Concepts and Methods of 2D Infrared Spectroscopy

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Answer Keys: Chapter 2

Problem 2.1: Verify Eq. 2.8

Solution: We substitute Eq. 2.7 into the left-hand side of Eq. 2.6 and apply the chain rule:

$$i\hbar\frac{\partial}{\partial t}\left(\sum_n c_n e^{-iE_nt/\hbar}|n\rangle\right) = i\hbar\sum_n \frac{\partial c_n}{\partial t}e^{-iE_nt/\hbar}|n\rangle + \sum_n E_n c_n e^{-iE_nt/\hbar}|n\rangle$$

The second term just equals $\hat{H}_0\Psi$, since the $|n\rangle$ are eigenfunctions of the system Hamiltonian, so:

$$i\hbar\sum_n \frac{\partial c_n}{\partial t}e^{-iE_nt/\hbar}|n\rangle = \hat{W}(t)\left(\sum_n c_n e^{-iE_nt/\hbar}|n\rangle\right)$$

We now multiply this equation from left with $\langle m|$, make use of the fact that the wavefunctions are orthonormal, $\langle m|n\rangle = \delta_{m,n}$, and obtain the final result Eq. 2.8.

Problem 2.2: With Eq. 2.37, show that the macroscopic polarization of state Eq. 2.30 is maximal, and that of an incoherent state Eq. 2.32 is zero.

Solution: We start with Eq. 2.32:

$$\mathrm{Tr}(\rho\mu) = \mathrm{Tr}\left(\begin{pmatrix} 1/2 & 0 \\ 0 & 1/2 \end{pmatrix}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\right) = \mathrm{Tr}\begin{pmatrix} 0 & 1/2 \\ 1/2 & 0 \end{pmatrix} = 0$$

For Eq. 2.30

$$\mathrm{Tr}(\rho\mu) = \mathrm{Tr}\left(\begin{pmatrix} 1/2 & -i/2 \\ +i/2 & 1/2 \end{pmatrix}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\right) = \mathrm{Tr}\begin{pmatrix} -i/2 & 1/2 \\ 1/2 & i/2 \end{pmatrix} = 0$$

we get zero as well. However, if we include the time propagation of such a density matrix:

$$\begin{aligned}\mathrm{Tr}(\rho\mu) &= \mathrm{Tr}\left(\left(\begin{array}{cc} 1/2 & -i/2e^{i\omega_{01}t} \\ +i/2e^{-i\omega_{01}t} & 1/2 \end{array}\right)\left(\begin{array}{cc} 0 & 1 \\ 1 & 0 \end{array}\right)\right) \\ &= \mathrm{Tr}\left(\begin{array}{cc} -i/2e^{i\omega t} & 1/2 \\ 1/2 & i/2e^{-i\omega t} \end{array}\right) = \sin\omega t\end{aligned}$$

we see that it oscillates with amplitude one.

Problem 2.3: Calculate the evolution of the density matrix for R_2 and R_5 in a manner that is analogous to Eq. 2.68. In what aspect are they different from R_1 and R_4?

Solution: For R_2 :

$$\begin{array}{l}\left(\begin{array}{cc} 1 & 0 \\ 0 & 0 \end{array}\right) \xrightarrow{i\rho\mu_0} \left(\begin{array}{cc} 0 & i \\ 0 & 0 \end{array}\right) \xrightarrow{t_1} \left(\begin{array}{cc} 0 & ie^{+i\omega_{01}t_1} \\ 0 & 0 \end{array}\right) \xrightarrow{i\rho\mu_0\mu_1} \\ \left(\begin{array}{cc} ie^{+i\omega_{01}t_1} & 0 \\ 0 & 0 \end{array}\right) \xrightarrow{i\mu_2\rho\mu_0\mu_1} \left(\begin{array}{cc} 0 & 0 \\ ie^{+i\omega_{01}t_1} & 0 \end{array}\right) \xrightarrow{t_3} \\ \left(\begin{array}{cc} 0 & 0 \\ ie^{-i\omega_{01}(t_3-t_1)} & 0 \end{array}\right) \xrightarrow{i\langle\mu_3\mu_2\rho\mu_0\mu_1\rangle} ie^{-i\omega_{01}(t_3-t_1)}\end{array}$$

and for R_5 :

$$\begin{array}{l}\left(\begin{array}{cc} 1 & 0 \\ 0 & 0 \end{array}\right) \xrightarrow{i\mu_0\rho} \left(\begin{array}{cc} 0 & 0 \\ i & 0 \end{array}\right) \xrightarrow{t_1} \left(\begin{array}{cc} 0 & 0 \\ ie^{-i\omega_{01}t_1} & 0 \end{array}\right) \xrightarrow{i\mu_1\mu_0\rho} \\ \left(\begin{array}{cc} ie^{-i\omega_{01}t_1} & 0 \\ 0 & 0 \end{array}\right) \xrightarrow{i\mu_2\mu_1\mu_0\rho} \left(\begin{array}{cc} 0 & 0 \\ ie^{-i\omega_{01}t_1} & 0 \end{array}\right) \xrightarrow{t_3} \\ \left(\begin{array}{cc} 0 & 0 \\ ie^{-i\omega_{01}(t_3+t_1)} & 0 \end{array}\right) \xrightarrow{i\langle\mu_3\mu_2\mu_1\mu_0\rho\rangle} ie^{-i\omega_{01}(t_3+t_1)}\end{array}$$

R_2 and R_5 have a ρ_{00} matrix element after the second field interaction, rather than a ρ_{11} matrix element. We say that these diagrams go through the ground state during the population time t_2.

