Assignment 3

Due Time : 13:01, March 31, 2020 (Tuesday)

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Score : ________

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 $\vec{E}(t)=\hat{z}\mathscr{E}[\delta(t-\tau_a-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})+\delta(t-\tau_b-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})]$. (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

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

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 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

$$\hat{\rho}^{(2)}(t)=\left(-\frac{i}{\hbar}\right)^2\hat{U}_0(t)\int_{-\infty}^{t}d\tau_1\int_{-\infty}^{\tau_1}d\tau_2\,[\hat{H}_I'(\tau_1),[\hat{H}_I'(\tau_2),\hat{\rho}_0]]\hat{U}_0(-t)$$

$$=\left(-\frac{i}{\hbar}\right)^2\hat{U}_0(t)\int_{-\infty}^{t}d\tau_1\int_{-\infty}^{\tau_1}d\tau_2\,[\hat{H}_I'(\tau_2)\hat{H}_I'(\tau_1)\hat{\rho}_0-\hat{H}_I'(\tau_2)\hat{\rho}_0\hat{H}_I'(\tau_1)-\hat{H}_I'(\tau_1)\hat{\rho}_0\hat{H}_I'(\tau_2)+\hat{\rho}_0\hat{H}_I'(\tau_1)\hat{H}_I'(\tau_2)]\hat{U}_0(-t)$$

$$=\left(-\frac{i}{\hbar}\right)^2\Big[\int_{-\infty}^{t}d\tau_2\int_{-\infty}^{\tau_2}d\tau_1\,\hat{U}_0(t-\tau_2)\hat{H}_I(\tau_2)\hat{U}_0(\tau_2-\tau_1)\hat{H}_I(\tau_1)\hat{\rho}_0\hat{U}(-(\tau_2-\tau_1))\hat{U}_0(-(t-\tau_2))$$
$$-\int_{-\infty}^{t}d\tau_2\int_{-\infty}^{\tau_2}d\tau_1\,\hat{U}_0(t-\tau_2)\hat{H}_I(\tau_2)\hat{U}_0(\tau_2-\tau_1)\hat{\rho}_0\hat{H}_I(\tau_1)\hat{U}_0(-(\tau_2-\tau_1))\hat{U}_0(-(t-\tau_2))$$
$$-\int_{-\infty}^{t}d\tau_2\int_{-\infty}^{\tau_2}d\tau_1\,\hat{U}_0(t-\tau_2)\hat{U}_0(\tau_2-\tau_1)\hat{H}_I(\tau_1)\hat{\rho}_0\hat{U}_0(-(\tau_2-\tau_1))\hat{H}_I(\tau_2)\hat{U}_0(-(t-\tau_2))$$
$$+\int_{-\infty}^{t}d\tau_2\int_{-\infty}^{\tau_2}d\tau_1\,\hat{U}_0(t-\tau_2)\hat{U}_0(\tau_2-\tau_1)\hat{\rho}_0\hat{H}_I(\tau_1)\hat{U}_0(-(\tau_2-\tau_1))\hat{H}_I(\tau_2)\hat{U}_0(-(t-\tau_2))\Big]$$

$$=\left(-\frac{i}{\hbar}\right)^2\Big[\int_{-\infty}^{t}d\tau_2\int_{-\infty}^{\tau_2}d\tau_1\,\hat{U}_0(t-\tau_2)\hat{H}_I(\tau_2)\hat{U}_0(\tau_2-\tau_1)[(-\vec{p}\cdot\vec{E}(\tau_1))_{12}|1\rangle\langle 2|+(-\vec{p}\cdot\vec{E}(\tau_1))_{21}|2\rangle\langle 1|]|1\rangle\langle 1|\hat{U}(-(\tau_2-\tau_1))\hat{U}_0(-(t-\tau_2))$$
$$-\int_{-\infty}^{t}d\tau_2\int_{-\infty}^{\tau_2}d\tau_1\,\hat{U}_0(t-\tau_2)\hat{H}_I(\tau_2)\hat{U}_0(\tau_2-\tau_1)|1\rangle\langle 1|[(-\vec{p}\cdot\vec{E}(\tau_1))_{12}|1\rangle\langle 2|+(-\vec{p}\cdot\vec{E}(\tau_1))_{21}|2\rangle\langle 1|]\hat{U}_0(-(\tau_2-\tau_1))\hat{U}_0(-(t-\tau_2))$$
$$-\int_{-\infty}^{t}d\tau_2\int_{-\infty}^{\tau_2}d\tau_1\,\hat{U}_0(t-\tau_2)\hat{U}_0(\tau_2-\tau_1)[(-\vec{p}\cdot\vec{E}(\tau_1))_{12}|1\rangle\langle 2|+(-\vec{p}\cdot\vec{E}(\tau_1))_{21}|2\rangle\langle 1|]|1\rangle\langle 1|\hat{U}_0(-(\tau_2-\tau_1))\hat{H}_I(\tau_2)\hat{U}_0(-(t-\tau_2))$$
$$+\int_{-\infty}^{t}d\tau_2\int_{-\infty}^{\tau_2}d\tau_1\,\hat{U}_0(t-\tau_2)\hat{U}_0(\tau_2-\tau_1)|1\rangle\langle 1|[(-\vec{p}\cdot\vec{E}(\tau_1))_{12}|1\rangle\langle 2|+(-\vec{p}\cdot\vec{E}(\tau_1))_{21}|2\rangle\langle 1|]\hat{U}_0(-(\tau_2-\tau_1))\hat{H}_I(\tau_2)\hat{U}_0(-(t-\tau_2))\Big]$$

$$=-\left(-\frac{i}{\hbar}\right)^2\mathscr{E}\Big[\int_{-\infty}^{t}d\tau_2\int_{-\infty}^{\tau_2}d\tau_1\,\hat{U}_0(t-\tau_2)\hat{H}_I(\tau_2)\hat{U}_0(\tau_2-\tau_1)[\delta(\tau_1-\tau_a-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})+\delta(\tau_1-\tau_b-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})]p_{21}|2\rangle\langle 1|$$

$$
\begin{aligned}
&\qquad \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{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_{12}|1\rangle\langle 2| \\
&\qquad \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)[\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| \\
&\qquad \hat{U}_0(-(\tau_2-\tau_1))\hat{H}_I(\tau_2)\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)[\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_{12}|1\rangle\langle 2| \\
&\qquad \hat{U}_0(-(\tau_2-\tau_1))\hat{H}_I(\tau_2)\hat{U}_0(-(t-\tau_2))\Big] \\
=&-\left(-\frac{i}{\hbar}\right)^2\mathscr{E}\Bigg[\int_{-\infty}^{t} d\tau_2\, \hat{U}_0(t-\tau_2)\hat{H}_I(\tau_2)[\theta(\tau_2-\tau_a-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})\hat{U}_0(\tau_2-\tau_a-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})p_{21}|2\rangle\langle 1|\hat{U}_0(-(\tau_2-\tau_a-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})) \\
&\qquad +\theta(\tau_2-\tau_b-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})\hat{U}_0(\tau_2-\tau_b-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})p_{21}|2\rangle\langle 1|\hat{U}_0(-(\tau_2-\tau_b-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}}))]\hat{U}_0(-(t-\tau_2)) \\
&\quad -\int_{-\infty}^{t} d\tau_2\, \hat{U}_0(t-\tau_2)\hat{H}_I(\tau_2)[\theta(\tau_2-\tau_a-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})\hat{U}_0(\tau_2-\tau_a-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})p_{12}|1\rangle\langle 2|\hat{U}_0(-(\tau_2-\tau_a-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})) \\
&\qquad +\theta(\tau_2-\tau_b-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})\hat{U}_0(\tau_2-\tau_b-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})p_{12}|1\rangle\langle 2|\hat{U}_0(-(\tau_2-\tau_b-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}}))]\hat{U}_0(-(t-\tau_2)) \\
&\quad -\int_{-\infty}^{t} d\tau_2\, \hat{U}_0(t-\tau_2)[\theta(\tau_2-\tau_a-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})\hat{U}_0(\tau_2-\tau_a-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})p_{21}|2\rangle\langle 1|\hat{U}_0(-(\tau_2-\tau_a-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})) \\
&\qquad +\theta(\tau_2-\tau_b-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})\hat{U}_0(\tau_2-\tau_b-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})p_{21}|2\rangle\langle 1|\hat{U}_0(-(\tau_2-\tau_b-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}}))]\hat{H}_I(\tau_2)\hat{U}_0(-(t-\tau_2)) \\
&\quad +\int_{-\infty}^{t} d\tau_2\, \hat{U}_0(t-\tau_2)[\theta(\tau_2-\tau_a-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})\hat{U}_0(\tau_2-\tau_a-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})p_{12}|1\rangle\langle 2|\hat{U}_0(-(\tau_2-\tau_a-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})) \\
&\qquad +\theta(\tau_2-\tau_b-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})\hat{U}_0(\tau_2-\tau_b-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})p_{12}|1\rangle\langle 2|\hat{U}_0(-(\tau_2-\tau_b-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}}))]\hat{H}_I(\tau_2)\hat{U}_0(-(t-\tau_2))\Bigg] \\
=&-\left(-\frac{i}{\hbar}\right)^2\mathscr{E}\Bigg[\int_{-\infty}^{t} d\tau_2\, \hat{U}_0(t-\tau_2)\hat{H}_I(\tau_2)[\theta(\tau_2-\tau_a-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})p_{21}\exp[-\frac{i}{\hbar}\hat{H}_0(\tau_2-\tau_a-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})]|2\rangle\langle 1|\exp[\frac{i}{\hbar}\hat{H}_0(\tau_2-\tau_a-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})] \\
&\qquad +\theta(\tau_2-\tau_b-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})p_{21}\exp[\frac{i}{\hbar}\hat{H}_0(\tau_2-\tau_b-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})]|2\rangle\langle 1|\exp[\frac{i}{\hbar}\hat{H}_0(\tau_2-\tau_b-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})]]\hat{U}_0(-(t-\tau_2)) \\
&\quad -\int_{-\infty}^{t} d\tau_2\, \hat{U}_0(t-\tau_2)\hat{H}_I(\tau_2)[\theta(\tau_2-\tau_a-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})p_{12}\exp[\frac{i}{\hbar}\hat{H}_0(\tau_2-\tau_a-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})]|1\rangle\langle 2|\exp[\frac{i}{\hbar}\hat{H}_0(\tau_2-\tau_a-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})] \\
&\qquad +\theta(\tau_2-\tau_b-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})p_{12}\exp[\frac{i}{\hbar}\hat{H}_0(\tau_2-\tau_b-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})]|1\rangle\langle 2|\exp[\frac{i}{\hbar}\hat{H}_0(\tau_2-\tau_b-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})]]\hat{U}_0(-(t-\tau_2)) \\
&\quad -\int_{-\infty}^{t} d\tau_2\, \hat{U}_0(t-\tau_2)[\theta(\tau_2-\tau_a-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})p_{21}\exp[\frac{i}{\hbar}\hat{H}_0(\tau_2-\tau_a-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})]|2\rangle\langle 1|\exp[\frac{i}{\hbar}\hat{H}_0(\tau_2-\tau_a-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})] \\
&\qquad +\theta(\tau_2-\tau_b-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})p_{21}\exp[\frac{i}{\hbar}\hat{H}_0(\tau_2-\tau_b-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})]|2\rangle\langle 1|\exp[\frac{i}{\hbar}\hat{H}_0(\tau_2-\tau_b-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})]]\hat{H}_I(\tau_2)\hat{U}_0(-(t-\tau_2)) \\
&\quad +\int_{-\infty}^{t} d\tau_2\, \hat{U}_0(t-\tau_2)[\theta(\tau_2-\tau_a-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})p_{12}\exp[\frac{i}{\hbar}\hat{H}_0(\tau_2-\tau_a-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})]|1\rangle\langle 2|\exp[\frac{i}{\hbar}\hat{H}_0(\tau_2-\tau_a-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})] \\
&\qquad +\theta(\tau_2-\tau_b-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})p_{12}\exp[\frac{i}{\hbar}\hat{H}_0(\tau_2-\tau_b-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})]|1\rangle\langle 2|\exp[\frac{i}{\hbar}\hat{H}_0(\tau_2-\tau_b-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})]]\hat{H}_I(\tau_2)\hat{U}_0(-(t-\tau_2))\Bigg] \\
=&-\left(-\frac{i}{\hbar}\right)^2\mathscr{E}\Bigg[\int_{-\infty}^{t} d\tau_2\, \hat{U}_0(t-\tau_2)\hat{H}_I(\tau_2)[\theta(\tau_2-\tau_a-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})p_{21}\exp[-\frac{i}{\hbar}E_2(\tau_2-\tau_a-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})]|2\rangle\langle 1|\exp[\frac{i}{\hbar}E_1(\tau_2-\tau_a-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})] \\
&\qquad +\theta(\tau_2-\tau_b-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})p_{21}\exp[\frac{i}{\hbar}E_2(\tau_2-\tau_b-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})]|2\rangle\langle 1|\exp[\frac{i}{\hbar}E_1(\tau_2-\tau_b-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})]]\hat{U}_0(-(t-\tau_2)) \\
&\quad -\int_{-\infty}^{t} d\tau_2\, \hat{U}_0(t-\tau_2)\hat{H}_I(\tau_2)[\theta(\tau_2-\tau_a-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})p_{12}\exp[\frac{i}{\hbar}E_1(\tau_2-\tau_a-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})]|1\rangle\langle 2|\exp[\frac{i}{\hbar}E_2(\tau_2-\tau_a-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})] \\
&\qquad +\theta(\tau_2-\tau_b-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})p_{12}\exp[\frac{i}{\hbar}E_1(\tau_2-\tau_b-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})]|1\rangle\langle 2|\exp[\frac{i}{\hbar}E_2(\tau_2-\tau_b-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})]]\hat{U}_0(-(t-\tau_2)) \\
&\quad -\int_{-\infty}^{t} d\tau_2\, \hat{U}_0(t-\tau_2)[\theta(\tau_2-\tau_a-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})p_{21}\exp[\frac{i}{\hbar}E_2(\tau_2-\tau_a-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})]|2\rangle\langle 1|\exp[\frac{i}{\hbar}E_1(\tau_2-\tau_a-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})] \\
&\qquad +\theta(\tau_2-\tau_b-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})p_{21}\exp[\frac{i}{\hbar}E_2(\tau_2-\tau_b-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})]|2\rangle\langle 1|\exp[\frac{i}{\hbar}E_1(\tau_2-\tau_b-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})]]\hat{H}_I(\tau_2)\hat{U}_0(-(t-\tau_2))
\end{aligned}
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\begin{aligned}
&+\int_{-\infty}^{t} d\tau_2\,\hat{U}_0(t-\tau_2)[\theta(\tau_2-\tau_a-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})p_{12}\exp[\frac{i}{\hbar}E_1(\tau_2-\tau_a-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})]|1\rangle\langle 2|\exp[\frac{i}{\hbar}E_2(\tau_2-\tau_a-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})]\\
&\qquad+\theta(\tau_2-\tau_b-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})p_{12}\exp[\frac{i}{\hbar}E_1(\tau_2-\tau_b-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})]|1\rangle\langle 2|\exp[\frac{i}{\hbar}E_2(\tau_2-\tau_b-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})]]\hat{H}_I(\tau_2)\hat{U}_0(-(t-\tau_2))\Bigg]\\
=&-\left(-\frac{i}{\hbar}\right)^2\mathscr{E}\Bigg[\int_{-\infty}^{t} d\tau_2\,\hat{U}_0(t-\tau_2)[(-\vec{p}\cdot\vec{E}(\tau_2))_{12}|1\rangle\langle 2|+(-\vec{p}\cdot\vec{E}(\tau_2))_{21}|2\rangle\langle 1|][\theta(\tau_2-\tau_a-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})p_{21}\exp[-\frac{i}{\hbar}(E_2-E_1)(\tau_2-\tau_a-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})]|2\rangle\langle 1|\\
&\qquad+\theta(\tau_2-\tau_b-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})p_{21}\exp[-\frac{i}{\hbar}(E_2-E_1)(\tau_2-\tau_b-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})]|2\rangle\langle 1|\hat{U}_0(-(t-\tau_2))\\
&-\int_{-\infty}^{t} d\tau_2\,\hat{U}_0(t-\tau_2)[(-\vec{p}\cdot\vec{E}(\tau_2))_{12}|1\rangle\langle 2|][\theta(\tau_2-\tau_a-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})p_{12}\exp[-\frac{i}{\hbar}(E_1-E_2)(\tau_2-\tau_a-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})]|1\rangle\langle 2|\\
&\qquad+\theta(\tau_2-\tau_b-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})p_{12}\exp[-\frac{i}{\hbar}(E_1-E_2)(\tau_2-\tau_b-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})]|1\rangle\langle 2|]\hat{U}_0(-(t-\tau_2))\\
&-\int_{-\infty}^{t} d\tau_2\,\hat{U}_0(t-\tau_2)[\theta(\tau_2-\tau_a-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})p_{21}\exp[-\frac{i}{\hbar}(E_2-E_1)(\tau_2-\tau_a-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})]|2\rangle\langle 1|\\
&\qquad+\theta(\tau_2-\tau_b-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})p_{21}\exp[-\frac{i}{\hbar}(E_2-E_1)(\tau_2-\tau_b-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})]|2\rangle\langle 1|][(-\vec{p}\cdot\vec{E}(\tau_2))_{12}|1\rangle\langle 2|+(-\vec{p}\cdot\vec{E}(\tau_2))_{21}|2\rangle\langle 1|]\hat{U}_0(-(t-\tau_2))\\
&+\int_{-\infty}^{t} d\tau_2\,\hat{U}_0(t-\tau_2)[\theta(\tau_2-\tau_a-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})p_{12}\exp[-\frac{i}{\hbar}(E_1-E_2)(\tau_2-\tau_a-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})]|1\rangle\langle 2|\\
&\qquad+\theta(\tau_2-\tau_b-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})p_{12}\exp[-\frac{i}{\hbar}(E_1-E_2)(\tau_2-\tau_b-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})]|1\rangle\langle 2|][(-\vec{p}\cdot\vec{E}(\tau_2))_{12}|1\rangle\langle 2|+(-\vec{p}\cdot\vec{E}(\tau_2))_{21}|2\rangle\langle 1|]\hat{U}_0(-(t-\tau_2))\Bigg]\\
=&\left(-\frac{i}{\hbar}\right)^2\mathscr{E}^2\Bigg[\int_{-\infty}^{t} d\tau_2\,\hat{U}_0(t-\tau_2)[\delta(\tau_2-\tau_a-\frac{\vec{k}\cdot\vec{E}}{\omega_{21}})+\delta(\tau_2-\tau_b-\frac{\vec{k}\cdot\vec{E}}{\omega_{21}})]\\
&\qquad[p_{12}|1\rangle\langle 2|+p_{21}|2\rangle\langle 1|][\theta(\tau_2-\tau_a-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})p_{21}\exp[-\frac{i}{\hbar}(E_2-E_1)(\tau_2-\tau_a-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})]|2\rangle\langle 1|\\
&\qquad+\theta(\tau_2-\tau_b-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})p_{21}\exp[-\frac{i}{\hbar}(E_2-E_1)(\tau_2-\tau_b-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})]|2\rangle\langle 1|]\hat{U}_0(-(t-\tau_2))\\
&-\int_{-\infty}^{t} d\tau_2\,\hat{U}_0(t-\tau_2)[\delta(\tau_2-\tau_a-\frac{\vec{k}\cdot\vec{E}}{\omega_{21}})+\delta(\tau_2-\tau_b-\frac{\vec{k}\cdot\vec{E}}{\omega_{21}})]\\
&\qquad[p_{12}|1\rangle\langle 2|+p_{21}|2\rangle\langle 1|][\theta(\tau_2-\tau_a-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})p_{12}\exp[-\frac{i}{\hbar}(E_1-E_2)(\tau_2-\tau_a-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})]|1\rangle\langle 2|\\
&\qquad+\theta(\tau_2-\tau_b-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})p_{12}\exp[-\frac{i}{\hbar}(E_1-E_2)(\tau_2-\tau_b-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})]|1\rangle\langle 2|]\hat{U}_0(-(t-\tau_2))\\
&-\int_{-\infty}^{t} d\tau_2\,\hat{U}_0(t-\tau_2)[\delta(\tau_2-\tau_a-\frac{\vec{k}\cdot\vec{E}}{\omega_{21}})+\delta(\tau_2-\tau_b-\frac{\vec{k}\cdot\vec{E}}{\omega_{21}})]\\
&\qquad[\theta(\tau_2-\tau_a-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})p_{21}\exp[-\frac{i}{\hbar}(E_2-E_1)(\tau_2-\tau_a-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})]|2\rangle\langle 1|\\
&\qquad+\theta(\tau_2-\tau_b-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})p_{21}\exp[-\frac{i}{\hbar}(E_2-E_1)(\tau_2-\tau_b-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})]|2\rangle\langle 1|][p_{12}|1\rangle\langle 2|+p_{21}|2\rangle\langle 1|]\hat{U}_0(-(t-\tau_2))\\
&+\int_{-\infty}^{t} d\tau_2\,\hat{U}_0(t-\tau_2)[\delta(\tau_2-\tau_a-\frac{\vec{k}\cdot\vec{E}}{\omega_{21}})+\delta(\tau_2-\tau_b-\frac{\vec{k}\cdot\vec{E}}{\omega_{21}})]\\
&\qquad[\theta(\tau_2-\tau_a-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})p_{12}\exp[-\frac{i}{\hbar}(E_1-E_2)(\tau_2-\tau_a-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})]|1\rangle\langle 2|\\
&\qquad+\theta(\tau_2-\tau_b-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})p_{12}\exp[-\frac{i}{\hbar}(E_1-E_2)(\tau_2-\tau_b-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})]|1\rangle\langle 2|][p_{12}|1\rangle\langle 2|+p_{21}|2\rangle\langle 1|]\hat{U}_0(-(t-\tau_2))\Bigg]\\
=&\left(-\frac{i}{\hbar}\right)^2\mathscr{E}^2\Bigg[\hat{U}_0(t-\tau_b-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})\sum_{j,m=1}^{2}p_{12}p_{21}\exp[-\frac{i}{\hbar}(E_2-E_1)(\tau_b-\tau_a)]|1\rangle\langle 1|\hat{U}_0(-(t-\tau_b-\frac{\vec{k}\cdot\vec{E}}{\omega_{21}}))\\
&-\hat{U}_0(t-\tau_b-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})p_{21}p_{12}\exp[-\frac{i}{\hbar}(E_1-E_2)(\tau_b-\tau_a)]|2\rangle\langle 2|\hat{U}_0(-(t-\tau_b-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}}))\\
&-\hat{U}_0(t-\tau_b-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})p_{21}p_{12}\exp[-\frac{i}{\hbar}(E_2-E_1)(\tau_b-\tau_a)]|2\rangle\langle 2|\hat{U}_0(-(t-\tau_b-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}}))\\
&+\hat{U}_0(t-\tau_b-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})p_{12}p_{21}\exp[-\frac{i}{\hbar}(E_1-E_2)(\tau_b-\tau_a)]|1\rangle\langle 1|\hat{U}_0(-(t-\tau_b-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}}))\Bigg]\\
=&\left(-\frac{i}{\hbar}\right)^2\mathscr{E}^2\Bigg[\exp[-\frac{i}{\hbar}\hat{H}_0(t-\tau_b-\frac{\vec{k}\cdot\vec{x}}{\omega_{21}})]p_{12}p_{21}\exp[-\frac{i}{\hbar}(E_2-E_1)(\tau_b-\tau_a)]|1\rangle\langle 1|\exp[\frac{i}{\hbar}\hat{H}_0(t-\tau_b-\frac{\vec{k}\cdot\vec{E}}{\omega_{21}})]
\end{aligned}
$$

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

+4

+1 +1 +1

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

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

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

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

+2

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

□

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:

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

We are interested in the third order contribution to the 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:

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

(b) Write down the density matrix at time t given by $t-\tau_c=\tau_b-\tau_a$.

(c) Suppose now that we have en 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 $(t-\tau_c)-(\tau_b-\tau_a)\gg\frac{1}{\Delta\omega_{21}}$.

  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 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

$$\begin{aligned}\hat{\rho}^{(2)}(t)=&-\left(-\frac{i}{\hbar}\right)^2\mathscr{E}\left[\int_{-\infty}^t d\tau_2\int_{-\infty}^{\tau_2}d\tau_1\,\hat{U}_0(t-\tau_2)\hat{H}_I(\tau_2)\hat{U}_0(\tau_2-\tau_1)[\delta(\tau_1-\tau_a-\frac{\vec{k}_a\cdot\vec{x}}{\omega_{21}})+\delta(\tau_1-\tau_b-\frac{\vec{k}_b\cdot\vec{x}}{\omega_{21}})]p_{21}|2\rangle\langle1|\right.\\&\hat{U}_0(-(\tau_2-\tau_1))\hat{U}_0(-(t-\tau_2))\\&-\int_{-\infty}^t d\tau_2\int_{-\infty}^{\tau_2}d\tau_1\,\hat{U}_0(t-\tau_2)\hat{H}_I(\tau_2)\hat{U}_0(\tau_2-\tau_1)[\delta(\tau_1-\tau_a-\frac{\vec{k}_a\cdot\vec{x}}{\omega_{21}})+\delta(\tau_1-\tau_b-\frac{\vec{k}_b\cdot\vec{x}}{\omega_{21}})]p_{12}|1\rangle\langle2|\\&\hat{U}_0(-(\tau_2-\tau_1))\hat{U}_0(-(t-\tau_2))\end{aligned}$$

$$
\begin{aligned}
&-\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)[\delta(\tau_1-\tau_a-\frac{\vec{k}_a\cdot\vec{x}}{\omega_{21}})+\delta(\tau_1-\tau_b-\frac{\vec{k}_b\cdot\vec{x}}{\omega_{21}})]p_{21}|2\rangle\langle 1|\\
&\qquad\hat{U}_0(-(\tau_2-\tau_1))\hat{H}_I(\tau_2)\hat{U}_0(-(t-\tau_2))\\
&+\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)[\delta(\tau_1-\tau_a-\frac{\vec{k}_a\cdot\vec{x}}{\omega_{21}})+\delta(\tau_1-\tau_b-\frac{\vec{k}_b\cdot\vec{x}}{\omega_{21}})]p_{12}|1\rangle\langle 2|\\
&\qquad\hat{U}_0(-(\tau_2-\tau_1))\hat{H}_I(\tau_2)\hat{U}_0(-(t-\tau_2))\Big]\\
=&-\left(-\frac{i}{\hbar}\right)^2\mathscr{E}\Bigg[\int_{-\infty}^{t}d\tau_2\,\hat{U}_0(t-\tau_2)\hat{H}_I(\tau_2)[\theta(\tau_2-\tau_a-\frac{\vec{k}_a\cdot\vec{x}}{\omega_{21}})\hat{U}_0(\tau_2-\tau_a-\frac{\vec{k}_a\cdot\vec{x}}{\omega_{21}})p_{21}|2\rangle\langle 1|\hat{U}_0(-(\tau_2-\tau_a-\frac{\vec{k}_a\cdot\vec{x}}{\omega_{21}}))\\
&\qquad+\theta(\tau_2-\tau_b-\frac{\vec{k}_b\cdot\vec{x}}{\omega_{21}})\hat{U}_0(\tau_2-\tau_b-\frac{\vec{k}_b\cdot\vec{x}}{\omega_{21}})p_{21}|2\rangle\langle 1|\hat{U}_0(-(\tau_2-\tau_b-\frac{\vec{k}_b\cdot\vec{x}}{\omega_{21}}))]\hat{U}_0(-(t-\tau_2))\\
&-\int_{-\infty}^{t}d\tau_2\,\hat{U}_0(t-\tau_2)\hat{H}_I(\tau_2)[\theta(\tau_2-\tau_a-\frac{\vec{k}_a\cdot\vec{x}}{\omega_{21}})\hat{U}_0(\tau_2-\tau_a-\frac{\vec{k}_a\cdot\vec{x}}{\omega_{21}})p_{12}|1\rangle\langle 2|\hat{U}_0(-(\tau_2-\tau_a-\frac{\vec{k}_a\cdot\vec{x}}{\omega_{21}}))\\
&\qquad+\theta(\tau_2-\tau_b-\frac{\vec{k}_b\cdot\vec{x}}{\omega_{21}})\hat{U}_0(\tau_2-\tau_b-\frac{\vec{k}_b\cdot\vec{x}}{\omega_{21}})p_{12}|1\rangle\langle 2|\hat{U}_0(-(\tau_2-\tau_b-\frac{\vec{k}_b\cdot\vec{x}}{\omega_{21}}))]\hat{U}_0(-(t-\tau_2))\\
&-\int_{-\infty}^{t}d\tau_2\,\hat{U}_0(t-\tau_2)[\theta(\tau_2-\tau_a-\frac{\vec{k}_a\cdot\vec{x}}{\omega_{21}})\hat{U}_0(\tau_2-\tau_a-\frac{\vec{k}_a\cdot\vec{x}}{\omega_{21}})p_{21}|2\rangle\langle 1|\hat{U}_0(-(\tau_2-\tau_a-\frac{\vec{k}_a\cdot\vec{x}}{\omega_{21}}))\\
&\qquad+\theta(\tau_2-\tau_b-\frac{\vec{k}_b\cdot\vec{x}}{\omega_{21}})\hat{U}_0(\tau_2-\tau_b-\frac{\vec{k}_b\cdot\vec{x}}{\omega_{21}})p_{21}|2\rangle\langle 1|\hat{U}_0(-(\tau_2-\tau_b-\frac{\vec{k}_b\cdot\vec{x}}{\omega_{21}}))]\hat{H}_I(\tau_2)\hat{U}_0(-(t-\tau_2))\\
&+\int_{-\infty}^{t}d\tau_2\,\hat{U}_0(t-\tau_2)[\theta(\tau_2-\tau_a-\frac{\vec{k}_a\cdot\vec{x}}{\omega_{21}})\hat{U}_0(\tau_2-\tau_a-\frac{\vec{k}_a\cdot\vec{x}}{\omega_{21}})p_{12}|1\rangle\langle 2|\hat{U}_0(-(\tau_2-\tau_a-\frac{\vec{k}_a\cdot\vec{x}}{\omega_{21}}))\\
&\qquad+\theta(\tau_2-\tau_b-\frac{\vec{k}_b\cdot\vec{x}}{\omega_{21}})\hat{U}_0(\tau_2-\tau_b-\frac{\vec{k}_b\cdot\vec{x}}{\omega_{21}})p_{12}|1\rangle\langle 2|\hat{U}_0(-(\tau_2-\tau_b-\frac{\vec{k}_b\cdot\vec{x}}{\omega_{21}}))]\hat{H}_I(\tau_2)\hat{U}_0(-(t-\tau_2))\Bigg]\\
=&-\left(-\frac{i}{\hbar}\right)^2\mathscr{E}\Bigg[\int_{-\infty}^{t}d\tau_2\,\hat{U}_0(t-\tau_2)\hat{H}_I(\tau_2)[\theta(\tau_2-\tau_a-\frac{\vec{k}_a\cdot\vec{x}}{\omega_{21}})p_{21}\exp[-\frac{i}{\hbar}\hat{H}_0(\tau_2-\tau_a-\frac{\vec{k}_a\cdot\vec{x}}{\omega_{21}})]|2\rangle\langle 1|\exp[\frac{i}{\hbar}\hat{H}_0(\tau_2-\tau_a-\frac{\vec{k}_a\cdot\vec{x}}{\omega_{21}})]\\
&\qquad+\theta(\tau_2-\tau_b-\frac{\vec{k}_b\cdot\vec{x}}{\omega_{21}})p_{21}\exp[\frac{i}{\hbar}\hat{H}_0(\tau_2-\tau_b-\frac{\vec{k}_b\cdot\vec{x}}{\omega_{21}})]|2\rangle\langle 1|\exp[\frac{i}{\hbar}\hat{H}_0(\tau_2-\tau_b-\frac{\vec{k}_b\cdot\vec{x}}{\omega_{21}})]]\hat{U}_0(-(t-\tau_2))\\
&-\int_{-\infty}^{t}d\tau_2\,\hat{U}_0(t-\tau_2)\hat{H}_I(\tau_2)[\theta(\tau_2-\tau_a-\frac{\vec{k}_a\cdot\vec{x}}{\omega_{21}})p_{12}\exp[\frac{i}{\hbar}\hat{H}_0(\tau_2-\tau_a-\frac{\vec{k}_a\cdot\vec{x}}{\omega_{21}})]|1\rangle\langle 2|\exp[\frac{i}{\hbar}\hat{H}_0(\tau_2-\tau_a-\frac{\vec{k}_a\cdot\vec{x}}{\omega_{21}})]\\
&\qquad+\theta(\tau_2-\tau_b-\frac{\vec{k}_b\cdot\vec{x}}{\omega_{21}})p_{12}\exp[\frac{i}{\hbar}\hat{H}_0(\tau_2-\tau_b-\frac{\vec{k}_b\cdot\vec{x}}{\omega_{21}})]|1\rangle\langle 2|\exp[\frac{i}{\hbar}\hat{H}_0(\tau_2-\tau_b-\frac{\vec{k}_b\cdot\vec{x}}{\omega_{21}})]]\hat{U}_0(-(t-\tau_2))\\
&-\int_{-\infty}^{t}d\tau_2\,\hat{U}_0(t-\tau_2)[\theta(\tau_2-\tau_a-\frac{\vec{k}_a\cdot\vec{x}}{\omega_{21}})p_{21}\exp[\frac{i}{\hbar}\hat{H}_0(\tau_2-\tau_a-\frac{\vec{k}_a\cdot\vec{x}}{\omega_{21}})]|2\rangle\langle 1|\exp[\frac{i}{\hbar}\hat{H}_0(\tau_2-\tau_a-\frac{\vec{k}_a\cdot\vec{x}}{\omega_{21}})]\\
&\qquad+\theta(\tau_2-\tau_b-\frac{\vec{k}_b\cdot\vec{x}}{\omega_{21}})p_{21}\exp[\frac{i}{\hbar}\hat{H}_0(\tau_2-\tau_b-\frac{\vec{k}_b\cdot\vec{x}}{\omega_{21}})]|2\rangle\langle 1|\exp[\frac{i}{\hbar}\hat{H}_0(\tau_2-\tau_b-\frac{\vec{k}_b\cdot\vec{x}}{\omega_{21}})]]\hat{H}_I(\tau_2)\hat{U}_0(-(t-\tau_2))\\
&+\int_{-\infty}^{t}d\tau_2\,\hat{U}_0(t-\tau_2)[\theta(\tau_2-\tau_a-\frac{\vec{k}_a\cdot\vec{x}}{\omega_{21}})p_{12}\exp[\frac{i}{\hbar}\hat{H}_0(\tau_2-\tau_a-\frac{\vec{k}_a\cdot\vec{x}}{\omega_{21}})]|1\rangle\langle 2|\exp[\frac{i}{\hbar}\hat{H}_0(\tau_2-\tau_a-\frac{\vec{k}_a\cdot\vec{x}}{\omega_{21}})]\\
&\qquad+\theta(\tau_2-\tau_b-\frac{\vec{k}_b\cdot\vec{x}}{\omega_{21}})p_{12}\exp[\frac{i}{\hbar}\hat{H}_0(\tau_2-\tau_b-\frac{\vec{k}_b\cdot\vec{x}}{\omega_{21}})]|1\rangle\langle 2|\exp[\frac{i}{\hbar}\hat{H}_0(\tau_2-\tau_b-\frac{\vec{k}_b\cdot\vec{x}}{\omega_{21}})]]\hat{H}_I(\tau_2)\hat{U}_0(-(t-\tau_2))\Bigg]\\
=&-\left(-\frac{i}{\hbar}\right)^2\mathscr{E}\Bigg[\int_{-\infty}^{t}d\tau_2\,\hat{U}_0(t-\tau_2)\hat{H}_I(\tau_2)[\theta(\tau_2-\tau_a-\frac{\vec{k}_a\cdot\vec{x}}{\omega_{21}})p_{21}\exp[-\frac{i}{\hbar}E_2(\tau_2-\tau_a-\frac{\vec{k}_a\cdot\vec{x}}{\omega_{21}})]|2\rangle\langle 1|\exp[\frac{i}{\hbar}E_1(\tau_2-\tau_a-\frac{\vec{k}_a\cdot\vec{x}}{\omega_{21}})]\\
&\qquad+\theta(\tau_2-\tau_b-\frac{\vec{k}_b\cdot\vec{x}}{\omega_{21}})p_{21}\exp[\frac{i}{\hbar}E_2(\tau_2-\tau_b-\frac{\vec{k}_b\cdot\vec{x}}{\omega_{21}})]|2\rangle\langle 1|\exp[\frac{i}{\hbar}E_1(\tau_2-\tau_b-\frac{\vec{k}_b\cdot\vec{x}}{\omega_{21}})]]\hat{U}_0(-(t-\tau_2))\\
&-\int_{-\infty}^{t}d\tau_2\,\hat{U}_0(t-\tau_2)\hat{H}_I(\tau_2)[\theta(\tau_2-\tau_a-\frac{\vec{k}_a\cdot\vec{x}}{\omega_{21}})p_{12}\exp[\frac{i}{\hbar}E_1(\tau_2-\tau_a-\frac{\vec{k}_a\cdot\vec{x}}{\omega_{21}})]|1\rangle\langle 2|\exp[\frac{i}{\hbar}E_2(\tau_2-\tau_a-\frac{\vec{k}_a\cdot\vec{x}}{\omega_{21}})]\\
&\qquad+\theta(\tau_2-\tau_b-\frac{\vec{k}_b\cdot\vec{x}}{\omega_{21}})p_{12}\exp[\frac{i}{\hbar}E_1(\tau_2-\tau_b-\frac{\vec{k}_b\cdot\vec{x}}{\omega_{21}})]|1\rangle\langle 2|\exp[\frac{i}{\hbar}E_2(\tau_2-\tau_b-\frac{\vec{k}_b\cdot\vec{x}}{\omega_{21}})]]\hat{U}_0(-(t-\tau_2))\\
&-\int_{-\infty}^{t}d\tau_2\,\hat{U}_0(t-\tau_2)[\theta(\tau_2-\tau_a-\frac{\vec{k}_a\cdot\vec{x}}{\omega_{21}})p_{21}\exp[\frac{i}{\hbar}E_2(\tau_2-\tau_a-\frac{\vec{k}_a\cdot\vec{x}}{\omega_{21}})]|2\rangle\langle 1|\exp[\frac{i}{\hbar}E_1(\tau_2-\tau_a-\frac{\vec{k}_a\cdot\vec{x}}{\omega_{21}})]\\
&\qquad+\theta(\tau_2-\tau_b-\frac{\vec{k}_b\cdot\vec{x}}{\omega_{21}})p_{21}\exp[\frac{i}{\hbar}E_2(\tau_2-\tau_b-\frac{\vec{k}_b\cdot\vec{x}}{\omega_{21}})]|2\rangle\langle 1|\exp[\frac{i}{\hbar}E_1(\tau_2-\tau_b-\frac{\vec{k}_b\cdot\vec{x}}{\omega_{21}})]]\hat{H}_I(\tau_2)\hat{U}_0(-(t-\tau_2))\\
&+\int_{-\infty}^{t}d\tau_2\,\hat{U}_0(t-\tau_2)[\theta(\tau_2-\tau_a-\frac{\vec{k}_a\cdot\vec{x}}{\omega_{21}})p_{12}\exp[\frac{i}{\hbar}E_1(\tau_2-\tau_a-\frac{\vec{k}_a\cdot\vec{x}}{\omega_{21}})]|1\rangle\langle 2|\exp[\frac{i}{\hbar}E_2(\tau_2-\tau_a-\frac{\vec{k}_a\cdot\vec{x}}{\omega_{21}})]\\
&\qquad+\theta(\tau_2-\tau_b-\frac{\vec{k}_b\cdot\vec{x}}{\omega_{21}})p_{12}\exp[\frac{i}{\hbar}E_1(\tau_2-\tau_b-\frac{\vec{k}_b\cdot\vec{x}}{\omega_{21}})]|1\rangle\langle 2|\exp[\frac{i}{\hbar}E_2(\tau_2-\tau_b-\frac{\vec{k}_b\cdot\vec{x}}{\omega_{21}})]]\hat{H}_I(\tau_2)\hat{U}_0(-(t-\tau_2))\Bigg]
\end{aligned}
$$

$$
\begin{aligned}
=&-\left(-\frac{i}{\hbar}\right)^2\mathscr{E}\left[\int_{-\infty}^{t}d\tau_2\,\hat{U}_0(t-\tau_2)[(-\vec{p}\cdot\vec{E}(\tau_2))_{12}|1\rangle\langle 2|+(-\vec{p}\cdot\vec{E}(\tau_2))_{21}|2\rangle\langle 1|][\theta(\tau_2-\tau_a-\frac{\vec{k}_a\cdot\vec{x}}{\omega_{21}})p_{21}\exp[-\frac{i}{\hbar}(E_2-E_1)(\tau_2-\tau_a-\frac{\vec{k}_a\cdot\vec{x}}{\omega_{21}})]|2\rangle\langle 1|\right.\\
&\qquad+\theta(\tau_2-\tau_b-\frac{\vec{k}_b\cdot\vec{x}}{\omega_{21}})p_{21}\exp[-\frac{i}{\hbar}(E_2-E_1)(\tau_2-\tau_b-\frac{\vec{k}_b\cdot\vec{x}}{\omega_{21}})]|2\rangle\langle 1|\hat{U}_0(-(t-\tau_2))\\
&-\int_{-\infty}^{t}d\tau_2\,\hat{U}_0(t-\tau_2)[(-\vec{p}\cdot\vec{E}(\tau_2))_{12}|1\rangle\langle 2|+(-\vec{p}\cdot\vec{E}(\tau_2))_{21}|2\rangle\langle 1|][\theta(\tau_2-\tau_a-\frac{\vec{k}_a\cdot\vec{x}}{\omega_{21}})p_{12}\exp[-\frac{i}{\hbar}(E_1-E_2)(\tau_2-\tau_a-\frac{\vec{k}_a\cdot\vec{x}}{\omega_{21}})]|1\rangle\langle 2|\\
&\qquad+\theta(\tau_2-\tau_b-\frac{\vec{k}_b\cdot\vec{x}}{\omega_{21}})p_{12}\exp[-\frac{i}{\hbar}(E_1-E_2)(\tau_2-\tau_b-\frac{\vec{k}_b\cdot\vec{x}}{\omega_{21}})]|1\rangle\langle 2|]\hat{U}_0(-(t-\tau_2))\\
&-\int_{-\infty}^{t}d\tau_2\,\hat{U}_0(t-\tau_2)[\theta(\tau_2-\tau_a-\frac{\vec{k}_a\cdot\vec{x}}{\omega_{21}})p_{21}\exp[-\frac{i}{\hbar}(E_2-E_1)(\tau_2-\tau_a-\frac{\vec{k}_a\cdot\vec{x}}{\omega_{21}})]|2\rangle\langle 1|\\
&\qquad+\theta(\tau_2-\tau_b-\frac{\vec{k}_b\cdot\vec{x}}{\omega_{21}})p_{21}\exp[-\frac{i}{\hbar}(E_2-E_1)(\tau_2-\tau_b-\frac{\vec{k}_b\cdot\vec{x}}{\omega_{21}})]|m\rangle\langle 1|][(-\vec{p}\cdot\vec{E}(\tau_2))_{12}|1\rangle\langle 2|-(-\vec{p}\cdot\vec{E}(\tau_2))_{21}|2\rangle\langle 1|]\hat{U}_0(-(t-\tau_2))\\
&+\int_{-\infty}^{t}d\tau_2\,\hat{U}_0(t-\tau_2)[\theta(\tau_2-\tau_a-\frac{\vec{k}_a\cdot\vec{x}}{\omega_{21}})p_{12}\exp[-\frac{i}{\hbar}(E_1-E_2)(\tau_2-\tau_a-\frac{\vec{k}_a\cdot\vec{x}}{\omega_{21}})]|1\rangle\langle 2|\\
&\qquad\left.+\theta(\tau_2-\tau_b-\frac{\vec{k}_b\cdot\vec{x}}{\omega_{21}})p_{12}\exp[-\frac{i}{\hbar}(E_1-E_2)(\tau_2-\tau_b-\frac{\vec{k}_b\cdot\vec{x}}{\omega_{21}})]|1\rangle\langle 2|][(-\vec{p}\cdot\vec{E}(\tau_2))_{12}|1\rangle\langle 2|+(-\vec{p}\cdot\vec{E}(\tau_2))_{21}|2\rangle\langle 1|]\hat{U}_0(-(t-\tau_2))\right]\\
=&\left(-\frac{i}{\hbar}\right)^2\mathscr{E}^2\left[\int_{-\infty}^{t}d\tau_2\,\hat{U}_0(t-\tau_2)[\delta(\tau_2-\tau_a-\frac{\vec{k}_a\cdot\vec{E}}{\omega_{21}})+\delta(\tau_2-\tau_b-\frac{\vec{k}_b\cdot\vec{E}}{\omega_{21}})]\right.\\
&\qquad[p_{12}|1\rangle\langle 2|+p_{21}|2\rangle\langle 1|][\theta(\tau_2-\tau_a-\frac{\vec{k}_a\cdot\vec{x}}{\omega_{21}})p_{21}\exp[-\frac{i}{\hbar}(E_2-E_1)(\tau_2-\tau_a-\frac{\vec{k}_a\cdot\vec{x}}{\omega_{21}})]|2\rangle\langle 1|\\
&\qquad+\theta(\tau_2-\tau_b-\frac{\vec{k}_b\cdot\vec{x}}{\omega_{21}})p_{21}\exp[-\frac{i}{\hbar}(E_2-E_1)(\tau_2-\tau_b-\frac{\vec{k}_b\cdot\vec{x}}{\omega_{21}})]|2\rangle\langle 1|]\hat{U}_0(-(t-\tau_2))\\
&-\int_{-\infty}^{t}d\tau_2\,\hat{U}_0(t-\tau_2)[\delta(\tau_2-\tau_a-\frac{\vec{k}_a\cdot\vec{E}}{\omega_{21}})+\delta(\tau_2-\tau_b-\frac{\vec{k}_b\cdot\vec{E}}{\omega_{21}})]\\
&\qquad[p_{12}|1\rangle\langle 2|+p_{21}|2\rangle\langle 1|][\theta(\tau_2-\tau_a-\frac{\vec{k}_a\cdot\vec{x}}{\omega_{21}})p_{12}\exp[-\frac{i}{\hbar}(E_1-E_2)(\tau_2-\tau_a-\frac{\vec{k}_a\cdot\vec{x}}{\omega_{21}})]|1\rangle\langle 2|\\
&\qquad+\theta(\tau_2-\tau_b-\frac{\vec{k}_b\cdot\vec{x}}{\omega_{21}})p_{12}\exp[-\frac{i}{\hbar}(E_1-E_2)(\tau_2-\tau_b-\frac{\vec{k}_b\cdot\vec{x}}{\omega_{21}})]|1\rangle\langle 2|]\hat{U}_0(-(t-\tau_2))\\
&-\int_{-\infty}^{t}d\tau_2\,\hat{U}_0(t-\tau_2)[\delta(\tau_2-\tau_a-\frac{\vec{k}_a\cdot\vec{E}}{\omega_{21}})+\delta(\tau_2-\tau_b-\frac{\vec{k}_b\cdot\vec{E}}{\omega_{21}})]\\
&\qquad[\theta(\tau_2-\tau_a-\frac{\vec{k}_a\cdot\vec{x}}{\omega_{21}})p_{21}\exp[-\frac{i}{\hbar}(E_2-E_1)(\tau_2-\tau_a-\frac{\vec{k}_a\cdot\vec{x}}{\omega_{21}})]|2\rangle\langle 1|\\
&\qquad+\theta(\tau_2-\tau_b-\frac{\vec{k}_b\cdot\vec{x}}{\omega_{21}})p_{21}\exp[-\frac{i}{\hbar}(E_2-E_1)(\tau_2-\tau_b-\frac{\vec{k}_b\cdot\vec{x}}{\omega_{21}})]|2\rangle\langle 1|][p_{12}|1\rangle\langle 2|+p_{21}|2\rangle\langle 1|]\hat{U}_0(-(t-\tau_2))\\
&+\int_{-\infty}^{t}d\tau_2\,\hat{U}_0(t-\tau_2)[\delta(\tau_2-\tau_a-\frac{\vec{k}_a\cdot\vec{E}}{\omega_{21}})+\delta(\tau_2-\tau_b-\frac{\vec{k}_b\cdot\vec{E}}{\omega_{21}})]\\
&\qquad[\theta(\tau_2-\tau_a-\frac{\vec{k}_a\cdot\vec{x}}{\omega_{21}})p_{12}\exp[-\frac{i}{\hbar}(E_1-E_2)(\tau_2-\tau_a-\frac{\vec{k}_a\cdot\vec{x}}{\omega_{21}})]|1\rangle\langle 2|\\
&\qquad\left.+\theta(\tau_2-\tau_b-\frac{\vec{k}_b\cdot\vec{x}}{\omega_{21}})p_{12}\exp[-\frac{i}{\hbar}(E_1-E_2)(\tau_2-\tau_b-\frac{\vec{k}_b\cdot\vec{x}}{\omega_{21}})]|1\rangle\langle 2|][p_{12}|1\rangle\langle 2|+p_{21}|2\rangle\langle 1|]\hat{U}_0(-(t-\tau_2))\right]\\
=&\left(-\frac{i}{\hbar}\right)^2\mathscr{E}^2\left[\hat{U}_0(t-\tau_b-\frac{\vec{k}_b\cdot\vec{x}}{\omega_{21}})p_{12}p_{21}\exp[-\frac{i}{\hbar}(E_2-E_1)(\tau_b-\tau_a+\frac{(\vec{k}_b-\vec{k}_a)\cdot\vec{x}}{\omega_{21}})]|1\rangle\langle 1|\hat{U}_0(-(t-\tau_b-\frac{\vec{k}_b\cdot\vec{E}}{\omega_{21}}))\right.\\
&-\hat{U}_0(t-\tau_b-\frac{\vec{k}_b\cdot\vec{x}}{\omega_{21}})p_{21}p_{12}\exp[-\frac{i}{\hbar}(E_1-E_2)(\tau_b-\tau_a+\frac{(\vec{k}_b-\vec{k}_a)\cdot\vec{x}}{\omega_{21}})]|2\rangle\langle 2|\hat{U}_0(t-\tau_b-\frac{\vec{k}_b\cdot\vec{x}}{\omega_{21}})\\
&-\hat{U}_0(t-\tau_b-\frac{\vec{k}_b\cdot\vec{x}}{\omega_{21}})p_{21}p_{12}\exp[-\frac{i}{\hbar}(E_2-E_1)(\tau_b-\tau_a+\frac{(\vec{k}_b-\vec{k}_a)}{\omega_{21}})]|2\rangle\langle k|\hat{U}_0(-(t-\tau_b-\frac{\vec{k}_b\cdot\vec{x}}{\omega_{21}}))\\
&\left.+\hat{U}_0(t-\tau_b-\frac{\vec{k}_b\cdot\vec{x}}{\omega_{21}})p_{12}p_{21}\exp[-\frac{i}{\hbar}(E_1-E_2)(\tau_b-\tau_a-\frac{(\vec{k}_b-\vec{k}_a)}{\omega_{21}})]|1\rangle\langle 1|\hat{U}_0(-(t-\tau_b-\frac{\vec{k}_b\cdot\vec{x}}{\omega_{21}}))\right]\\
=&\left(-\frac{i}{\hbar}\right)^2\mathscr{E}^2\left[\exp[-\frac{i}{\hbar}\hat{H}_0(t-\tau_b-\frac{\vec{k}_b\cdot\vec{x}}{\omega_{21}})]p_{12}p_{21}\exp[-\frac{i}{\hbar}(E_2-E_1)(\tau_b-\tau_a+\frac{(\vec{k}_b-\vec{k}_a)\cdot\vec{x}}{\omega_{21}})]|1\rangle\langle 1|\exp[\frac{i}{\hbar}\hat{H}_0(t-\tau_b-\frac{\vec{k}_b\cdot\vec{E}}{\omega_{21}})]\right.\\
&-\exp[-\frac{i}{\hbar}\hat{H}_0(t-\tau_b-\frac{\vec{k}_b\cdot\vec{x}}{\omega_{21}})]p_{21}p_{12}\exp[-\frac{i}{\hbar}(E_1-E_2)(\tau_b-\tau_a+\frac{(\vec{k}_b-\vec{k}_a)\cdot\vec{x}}{\omega_{21}})]|2\rangle\langle 2|\exp[\frac{i}{\hbar}\hat{H}_0(t-\tau_b-\frac{\vec{k}_b\cdot\vec{x}}{\omega_{21}})]\\
&-\exp[-\frac{i}{\hbar}\hat{H}_0(t-\tau_b-\frac{\vec{k}_b\cdot\vec{x}}{\omega_{21}})]p_{21}p_{12}\exp[-\frac{i}{\hbar}(E_2-E_1)(\tau_b-\tau_a+\frac{(\vec{k}_b-\vec{k}_a)}{\omega_{21}})]|2\rangle\langle 2|\exp[\frac{i}{\hbar}\hat{H}_0(t-\tau_b-\frac{\vec{k}_b\cdot\vec{x}}{\omega_{21}})]
\end{aligned}
$$

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

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)\mathscr{E}\Bigg[\int_{\tau_b}^{t}d\tau_3\,\exp[-\frac{i}{\hbar}\hat{H}_0(t-\tau_3)]\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[\frac{i}{\hbar}\hat{H}_0(t-\tau_3)]\\
&-\int_{\tau_b}^{t}d\tau_3\,\exp[-\frac{i}{\hbar}\hat{H}_0(t-\tau_3)][\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[\frac{i}{\hbar}\hat{H}_0(t-\tau_3)]\Bigg]\\
=&-\left(-\frac{i}{\hbar}\right)\mathscr{E}\Bigg[\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[-\frac{i}{\hbar}(E_1-E_2)(t-\tau_3)]|1\rangle\langle 2|+p_{21}\rho_{11}(\tau_b)\exp[\frac{i}{\hbar}(E_2-E_1)(t-\tau_3)]|2\rangle\langle 1|]\\
&-\int_{\tau_b}^{t}d\tau_3\,[\rho_{11}(\tau_b)p_{12}\exp[-\frac{i}{\hbar}(E_1-E_2)(t-\tau_3)]|1\rangle\langle 2|+\rho_{22}(\tau_b)p_{21}\exp[\frac{i}{\hbar}(E_2-E_1)(t-\tau_3)]|2\rangle\langle 1|]\delta(\tau_3-\tau_c-\frac{\vec{k}_c\cdot\vec{x}}{\omega_{21}})\Bigg]\\
=&-\left(-\frac{i}{\hbar}\right)\mathscr{E}\Bigg[p_{12}\rho_{22}(\tau_3)\exp[-\frac{i}{\hbar}(E_1-E_2)(t-\tau_c-\frac{\vec{k}_c\cdot\vec{x}}{\omega_{21}})]|1\rangle\langle 2|+p_{21}\rho_{11}(\tau_3)\exp[-\frac{i}{\hbar}(E_2-E_1)(t-\tau_c-\frac{\vec{k}_c\cdot\vec{x}}{\omega_{21}}))]|2\rangle\langle 1|\\
&-\rho_{11}(\tau_3)p_{12}\exp[-\frac{i}{\hbar}(E_1-E_2)(t-\tau_c-\frac{\vec{k}_c\cdot\vec{x}}{\omega_{21}})]|1\rangle\langle 2|-\rho_{22}(\tau_3)p_{21}\exp[-\frac{i}{\hbar}(E_2-E_1)(t-\tau_c-\frac{\vec{k}_c\cdot\vec{x}}{\omega_{21}})]|2\rangle\langle 1|\Bigg]\hat{U}_0(-t)\\
=&-\left(-\frac{i}{\hbar}\right)\mathscr{E}\Bigg[p_{12}(\rho_{22}(\tau_b)-\rho_{11}(\tau_3))\exp[-\frac{i}{\hbar}(E_1-E_2)(t-\tau_c-\frac{\vec{k}_c\cdot\vec{x}}{\omega_{21}})]|1\rangle\langle 2|\\
&p_{21}(\rho_{11}(\tau_3)-\rho_{22}(\tau_3))\exp[-\frac{i}{\hbar}(E_2-E_1)(t-\tau_c-\frac{\vec{k}_c\cdot\vec{x}}{\omega_{21}}))]|2\rangle\langle 1|\Bigg]
\end{aligned}
$$

+5

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

+1

$$
\begin{aligned}
=&4\left(-\frac{i}{\hbar}\right)^3\mathscr{E}p_{12}p_{21}\begin{pmatrix}0&p_{12}\exp\left[-\frac{i}{\hbar}(E_1-E_2)(t-\tau_c-\frac{\vec{k}_c\cdot\vec{x}}{\omega_{21}})\right]\\-p_{21}\exp[-\frac{i}{\hbar}(E_2-E_1)(t-\tau_c-\frac{\vec{k}_c\cdot\vec{x}}{\omega_{21}}))]&0\end{pmatrix}\\
&\times\left\{\exp\left[\frac{i}{\hbar}(E_2-E_1)(\tau_b-\tau_a+\frac{(\vec{k}_b-\vec{k}_a)\cdot\vec{x}}{\omega_{21}})\right]+\exp\left[-\frac{i}{\hbar}(E_2-E_1)(\tau_b-\tau_a+\frac{(\vec{k}_b-\vec{k}_a)\cdot\vec{x}}{\omega_{21}})\right]\right\}
\end{aligned}\tag{8}
$$

+5

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

+1

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

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

+2

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

(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

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

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

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

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

+2

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

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

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

□