat{H}_0(t-\tau_a-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})\right] \right. \\
& \quad \left. -\exp\left[-\frac{i}{\hbar}\hat{H}_0(t-\tau_b-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})\right]p_{12}|1\rangle\langle 2|\exp\left[\frac{i}{\hbar}\hat{H}_0(t-\tau_b-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})\right]\right] \\
& =-\left(-\frac{i}{\hbar}\right)\mathcal{E}\left[\exp\left[-\frac{i}{\hbar}(E_2-E_1)(t-\tau_a-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})\right]p_{21}|2\rangle\langle 1|+\exp\left[-\frac{i}{\hbar}(E_2-E_1)(t-\tau_b-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})\right]p_{21}|2\rangle\langle 1| \right. \\
& \quad \left.-\exp\left[-\frac{i}{\hbar}(E_1-E_2)(t-\tau_a-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})\right]p_{12}|1\rangle\langle 2|-\exp\left[-\frac{i}{\hbar}(E_1-E_2)(t-\tau_b-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})\right]p_{12}|1\rangle\langle 2|\right] \\
& =\left(-\frac{i}{\hbar}\right)\mathcal{E}\begin{pmatrix} 0 & p_{12}\begin{bmatrix}\exp\left[-\frac{i}{\hbar}(E_1-E_2)(t-\tau_a-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})\right] \\ +\exp\left[-\frac{i}{\hbar}(E_1-E_2)(t-\tau_b-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})\right] \end{bmatrix} \\ -p_{21}\begin{bmatrix}\exp\left[-\frac{i}{\hbar}(E_2-E_1)(t-\tau_a-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})\right] \\ +\exp\left[-\frac{i}{\hbar}(E_2-E_1)(t-\tau_b-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})\right] \end{bmatrix} & 0 \end{pmatrix}. \tag{3}
\end{aligned}$$

The zeroth-order density matrix is

$$\hat{\rho}^{(0)}(t)=\begin{pmatrix}1 & 0 \\ 0 & 0\end{pmatrix}. \tag{4}$$

The entire density matrix is

$$\begin{aligned} \hat{\rho}(t) &= \hat{\rho}^{(0)}(t) + \hat{\rho}^{(1)}(t) + \hat{\rho}^{(2)}(t) \\ &= \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} + \left(-\frac{i}{\hbar}\right) \mathcal{E} \begin{pmatrix} 0 & p_{12} \left[\exp\left[-\frac{i}{\hbar}(E_1 - E_2)(t - \tau_a - \frac{\vec{k} \cdot \vec{x}}{\omega_{21}})\right] \right. \\ \left. + \exp\left[-\frac{i}{\hbar}(E_1 - E_2)(t - \tau_b - \frac{\vec{k} \cdot \vec{x}}{\omega_{21}})\right] \right] \\ -p_{21} \left[\exp\left[-\frac{i}{\hbar}(E_2 - E_1)(t - \tau_a - \frac{\vec{k} \cdot \vec{x}}{\omega_{21}})\right] \right. \\ \left. + \exp\left[-\frac{i}{\hbar}(E_2 - E_1)(t - \tau_b - \frac{\vec{k} \cdot \vec{x}}{\omega_{21}})\right] \right] & 0 \end{pmatrix} \\ &\quad + 2 \left(-\frac{i}{\hbar}\right)^2 \mathcal{E}^2 p_{12} p_{21} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \cos \left[\frac{(E_2 - E_1)(\tau_b - \tau_a)}{\hbar} \right]. \end{aligned} \quad (5)$$

The part that depends on the time difference $\tau_b - \tau_a$ is just the second-order density matrix, i.e., equation (2).

(b) The value of the expectation value of the dipole moment operator is

$$\langle \hat{p}(t) \rangle = \text{Tr}(\hat{\rho}(t) \hat{p}) = \frac{2}{\hbar} \mathcal{E} p_{12} p_{21} \left\{ \sin \left[\frac{(E_2 - E_1)(t - \tau_a - \frac{\vec{k} \cdot \vec{x}}{\omega_{21}})}{\hbar} \right] + \sin \left[\frac{(E_2 - E_1)(t - \tau_b - \frac{\vec{k} \cdot \vec{x}}{\omega_{21}})}{\hbar} \right] \right\}. \quad (6)$$

□

Problem 2 ((20 points) The third-order density matrix) Score: _____. 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 direction:

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

We are interested in the third order contribution to the 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 pulse 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 just place our detector in the 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 pulse.

Your tasks are the following:

- Calculate the entire density matrix (but only that part characterized by the wave vector specified above) at times $t > \tau_c + \frac{\vec{k}_c \cdot \vec{x}}{\omega_{21}}$.
- Write down the density matrix at time t given by $t - \tau_c = \tau_b - \tau_a$.
- 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.
 - Write down the density matrix at time $(t - \tau_c) - (\tau_b - \tau_a) \gg \frac{1}{\Delta\omega_{21}}$.
 - 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 precise answer, just a reasonable estimate. If you really want a distribution, you can assume a Gaussian distribution.

Solution: (a) Without loss of generality, we set $\tau_a < \tau_b < \tau_c$. Using some part of problem 1's process, the second-order density matrix between the the second and the third pulses ($\tau_b < \tau_3 < \tau_c$) is

$$\begin{aligned} \hat{\rho}^{(2)}(t) &= - \left(-\frac{i}{\hbar}\right)^2 \mathcal{E} \left[\int_{-\infty}^t d\tau_2 \int_{-\infty}^{\tau_2} d\tau_1 \hat{U}_0(t - \tau_2) \hat{H}_I(\tau_2) \hat{U}_0(\tau_2 - \tau_1) \left[\delta\left(\tau_1 - \tau_a - \frac{\vec{k}_a \cdot \vec{x}}{\omega_{21}}\right) + \delta\left(\tau_1 - \tau_b - \frac{\vec{k}_b \cdot \vec{x}}{\omega_{21}}\right) \right] p_{21} |2\rangle \langle 1| \right. \\ &\quad \left. \hat{U}_0(-(\tau_2 - \tau_1)) \hat{U}_0(-(t - \tau_2)) \right. \\ &\quad \left. - \int_{-\infty}^t d\tau_2 \int_{-\infty}^{\tau_2} d\tau_1 \hat{U}_0(t - \tau_2) \hat{H}_I(\tau_2) \hat{U}_0(\tau_2 - \tau_1) \left[\delta\left(\tau_1 - \tau_a - \frac{\vec{k}_a \cdot \vec{x}}{\omega_{21}}\right) + \delta\left(\tau_1 - \tau_b - \frac{\vec{k}_b \cdot \vec{x}}{\omega_{21}}\right) \right] p_{12} |1\rangle \langle 2| \right. \\ &\quad \left. \hat{U}_0(-(\tau_2 - \tau_1)) \hat{U}_0(-(t - \tau_2)) \right] \end{aligned}$$

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$$\begin{aligned}
& + \exp\left[-\frac{i}{\hbar}\hat{H}_0(t-\tau_b - \frac{\vec{k}_b \cdot \vec{x}}{\omega_{21}})\right] p_{12} p_{21} \exp\left[-\frac{i}{\hbar}(E_1 - E_2)(\tau_b - \tau_a + \frac{(\vec{k}_b - \vec{k}_a) \cdot \vec{x}}{\omega_{21}})\right] |1\rangle\langle 1| \exp\left[\frac{i}{\hbar}\hat{H}_0(t-\tau_b - \frac{\vec{k}_b \cdot \vec{x}}{\omega_{21}})\right] \\
& = \left(-\frac{i}{\hbar}\right)^2 \mathcal{E}^2 \left[p_{12} p_{21} \exp\left[-\frac{i}{\hbar}(E_2 - E_1)(\tau_b - \tau_a + \frac{(\vec{k}_b - \vec{k}_a) \cdot \vec{x}}{\omega_{21}})\right] |1\rangle\langle 1| \right. \\
& \quad - p_{21} p_{12} \exp\left[-\frac{i}{\hbar}(E_1 - E_2)(\tau_b - \tau_a + \frac{(\vec{k}_b - \vec{k}_a) \cdot \vec{x}}{\omega_{21}})\right] |2\rangle\langle 2| \\
& \quad - p_{21} p_{12} \exp\left[-\frac{i}{\hbar}(E_2 - E_1)(\tau_b - \tau_a + \frac{(\vec{k}_b - \vec{k}_a) \cdot \vec{x}}{\omega_{21}})\right] |2\rangle\langle 2| \\
& \quad \left. + p_{12} p_{21} \exp\left[-\frac{i}{\hbar}(E_1 - E_2)(\tau_b - \tau_a + \frac{(\vec{k}_b - \vec{k}_a) \cdot \vec{x}}{\omega_{21}})\right] |1\rangle\langle 1| \right] \\
& = 2 \left(-\frac{i}{\hbar}\right)^2 \mathcal{E}^2 p_{12} p_{21} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \cos \left[\frac{(E_2 - E_1)(\tau_b - \tau_a + \frac{(\vec{k}_b - \vec{k}_a) \cdot \vec{x}}{\omega_{21}})}{\hbar} \right]. \tag{7}
\end{aligned}$$

The third-order density matrix at time t is

$$\begin{aligned}
\hat{\rho}^{(3)}(t) & = \left(-\frac{i}{\hbar}\right) \hat{U}_0(t) \int_{\tau_b}^t d\tau_3 [\hat{H}'_I(\tau_3), \hat{\rho}^{(2)'}(\tau_3)] \hat{U}_0(-t) \\
& = \left(-\frac{i}{\hbar}\right) \left[\int_{\tau_b}^t d\tau_c \hat{U}_0(t-\tau_3) \hat{H}(-\tau_3) \hat{\rho}^{(2)}(\tau_3) \hat{U}_0(-(t-\tau_3)) - \int_{\tau_b}^t d\tau_c \hat{U}_0(t-\tau_3) \hat{\rho}^{(2)}(\tau_3) \hat{H}(-\tau_3) \hat{U}_0(-(t-\tau_3)) \right] \\
& = -\left(-\frac{i}{\hbar}\right) \mathcal{E} \left[\int_{\tau_b}^t d\tau_3 \exp\left[-\frac{i}{\hbar}\hat{H}_0(t-\tau_3)\right] \delta(\tau_3 - \tau_c - \frac{\vec{k}_c \cdot \vec{x}}{\omega_{21}}) [p_{12}|1\rangle\langle 2| + p_{21}|2\rangle\langle 1|] [\rho_{11}^{(2)}(\tau_3)|1\rangle\langle 1| + \rho_{22}^{(2)}(\tau_3)|2\rangle\langle 2|] \exp\left[\frac{i}{\hbar}\hat{H}_0(t-\tau_3)\right] \right. \\
& \quad \left. - \int_{\tau_b}^t d\tau_3 \exp\left[-\frac{i}{\hbar}\hat{H}_0(t-\tau_3)\right] [\rho_{11}^{(2)}(\tau_3)|1\rangle\langle 1| + \rho_{22}^{(2)}(\tau_3)|2\rangle\langle 2|] \delta(\tau_3 - \tau_c - \frac{\vec{k}_c \cdot \vec{x}}{\omega_{21}}) [p_{12}|1\rangle\langle 2| + p_{21}|2\rangle\langle 1|] \exp\left[\frac{i}{\hbar}\hat{H}_0(t-\tau_3)\right] \right] \\
& = -\left(-\frac{i}{\hbar}\right) \mathcal{E} \left[\int_{\tau_b}^t d\tau_3 \delta(\tau_3 - \tau_c - \frac{\vec{k}_c \cdot \vec{x}}{\omega_{21}}) [p_{12}\rho_{22}(\tau_3) \exp\left[-\frac{i}{\hbar}(E_1 - E_2)(t-\tau_3)\right] |1\rangle\langle 2| + p_{21}\rho_{11}(\tau_b) \exp\left[\frac{i}{\hbar}(E_2 - E_1)(t-\tau_3)\right] |2\rangle\langle 1|] \right. \\
& \quad \left. - \int_{\tau_b}^t d\tau_3 [\rho_{11}(\tau_b) p_{12} \exp\left[-\frac{i}{\hbar}(E_1 - E_2)(t-\tau_3)\right] |1\rangle\langle 2| + \rho_{22}(\tau_b) p_{21} \exp\left[\frac{i}{\hbar}(E_2 - E_1)(t-\tau_3)\right] |2\rangle\langle 1|] \delta(\tau_3 - \tau_c - \frac{\vec{k}_c \cdot \vec{x}}{\omega_{21}}) \right] \\
& = -\left(-\frac{i}{\hbar}\right) \mathcal{E} \left[p_{12}\rho_{22}(\tau_3) \exp\left[-\frac{i}{\hbar}(E_1 - E_2)(t-\tau_c - \frac{\vec{k}_c \cdot \vec{x}}{\omega_{21}})\right] |1\rangle\langle 2| + p_{21}\rho_{11}(\tau_3) \exp\left[-\frac{i}{\hbar}(E_2 - E_1)(t-\tau_c - \frac{\vec{k}_c \cdot \vec{x}}{\omega_{21}})\right] |2\rangle\langle 1| \right. \\
& \quad \left. - \rho_{11}(\tau_3) p_{12} \exp\left[-\frac{i}{\hbar}(E_1 - E_2)(t-\tau_c - \frac{\vec{k}_c \cdot \vec{x}}{\omega_{21}})\right] |1\rangle\langle 2| - \rho_{22}(\tau_3) p_{21} \exp\left[-\frac{i}{\hbar}(E_2 - E_1)(t-\tau_c - \frac{\vec{k}_c \cdot \vec{x}}{\omega_{21}})\right] |2\rangle\langle 1| \right] \hat{U}_0(-t) \\
& = -\left(-\frac{i}{\hbar}\right) \mathcal{E} \left[p_{12}(\rho_{22}(\tau_b) - \rho_{11}(\tau_3)) \exp\left[-\frac{i}{\hbar}(E_1 - E_2)(t-\tau_c - \frac{\vec{k}_c \cdot \vec{x}}{\omega_{21}})\right] |1\rangle\langle 2| \right. \\
& \quad \left. p_{21}(\rho_{11}(\tau_3) - \rho_{22}(\tau_b)) \exp\left[-\frac{i}{\hbar}(E_2 - E_1)(t-\tau_c - \frac{\vec{k}_c \cdot \vec{x}}{\omega_{21}})\right] |2\rangle\langle 1| \right] \\
& = 4 \left(-\frac{i}{\hbar}\right)^3 \mathcal{E} p_{12} p_{21} \begin{pmatrix} 0 & p_{12} \exp\left[-\frac{i}{\hbar}(E_1 - E_2)(t-\tau_c - \frac{\vec{k}_c \cdot \vec{x}}{\omega_{21}})\right] \\ -p_{21} \exp\left[-\frac{i}{\hbar}(E_2 - E_1)(t-\tau_c - \frac{\vec{k}_c \cdot \vec{x}}{\omega_{21}})\right] & 0 \end{pmatrix} \\
& \quad \times \cos \left[\frac{(E_2 - E_1)(\tau_b - \tau_a + \frac{(\vec{k}_b - \vec{k}_a) \cdot \vec{x}}{\omega_{21}})}{\hbar} \right] \\
& = 4 \left(-\frac{i}{\hbar}\right)^3 \mathcal{E} p_{12} p_{21} \begin{pmatrix} 0 & p_{12} \exp\left[-\frac{i}{\hbar}(E_1 - E_2)(t-\tau_c - \frac{\vec{k}_c \cdot \vec{x}}{\omega_{21}})\right] \\ -p_{21} \exp\left[-\frac{i}{\hbar}(E_2 - E_1)(t-\tau_c - \frac{\vec{k}_c \cdot \vec{x}}{\omega_{21}})\right] & 0 \end{pmatrix} \\
& \quad \times \left\{ \exp\left[\frac{i}{\hbar}(E_2 - E_1)(\tau_b - \tau_a + \frac{(\vec{k}_b - \vec{k}_a) \cdot \vec{x}}{\omega_{21}})\right] + \exp\left[-\frac{i}{\hbar}(E_2 - E_1)(\tau_b - \tau_a + \frac{(\vec{k}_b - \vec{k}_a) \cdot \vec{x}}{\omega_{21}})\right] \right\} \tag{8}
\end{aligned}$$

In the above density matrix, the part characterized by $\vec{k}_c + \vec{k}_b - \vec{k}_a$ is

$$\begin{aligned}
& \hat{\rho}_{\vec{k}_c + \vec{k}_b - \vec{k}_a}^{(3)}(t) \\
& = 4 \left(-\frac{i}{\hbar}\right)^3 \mathcal{E} p_{12} p_{21} \begin{pmatrix} 0 & p_{12} \exp\left[-\frac{i}{\hbar}(E_1 - E_2)(t-\tau_c - \tau_b + \tau_a - \frac{(\vec{k}_c + \vec{k}_b - \vec{k}_a) \cdot \vec{x}}{\omega_{21}})\right] \\ -p_{21} \exp\left[-\frac{i}{\hbar}(E_2 - E_1)(t-\tau_c - \tau_b + \tau_a - \frac{(\vec{k}_c + \vec{k}_b - \vec{k}_a) \cdot \vec{x}}{\omega_{21}})\right] & 0 \end{pmatrix}. \tag{9}
\end{aligned}$$

(b) The density matrix at time t given by $t - \tau_c = \tau_b - \tau_a$ is

$$\hat{\rho}_{\vec{k}_c + \vec{k}_b - \vec{k}_a}^{(3)}(t = \tau_c + \tau_b - \tau_a) = 4 \left(-\frac{i}{\hbar} \right)^3 \mathcal{E} p_{12} p_{21} \begin{pmatrix} 0 & p_{12} \exp \left[-\frac{i}{\hbar} (E_2 - E_1) \frac{(\vec{k}_c + \vec{k}_b - \vec{k}_a) \cdot \vec{x}}{\omega_{21}} \right] \\ -p_{21} \exp \left[-\frac{i}{\hbar} (E_1 - E_2) \frac{(\vec{k}_c + \vec{k}_b - \vec{k}_a) \cdot \vec{x}}{\omega_{21}} \right] & 0 \end{pmatrix}. \quad (10)$$

(c) Without loss of generality, we set $E_2 > E_1$ and thus $\hbar(\omega_{21} - \Delta\omega_{21}/2) \leq E_2 - E_1 \leq \hbar(\omega_{21} + \Delta\omega_{21}/2)$.

i. The density matrix at time t is

$$\begin{aligned} & \hat{\rho}_{\vec{k}_c + \vec{k}_b - \vec{k}_a}(t) \\ &= \int_{\omega_{21} - \Delta\omega_{21}/2}^{\omega_{21} + \Delta\omega_{21}/2} d\omega g(\omega) \\ & \times 4 \left(-\frac{i}{\hbar} \right)^3 \mathcal{E} p_{12} p_{21} \begin{pmatrix} 0 & p_{12} \exp \left[-i\omega(t - \tau_c - \tau_b + \tau_a - \frac{(\vec{k}_c + \vec{k}_b - \vec{k}_a) \cdot \vec{x}}{\omega_{21}}) \right] \\ -p_{21} \exp \left[i\omega(t - \tau_c - \tau_b + \tau_a - \frac{(\vec{k}_c + \vec{k}_b - \vec{k}_a) \cdot \vec{x}}{\omega_{21}}) \right] & 0 \end{pmatrix}. \end{aligned} \quad (11)$$

Since $(t - \tau_c) - (\tau_b - \tau_a) \gg \frac{1}{\Delta\omega_{21}} \gg \frac{1}{\omega_{21}}$, $(t - \tau_c - \tau_b + \tau_a - \frac{(\vec{k}_c + \vec{k}_b - \vec{k}_a) \cdot \vec{x}}{\omega_{21}})$ can be approximately regarded as $(t - \tau_c - \tau_b + \tau_a)$. In this way, we have

$$\begin{aligned} & \hat{\rho}_{\vec{k}_c + \vec{k}_b - \vec{k}_a}(t \gg \tau_c + \tau_b - \tau_a + \frac{1}{\Delta\omega_{21}}) \\ & \approx 4 \left(-\frac{i}{\hbar} \right)^3 \mathcal{E} p_{12} p_{21} \int_{\omega_{21} - \Delta\omega_{21}/2}^{\omega_{21} + \Delta\omega_{21}/2} d\omega g(\omega) \begin{pmatrix} 0 & p_{12} \exp \left[-i\omega(t - \tau_c - \tau_b + \tau_a) \right] \\ -p_{21} \exp \left[i\omega(t - \tau_c - \tau_b + \tau_a) \right] & 0 \end{pmatrix}. \\ & \approx 0 \end{aligned} \quad (12)$$

ii. The density matrix at time $t - \tau_c = \tau_b - \tau_a$ is

$$\begin{aligned} & \hat{\rho}_{\vec{k}_c + \vec{k}_b - \vec{k}_a}(t = \tau_c + \tau_b - \tau_a) \\ &= \int_{\omega_{21} - \Delta\omega_{21}/2}^{\omega_{21} + \Delta\omega_{21}/2} d\omega g(\omega) \times 4 \left(-\frac{i}{\hbar} \right)^3 \mathcal{E} p_{12} p_{21} \begin{pmatrix} 0 & p_{12} \exp \left[-i\omega \frac{(\vec{k}_c + \vec{k}_b - \vec{k}_a) \cdot \vec{x}}{\omega_{21}} \right] \\ -p_{21} \exp \left[i\omega \frac{(\vec{k}_c + \vec{k}_b - \vec{k}_a) \cdot \vec{x}}{\omega_{21}} \right] & 0 \end{pmatrix}. \end{aligned} \quad (13)$$

Since the oscillators are almost same, $\Delta\omega_{21} \ll \omega_{21}$, we have

$$\hat{\rho}_{\vec{k}_c + \vec{k}_b - \vec{k}_a}(t = \tau_c + \tau_b - \tau_a) \approx 4 \left(-\frac{i}{\hbar} \right)^3 \mathcal{E} p_{12} p_{21} \begin{pmatrix} 0 & p_{12} \exp \left[-i(\vec{k}_c + \vec{k}_b - \vec{k}_a) \cdot \vec{x} \right] \\ -p_{21} \exp \left[i(\vec{k}_c + \vec{k}_b - \vec{k}_a) \cdot \vec{x} \right] & 0 \end{pmatrix}. \quad (14)$$

□