Problem 2.4: Repeat the calculation of the propagation of the density matrix analogous to Eqns. 2.43, 2.44 and 2.50 with the first field interaction acting from the left, however, now starting out from an excited state with:

$$\rho(-\infty) = \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}.$$

Prove that $E^*(t) \propto e^{+i\omega_{01}t}$ now survives the rotating wave approximation, whereas the term related to $E(t) \propto e^{-i\omega_{01}t}$ vanishes. Draw the corresponding Feynman diagram.

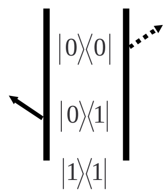
Solution:

$$\begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix} \xrightarrow{i\mu_0\rho} \begin{pmatrix} 0 & i \\ 0 & 0 \end{pmatrix} \xrightarrow{t_1} \begin{pmatrix} 0 & ie^{i\omega_{01}t_1} \\ 0 & 0 \end{pmatrix} \xrightarrow{i\mu_0\rho\mu_1}$$
$$\begin{pmatrix} ie^{i\omega_{01}t_1} & 0 \\ 0 & 0 \end{pmatrix} \xrightarrow{i\langle\mu_0\rho\mu_1\rangle} ie^{i\omega_{01}(t_1)}$$

Plugging this into Eq. 2.56, we get:

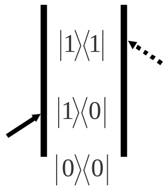
$$P^{(1)}(t) \propto \; ie^{-i\omega t} \int\limits_0^\infty dt_1 E'(t-t_1) e^{-t_1/T_2} e^{+2i\omega t_1}$$
$$+ie^{+i\omega t} \int\limits_0^\infty dt_1 E'(t-t_1) e^{-t_1/T_2}. \tag{0.1}$$

The term in the first integral is highly oscillating, hence the integral will be very small. The corresponding Feynman diagram is:



Problem 2.5: The trace is invariant under cyclic permutation, so $\langle \mu(t_1)\mu(0)\rho(-\infty)\rangle = \langle \mu(0)\rho(-\infty)\mu(t_1)\rangle$. By convention we choose the left term, but the right one is mathematically identical. Plot the corresponding Feynman diagram for the right term, taking into account the rotating wave approximation, and discuss how it might be interpreted.

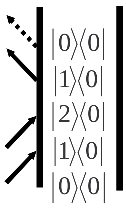
Solution: The corresponding Feynman diagram would be:



hence, it ends in an excited state $|1\rangle\langle 1|$. This is often used as another answer to resolve the paradox in Sect. 2.5. That is, the fact that we end in the ground state $|0\rangle\langle 0|$ is the result of an arbitrary (but common) convention of plotting Feynman diagram. If one were to use the other representation, which is mathematically equivalent, energy conservation is guaranteed.

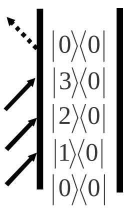
Problem 2.6: Draw a Feynman-diagram that emits in $+\vec{k}_1 + \vec{k}_2 - \vec{k}_3$ direction.

Solution:



Problem 2.7: Draw a Feynman-diagram that emits in $+\vec{k}_1 + \vec{k}_2 + \vec{k}_3$ direction. At what frequency will it emit?

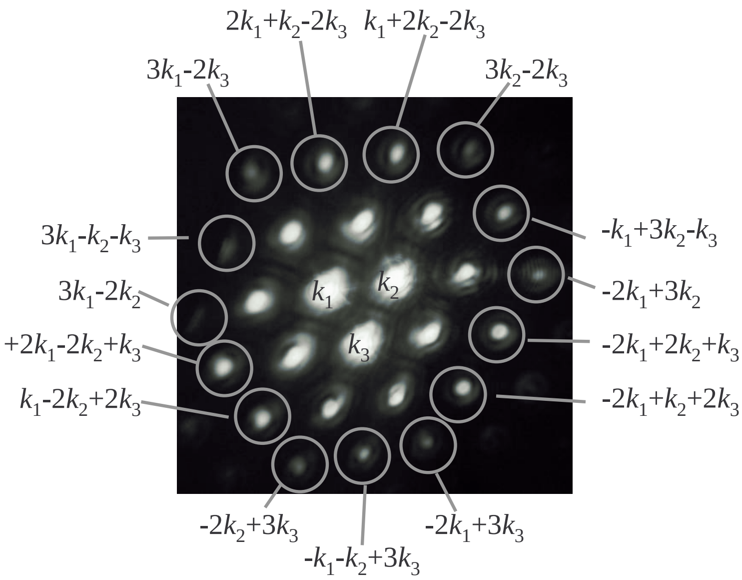
Solution:



This diagram will emit at three times the incident laser frequency (third harmonic).

Problem 2.8: In Fig. 2.14, find the phase matching conditions for the 5^{th}-order beams. In each case, think of a corresponding Feynman diagram, assuming that you can apply the rotating wave approximation. Hint: In some cases, you will need more than a two-level system, e.g. a slightly anharmonic oscillator with a set of almost equidistant quantum states.

Solution:



For example, one possible Feynman diagram observed in the $2k_1 - 2k_2 + k_3$ phase matching direction would be: