# Concepts and Methods of 2D Infrared Spectroscopy

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## Answer Keys: Chapter 3

**Problem 3.1:** Show that one obtains $\rho = \rho^2$ for the density matrix of a pure state. Show that this is no longer true for a density matrix of a statistical average. Verify these results for the examples $\rho = \begin{pmatrix} 1/2 & 1/2 \\ 1/2 & 1/2 \end{pmatrix}$ and $\rho = \begin{pmatrix} 1/2 & 0 \\ 0 & 1/2 \end{pmatrix}$.

**Solution:**

For the density matrix of a pure state described by a wavefunction $\Psi$, we have:

$$\rho = |\Psi\rangle\langle\Psi|$$

so

$$\rho^2 = |\Psi\rangle\langle\Psi|\Psi\rangle\langle\Psi| = |\Psi\rangle\langle\Psi|$$

since the middle part, $\langle\Psi|\Psi\rangle$, is the norm of the wavefunction, which we assume to be one.

For $\rho = \begin{pmatrix} 1/2 & 1/2 \\ 1/2 & 1/2 \end{pmatrix}$, we get:

$$\rho^2 = \begin{pmatrix} 1/2 & 1/2 \\ 1/2 & 1/2 \end{pmatrix} \cdot \begin{pmatrix} 1/2 & 1/2 \\ 1/2 & 1/2 \end{pmatrix} = \begin{pmatrix} 1/2 & 1/2 \\ 1/2 & 1/2 \end{pmatrix}$$

and for $\rho = \begin{pmatrix} 1/2 & 0 \\ 0 & 1/2 \end{pmatrix}$:

$$\rho^2 = \begin{pmatrix} 1/2 & 0 \\ 0 & 1/2 \end{pmatrix} \cdot \begin{pmatrix} 1/2 & 0 \\ 0 & 1/2 \end{pmatrix} = \begin{pmatrix} 1/4 & 0 \\ 0 & 1/4 \end{pmatrix}$$

**Problem 3.2:** Verify that there is no wavefunction $|\psi\rangle$ whose density matrix would be $\rho = \begin{pmatrix} 1/2 & 0 \\ 0 & 1/2 \end{pmatrix}$

**Solution:** The diagonal elements of a density matrix are defined as $c_n c_m^*$. From the two diagonal element, one would conclude $c_0 = 1/\sqrt{2}$ and $c_1 = 1/\sqrt{2}$ (modulo an undetermined phase factor, but then, if it were a pure state, the off-diagonal element would be $\rho_{01} = c_0 c_1^*$.

**Problem 3.3:** Show that exactly one eigenvalue of a $n \times n$-density matrix of a pure state is 1, while all others are zero. Hint: Start with $\rho = \rho^2$. Diagonalize with a matrix $Q$ and compare the diagonal elements.

**Solution:**

Let $Q$ be the unitary transformation matrix that diagonalizes $\rho$ (which exists since $\rho$ is hermitian). Then:

$$Q^{-1}\rho Q = D$$

with $D$ a diagonal matrix with the real eigenvalues of $\rho$. We calculate

$$D^2 = Q^{-1}\rho Q Q^{-1}\rho Q = Q^{-1}\rho\rho Q = Q^{-1}\rho Q = D.$$

Since $D$ is diagonal, each diagonal element must fulfill $d_{ii}^2 = d_{ii}$. The only numbers which fulfill this equation are $d_{ii} = 0$ or $d_{ii} = 1$. Furthermore, the transformation preserves the trace:

$$\mathrm{Tr(D)} = \mathrm{Tr(Q^{-1}\rho Q)} = \mathrm{Tr(\rho Q Q^{-1})} = \mathrm{Tr}(\rho) = 1.$$

Since the diagonal elements of $D$ are either 0 or 1, and their sum is 1, only one diagonal element can be 1 and all other are 0.

**Problem 3.4:** Starting from the definition of the trace of a matrix, $\mathrm{Tr\,(A)} \equiv \sum_\mathrm{n} \mathrm{A_{nn}}$, show that $\mathrm{Tr\,(AB)} = \mathrm{Tr\,(BA)}$. Show furthermore that the trace is invariant to cyclic permutation, $\mathrm{Tr}\,(ABC) = \mathrm{Tr}\,(CAB) = \mathrm{Tr}\,(BCA)$.

**Solution:** One particular element of the product of two matrices $A$ and $B$ is:

$$(AB)_{nm} = \sum_k A_{nk} B_{km}$$

With that:

$$\mathrm{Tr}(\mathrm{AB}) \equiv \sum_{\mathrm{n}} (\mathrm{AB})_{\mathrm{nn}} = \sum_{\mathrm{n,k}} \mathrm{A_{nk}B_{kn}} = \sum_{\mathrm{n,k}} \mathrm{B_{kn}A_{nk}} = \mathrm{Tr}(\mathrm{BA}).$$

Then:

$$\mathrm{Tr}\left((\mathrm{AB})\mathrm{C}\right) = \mathrm{Tr}\left(\mathrm{C}(\mathrm{AB})\right).$$

etc.

**Problem 3.5:** Show that the trace of any density matrix is indeed $\mathrm{Tr}(\rho) = 1$.

**Solution:** For a pure state:

$$\mathrm{Tr}\left(\rho\right) = \sum_{\mathrm{i}} \mathrm{c_i c_i^*} = 1$$

results from the normalization of the wave function. For a mixed state, Eq. 3.22, the same holds as long as each wavefunction $\psi_s$ is normalized and the statistical distribution is normalized as well, $\sum_s p_s = 1$.

**Problem 3.6:** Show that the length of a Bloch vector corresponding to a pure state is unity.

**Solution:** With Eq. 2.16, one obtains with a little bit of algebra for the length of the Bloch vector:

$$B_x^2 + B_y^2 + B_z^2 = (c_0 c_0^* + c_1 c_1^*)^2 = 1$$

due to the normalization of the wavefunction.

**Problem 3.7:** Derive Eq. 3.33 starting from Eq. 3.32. Hint: Do a change of variables using $\rho_{nm}^{(1)}(\tau) = S_{nm}^{(1)}(\tau) e^{-\left(i\omega_{mn} + \frac{1}{T_2}\right)\tau}$. Then integrate from $\tau' = -\infty$ to $\tau$. Finally, switch to relative time-delays.

**Solution:** This solution follows that of Boyd[16]. Start by doing a change of in Eq. 3.32 using

$$\rho_{nm}^{(1)}(\tau) = S_{nm}^{(1)}(\tau) e^{-\left(i\omega_{mn} + \frac{1}{T_2}\right)\tau} \tag{0.1}$$

$$\dot{\rho}_{nm}^{(1)}(\tau) = -\left(i\omega_{mn} + \frac{1}{T_2}\right) S_{nm}^{(1)}(\tau) e^{-\left(i\omega_{mn}+\frac{1}{T_2}\right)\tau} + \dot{S}_{nm}^{(1)}(\tau) e^{-\left(i\omega_{mn}+\frac{1}{T_2}\right)\tau}$$

Substitute

$$-\left(i\omega_{mn} + \frac{1}{T_2}\right) S_{nm}^{(1)}(\tau) e^{-\left(i\omega_{mn}+\frac{1}{T_2}\right)\tau} + \dot{S}_{nm}^{(1)}(\tau) e^{-\left(i\omega_{mn}+\frac{1}{T_2}\right)\tau} = \\ -\left(i\omega_{mn} + \frac{1}{T_2}\right) S_{nm}^{(1)}(\tau) e^{-\left(i\omega_{mn}+\frac{1}{T_2}\right)\tau} - \frac{i}{\hbar}\left[\hat{W}(\tau), \rho^{(0)}\right]_{nm} \quad (0.2)$$

to get

$$\dot{S}_{nm}^{(1)}(\tau) = -\frac{i}{\hbar}\left[\hat{W}(\tau), \rho^{(0)}\right]_{nm} e^{+\left(i\omega_{mn}+\frac{1}{T_2}\right)\tau} \quad (0.3)$$

Integrate

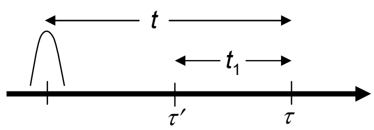
$$S_{nm}^{(1)}(\tau) = -\frac{i}{\hbar}\int_{-\infty}^{\tau}\left[\hat{W}(\tau'), \rho^{(0)}\right]_{nm} e^{+\left(i\omega_{mn}+\frac{1}{T_2}\right)\tau'} d\tau' \quad (0.4)$$

Change variables back by substituting into Eq. 0.1

$$\rho_{nm}^{(1)}(\tau) = -\frac{i}{\hbar}\int_{\tau'=-\infty}^{\tau'=\tau}\left[\hat{W}(\tau'), \rho^{(0)}\right]_{nm} e^{-\left(i\omega_{mn}+\frac{1}{T_2}\right)(\tau-\tau')} d\tau' \quad (0.5)$$

Put into relative delay times using $t$=$\tau$ and $t_1$=$\tau - \tau'$ so that when $\tau'$=-$\infty$ then $t$=+$\infty$ and when $\tau'$=$\tau$, $t$=0 (see figure below), which gives

$$\rho_{nm}^{(1)}(t) = +\frac{i}{\hbar}\int_{0}^{\infty}\left[\hat{W}(t-t_1), \rho^{(0)}\right]_{nm} e^{-\left(i\omega_{mn}+\frac{1}{T_2}\right)t_1} dt_1 \quad (0.6)$$




**Problem 3.8:** Derive Eq. 3.49.

**Solution:** We define the density matrix of a pure state in the interaction picture:

$$\rho_I = |\psi_I\rangle\langle\psi_i|$$

Eq. 3.40 is formally equivalent to the time-dependent Schrödinger equation Eq. 3.18, replacing $\psi$ by $\psi_I$ and $\hat{H}$ by $\hat{W}_I$. Performing the same steps as

Eqs. 3.19 and 3.20, we obtain Eq. 3.49 for a pure state. Since this equation is linear in $\rho_I$, it also holds for a statistical average with

$$\rho_I = \sum_s p_s \rho_I^{(s)}$$