Chapter 4. Density operator and quantum dynamics in Liouville space

4.1 Why do we need the density operator?

So far, we have considered quantum mechanics in the Schrödinger (wavefunction) picture: the quantum state of the system is completely described by a wavefunction $|\psi(q,t)\rangle$, where $q$ describes a set of coordinates for the system, whose time-dependence describes the evolution of the system. We solve the time-dependent Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} |\psi(q,t)\rangle = \hat{H}(q)|\psi(q,t)\rangle$$

($\hat{H}(q)$ indicates that the Hamiltonian operator acts on variables $q$), find $|\psi(q,t)\rangle$, and then use it to calculate physical observables of the system such as energy, angular momentum, dipole moment, etc. For an observable $A$ described by operator $\hat{A}$, the expectation value at time $t$ is

$$\langle A \rangle(t) = \langle \psi(q,t) | \hat{A} | \psi(q,t) \rangle$$

(Alternatively, we can use the Heisenberg picture, where we solve the equation of motion for the time-dependent Heisenberg-picture operator $\hat{A}_H(t)$ and then compute $\langle A \rangle(t) = \langle \psi(q,0) | \hat{A}_H(t) | \psi(q,0) \rangle$ for the initial state $|\psi(0)\rangle$).

However, the wavefunction description is not the only possible way to specify the quantum state of the system, and, in many cases, not the best one! Consider the following example: we have an ensemble of $N$ nearly identical systems (e.g., $N$ molecules). Each molecule ($i$) has its own set of coordinates $q_i$, and thus the complete wavefunction for such system will be $|\psi(q_1,q_2,...,q_N,t)\rangle$. Since $N$ is usually rather large for a macroscopic ensemble (typically, spectroscopic measurements require at least $>10^6$ chromophores), solving the Schrödinger equation for the whole system would be a hopeless task (for a partial differential equation in $N$ variables, the computational cost scales exponentially with $N$).

Even if we neglect interactions between the molecules, i.e. assume that the Hamiltonian breaks up into sum of individual molecules’ Hamiltonians,

$$\hat{H}(q_1,q_2,...,q_N) = \hat{H}_1(q_1) + \hat{H}_2(q_2) + ... + \hat{H}_N(q_N)$$

---

\[a\] That is, if we work in coordinate representation. $r$ can represent any set of quantum variables for the system, e.g. momenta if we choose to work in momentum representation, spin variables, etc.
and thus the total wavefunction factorizes into a product of the individual molecules’
wavefunctions,
\[
|\psi(q_1, q_2, \ldots, q_N, t)\rangle = |\psi_1(q_1, t)\rangle |\psi_2(q_2, t)\rangle \cdots |\psi_N(q_N, t)\rangle = \prod_{i=1}^{N} |\psi_i(q_i, t)\rangle,
\]
we would still need to specify the relative phases between the wavefunctions \( |\psi_i(q_i, t)\rangle \)
in order to calculate the expectation values of physical observables. For example, for an
additive observable \( A \) represented by operator \( \hat{A} \) (e.g., the total dipole moment of the
ensemble equal to the sum of the individual molecules’ dipole moments),
\[
\langle A \rangle(t) = \langle \psi(q_1, q_2, \ldots, q_N, t) | \hat{A}(q_1) + \hat{A}(q_2) + \cdots + \hat{A}(q_N) | \psi(q_1, q_2, \ldots, q_N, t) \rangle = \\
\sum_{k=1}^{N} \langle \psi(q_1, q_2, \ldots, q_N, t) | \hat{A}(q_k) | \psi(q_1, q_2, \ldots, q_N, t) \rangle
\]
Indeed, solving the Schrödinger equation for one molecule
\[
\frac{i\hbar}{\partial t} |\psi_i(q_i, t)\rangle = \hat{H}_i(q_i) |\psi_i(q_i, t)\rangle
\]
yields the wavefunction to within an arbitrary phase factor: if \( |\psi_i(q_i, t)\rangle \) satisfies (4.6),
then a function \( |\psi_i(q_i, t)e^{i\varphi_i}\rangle \) also satisfies (4.6) for any constant \( \varphi_i \). Thus, our theory
would need to keep track of at least \( N \) parameters \( \varphi_i \), since the result of integration in
(4.5) will certainly depend on these phases (they will determine the phases of the
different terms in the sum (4.5)). That’s a lot of parameters to keep track of!

If the molecules do interact with one another, the wavefunction, in general, will
not factorize, and we are going to have even harder time constructing a theory (even a
phenomenological theory!) to describe the behavior of such ensemble.

On the other hand, we may not actually care about the details of what every single
molecule in the ensemble is doing, as long as our spectroscopic observables do not depend on them! Since the spectroscopic observables are going to be some kind of statistically averaged values for the ensemble (as we’ll discuss later), we may wish to
describe the ensemble in a statistical fashion – that is, construct the equations of motion
describing what a molecule in the ensemble is doing on average. This way, we do not have to deal with \( N \) sets of variables \( q_i \) for different molecules, but write the equations of
motion for a single set of variables \( q \) for an average molecule.

However, we immediately see the problem with the wavefunction description for
such strategy: the wavefunction for an ensemble of systems is not additive – even in the
best case, it involves multiplying wavefunctions for individual molecules (4.4). Instead
of a wavefunction, we would like to have some object \( \rho_i \) defining quantum state of
molecule \( i \) that would be additive, so it’s easy to calculate ensemble average:
\[
\rho(q_1, q_2, \ldots, q_N, t) = \frac{1}{N} \sum_{i=1}^{N} \rho_i(q, t)
\]
One such object is the density operator introduced in the next section. The additivity property, as we will see, not only allows us to easily treat statistical ensembles, but also permits calculating properties of sub-ensembles of molecules, for example sub-ensemble of spectroscopically active ‘chromophore’ molecules in a larger ensemble of ‘bath’ (e.g., solvent) molecules, through the so-called reduced density operator description.

The density operator also allows us to write equations of motion that are more general than the Schodinger or Heisenberg equations of motion. Thus we can describe richer dynamics of the system using the density operator description, in particular, we can include dephasing and relaxation. This can be done either by deriving various approximations to the rigorous first-principles equations of motion, or phenomenologically (i.e., writing equations of motion not from first principles, but using our physical intuition and/or general ideas about the behavior of the system gained from previous observations).

Below, we begin by introducing the formal definition of the density operator for a single quantum system (the so-called pure state), section 4.2, then generalize it to mixed states (section 4.3), and discuss its general properties.

### 4.2 Definition and properties of the density operator for pure states

Let’s start with a simple case of a system in a quantum state described by a wavefunction \(|\psi\rangle\). (Such states are called pure states). We define the density operator as

\[
\hat{\rho} = |\psi\rangle \langle \psi |
\]

Let’s work in some (complete and orthonormal) basis set of states \(\{|n\rangle\}\):

\[
|\psi(t)\rangle = \sum_{n} c_n(t) |n\rangle, \text{ or, in vector notation, } |\psi(t)\rangle = \begin{pmatrix} c_1 \\ c_2 \\ \vdots \end{pmatrix}
\]

(For example, if the system’s Hamiltonian \(\hat{H}\) is time-independent, a convenient choice is to work in the basis set of stationary states \(\hat{H} |n\rangle = E_n |n\rangle\)).

Substituting (4.9) in our definition of the density operator (4.8), we have for the pure state

\[
\dot{\hat{\rho}} = \sum_{i,j} c_i^* (t)c_j (t) |j\rangle \langle i|
\]

The matrix elements of the density operator in the basis set \(\{|n\rangle\}\) are

\[
\rho_{mn} (t) = \langle m | \hat{\rho} | n \rangle = \sum_{i,j} c_j^* (t)c_i (t) \langle j | n \rangle \langle m | i \rangle = \sum_{i,j} c_j^* (t)c_i (t) \delta_{jm} \delta_{mi} = c_n^* (t)c_m (t)
\]
Thus, in the basis set \( \{ |n\rangle \} \) the density operator for a pure state \( |\psi\rangle \) is represented by the density matrix

\[
\rho = \begin{pmatrix}
\rho_{11} & \rho_{12} & \cdots \\
\rho_{21} & \rho_{22} & \cdots \\
\vdots & \vdots & \ddots
\end{pmatrix} = \begin{pmatrix}
c_1^*c_1 & c_1^*c_2 & \cdots \\
c_2^*c_1 & c_2^*c_2 & \cdots \\
\vdots & \vdots & \ddots
\end{pmatrix}
\]

(which literally is the outer product of \( |\psi(t)\rangle = \begin{pmatrix} c_1 \\ c_2 \\ \vdots \end{pmatrix} \) and \( \langle \psi(t) | = (c_1^* \ c_2^* \ \cdots) \), as implied by our definition (4.8)).

In the wavefunction picture, the quantum state of our system is defined as a vector in the Hilbert space of our basis set vectors \( \{ |n\rangle \} \). That is, the quantum state is completely defined by a set of numbers \((c_1, c_2, \ldots)\). We see that the same numbers are contained in the density matrix (4.12), just in a different format. If our basis set consists of \( M \) vectors, the wavefunction is defined by \( M \) coefficients (which may be complex), so \( 2M \) real numbers. The density matrix contains \( M^2 \) numbers (the diagonal elements of \( \rho \) are real, as we see from (4.12), but the off-diagonal elements may be complex), so the density matrix contains \( M(2M-1) \) real numbers, which is always greater than \( 2M \) (for \( M\geq2 \)). We therefore see that specifying all of the density matrix elements contains more information than specifying the wavefunction. That is, specifying the density matrix seems to be a more general way to describe the quantum state of the system that specifying its wavefunction. As we will see, this extra information contained in the density matrix (specifically, in its off-diagonal matrix elements) can be indeed used to describe systems such as statistical ensembles, in a more general way than a wavefunction description would allow.

**Normalization**

Per our usual quantum mechanical interpretation of a superposition state (4.10), the diagonal elements of the density matrix

\[
\rho_{nn}(t) = c_n^*(t)c_n(t)
\]

can be thought of as probabilities of finding the system in the state \( |n\rangle \) at time \( t \). The diagonal elements of the density matrix are thus referred to as populations. Note that the diagonal elements are real positive numbers. Moreover, since the total probability of finding the system in one of the basis set states is one (for a complete basis set), we have

\[
\text{Tr} \rho = \sum_n \rho_{nn} = 1
\]
The *trace* of a density matrix (the sum of the diagonal elements) must equal 1. This is the normalization condition, which is equivalent to $\langle \psi | \psi \rangle = 1$ in the wavefunction picture.

The *off-diagonal elements* of the density matrix $\rho_{mn}(t)$ ($i \neq j$) are known as *coherences*. Note that, per (4.11), $\rho_{mn} = \rho_{nm}^*$. When the system is described by a time-independent Hamiltonian and we work in the basis set of the stationary states, the only time-dependence of the coefficients is in the phase terms, $c_n(t) = c_n^0 \exp \left( -\frac{i}{\hbar} E_n t \right)$. In this situation, the coherences oscillate at the transitions frequencies between the levels, $\omega_{mn} = \frac{E_m - E_n}{\hbar}$;

$$\rho_{mn}(t) = c_m^0 c_n^0 \exp(-i\omega_{mn} t)$$  \hspace{1cm} (4.15)

*Calculating expectation values*

The density operator can be used to easily calculate expectation values of physical observables. For an observable $A$ represented by operator $\hat{A}$, the expectation value is

$$\langle A \rangle (t) = \langle \psi | \hat{A} | \psi \rangle = \sum_{m,n} c_m^* (t) c_n (t) A_{mn} = \sum_{m,n} c_m^*(t) c_n (t) \rho_{mn} A_{mn}$$  \hspace{1cm} (4.16)

where $A_{mn} = \langle m | \hat{A} | n \rangle$ are elements of the matrix $A$ representing operator $\hat{A}$ in the basis set $\{ |n \rangle \}$.

Equation (4.16) can be written in a more succinct form by noting that the matrix product $A \rho$ has elements

$$\left( A \rho \right)_{ij} = \sum_n \rho_{in} A_{nj}$$

By comparing this with (4.16), we see that the sum over $m$ in (4.16) gives the $n$-th diagonal matrix element of $A \rho$, $\sum_n \rho_{mn} A_{nn} = \left( A \rho \right)_{nn}$, and therefore the sum over $n$ gives the trace of the matrix $A \rho$. Thus,

$$\langle A \rangle (t) = \text{Tr} \left( A \rho \right)$$  \hspace{1cm} (4.17)

*Time evolution*

The wavefunction $| \psi(t) \rangle$ obeys the time-dependent Schrödinger equation

$$i\hbar \frac{\partial | \psi(t) \rangle}{\partial t} = \hat{H} | \psi(t) \rangle.$$  \hspace{1cm} As we discussed in Chapter 3, the quantum dynamics can be
conveniently described by the time evolution operator \( \hat{U}(t,t_0) \) which propagates the wavefunction from time \( t_0 \) to time \( t \), \( \ket{\psi(t)} = \hat{U}(t,t_0)\ket{\psi(t_0)} \). Substituting this expression and its Hermitian conjugate into our definition of the density operator (4.8), \( \hat{\rho} = \ket{\psi}\bra{\psi} \), we obtain the time evolution of the density operator:

\[
\dot{\hat{\rho}}(t) = \ket{\psi(t)}\bra{\psi(t)} - \hat{U}(t,t_0)\ket{\psi(t_0)}\bra{\psi(t_0)}\hat{U}^\dagger(t,t_0)
\]

i.e.

\[
\text{(4.18)} \quad \dot{\hat{\rho}}(t) = \hat{U}(t,t_0)\dot{\hat{\rho}}(t_0)\hat{U}^\dagger(t,t_0)
\]

Alternatively, we can come up with an equation of motion for \( \dot{\hat{\rho}}(t) \) by calculating its time derivative:

\[
\frac{\partial \rho(t)}{\partial t} = \frac{\partial}{\partial t} \left( \ket{\psi(t)}\bra{\psi(t)} \right) = \frac{\partial \ket{\psi(t)}}{\partial t} \bra{\psi(t)} + \ket{\psi(t)} \frac{\partial \bra{\psi(t)}}{\partial t}
\]

and substituting \( \frac{\partial \ket{\psi(t)}}{\partial t} \) and \( \frac{\partial \bra{\psi(t)}}{\partial t} \) from the time-dependent Schrödinger equation:

\[
i\hbar \frac{\partial \ket{\psi(t)}}{\partial t} = \hat{H}\ket{\psi(t)}
\]

\[
- i\hbar \frac{\partial \bra{\psi(t)}}{\partial t} = \bra{\psi(t)}\hat{H}^\dagger = \bra{\psi(t)}\hat{H}
\]

(since \( \hat{H} \) is Hermitian). Combining these, we obtain

\[
i\hbar \frac{\partial \rho(t)}{\partial t} = \hat{H}\ket{\psi(t)}\bra{\psi(t)} - \ket{\psi(t)}\bra{\psi(t)}\hat{H}
\]

i.e.

\[
\text{(4.19)} \quad i\hbar \frac{\partial \rho(t)}{\partial t} = \left[ \hat{H}, \rho(t) \right]
\]

This is known as the Liouville-von Neumann equation. We can verify by direct substitution that the expression (4.18) for \( \dot{\hat{\rho}}(t) \) obeys the Liouville-von Neumann equation (recall from Chapter 3 that the time evolution operator obeys the Heisenberg equation of motion \( i\hbar \frac{\partial \hat{U}(t,t_0)}{\partial t} = \hat{H}\hat{U}(t,t_0) \)).

Note also that in order to calculate the time-dependent expectation value \( \langle A \rangle (t) \), we can use either the Schrödinger or the Heisenberg picture:

\[
\text{(4.20)} \quad \langle A \rangle (t) = \text{Tr} \left( \hat{A}\dot{\hat{\rho}}(t) \right) =
\]

in the Schrödinger picture (time dependence is in the density operator), or
\[ (4.21) \quad \text{Tr} \left( \hat{A} \hat{U} (t, t_0) \hat{\rho} (t_0) \hat{U}^\dagger (t, t_0) \right) = \text{Tr} \left( \hat{U}^\dagger (t, t_0) \hat{A} \hat{U} (t, t_0) \hat{\rho} (t_0) \right) = \text{Tr} \left( \hat{A}_\eta (t) \hat{\rho} (t_0) \right) \]

in the Heisenberg picture (time dependence is in the operator \( \hat{A}_\eta (t) \)).

**Some basic properties of a trace of a matrix:**

1. Trace is a linear operation:
   \[
   (4.22) \quad \text{Tr} (A + B) = \text{Tr} (A) + \text{Tr} (B) \\
   \text{Tr} (cA) = c \text{Tr} (A)
   \]

2. Trace of a product of several matrices is invariant to cyclic permutation, e.g.
   \[
   (4.23) \quad \text{Tr} (ABC) = \text{Tr} (CAB) = \text{Tr} (BCA)
   \]
   (This holds for a product of two, three, or more matrices). Thus, in (4.17) we can compute the trace of either \( A\rho \) or \( \rho A \) to obtain the expectation value of \( A \).

3. A consequence of the previous property is that trace is invariant to unitary transformations of a matrix. Indeed, if \( S \) is unitary, i.e. \( S^\dagger = S^{-1} \), the transformation of the basis set under \( S \) yields \( A' = SAS^\dagger \). But
   \[
   (4.24) \quad \text{Tr} (A') = \text{Tr} (SAS^\dagger) = \text{Tr} (S^\dagger SA) = \text{Tr} (A)
   \]
   One particularly important unitary operator we encountered in Chapter 3 is the time-evolution operator \( \hat{U} (t, t_0) \). Thus, time evolution of the density operator \( \hat{\rho} (t) = \hat{U} (t, t_0) \hat{\rho} (t_0) \hat{U}^\dagger (t, t_0) \) preserves normalization (as it should, of course!):
   \[
   (4.25) \quad \text{Tr} (\rho (t)) = \text{Tr} (\hat{\rho} (t_0)) = 1
   \]

### 4.3 Density operator for mixed states

Now, let’s consider an *ensemble* of \( N \) molecules, each in a pure state \( \ket{\psi_i (q_i, t)} \), an \( M \)-dimensional vector in the Hilbert space of \( M \) basis set functions \( \{| \eta \rangle \} \). The corresponding density matrix for a single molecule is an \( M \times M \) matrix \( \hat{\rho}_i = \ket{\psi_i (q_i, t)} \bra{\psi_i (q_i, t)} = \begin{pmatrix} c_{i_1}^* c_{i_1} & c_{i_1}^* c_{i_2} & \cdots \\ c_{i_2}^* c_{i_1} & c_{i_2}^* c_{i_2} & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix} \).

We can surely construct a grand wavefunction for the whole ensemble, simply by combining the \( \ket{\psi_i (q_i, t)} \) vectors for individual molecules in one grand vector
If we have $N$ molecules and the basis set is $M$-dimensional, this grand wavefunction will be defined by $MN$ coefficients (we have $N$ $M$-dimensional blocks each representing a molecule). This would be a pure state description of the entire ensemble, and we could also construct the density matrix for this pure state,

\[
\hat{\mathbf{R}}(q_1, q_2, \ldots, t) = |\Psi\rangle \langle \Psi| = \begin{pmatrix}
\begin{bmatrix}
 c_{11}(t) \\
c_{i2}(t) \\
\vdots \\
c_{iM}(t) \\
c_{21}(t) \\
\vdots \\
c_{2M}(t)
\end{bmatrix} & \begin{bmatrix}
\psi_1(q_1, t) \\
\psi_2(q_2, t) \\
\vdots \\
\psi_i(q_i, t) \\
\psi_M(q_M, t)
\end{bmatrix}
\end{pmatrix}
\]

for molecule 1

for molecule $i$

\[
(4.26)
\]

which would be a $MN \times MN$ matrix that contains the complete information about the quantum state of the ensemble. This matrix would consist of $M \times M$ blocks. The blocks on the diagonal represent density matrices for individual molecules $\hat{\rho}_i$. The off-diagonal $M \times M$ blocks fully describe coherences (i.e., phase relationships) between different molecules. However, as discussed earlier (Section 4.1), this would be impractical for a large ensemble, and it is also not necessary since it contains more details than we (i.e., our spectroscopic observables) care about.

Instead, let’s consider the $M \times M$ density matrix for the whole ensemble:

\[
\hat{\rho} = \frac{1}{N} \sum_{i=1}^{N} \hat{\rho}_i = \frac{1}{N} \sum_{i=1}^{N} |\psi_i\rangle \langle \psi_i| = \begin{pmatrix}
\frac{1}{N} \sum_{i=1}^{N} c_{i1}^* c_{i1} & \frac{1}{N} \sum_{i=1}^{N} c_{i2}^* c_{i2} & \ldots \\
\frac{1}{N} \sum_{i=1}^{N} c_{i1}^* c_{i2} & \frac{1}{N} \sum_{i=1}^{N} c_{i1}^* c_{i3} & \ldots \\
\vdots & \vdots & \ddots
\end{pmatrix}
\]

That is, each matrix element of the ensemble density matrix $\hat{\rho}$ is simply an average of the corresponding elements of the pure state density matrices for individual molecules $\hat{\rho}_i$. 

\[
(4.28)
\]
More generally, for an ensemble of quantum systems where a certain (pure) quantum state \( |\psi_k\rangle \) occurs with probability \( P_k \) \( (\sum_k P_k = 1) \) we define the density matrix as

\[
\hat{\rho} = \sum_k P_k |\psi_k\rangle \langle \psi_k| = \sum_k P_k \hat{\rho}_k
\]

This situation is referred to as a mixed state. A mixed state can be described by a density operator, but it cannot be represented by a wavefunction. (HW 3, Problem 3).

Our rationale for defining the mixed state \( \hat{\rho} \) according to (4.29) is as follows. Consider expectation value of some observable \( A \) (after all, all we require from our theory is that it correctly calculates expectation values!) For a statistical ensemble, we would expect

\[
\langle A \rangle = \sum_k P_k \langle A \rangle_k
\]

(average over the ensemble distribution of expectation value for state \( k \), \( \langle A \rangle_k = \langle \psi_k | \hat{A} | \psi_k \rangle = \text{Tr} \left( \hat{A} \hat{\rho}_k \right) \), with the probability of that state \( P_k \)). Our expression (4.17) for the pure state expectation value, \( \langle A \rangle = \text{Tr} \left( \hat{A} \hat{\rho} \right) \), works for the mixed state as well: it indeed correctly yields such ensemble-averaged result:

\[
\langle A \rangle = \text{Tr} \left( \hat{A} \hat{\rho} \right) = \text{Tr} \left( \hat{A} \sum_k P_k \hat{\rho}_k \right) = \sum_k P_k \text{Tr} \left( \hat{A} \hat{\rho}_k \right) = \sum_k P_k \langle A \rangle_k
\]

(since \( \text{Tr}(\ldots) \) is a linear operation).

Here are some important basic properties of the density operator \( \hat{\rho} \) for either pure or mixed states, stemming from the properties of pure state density operators (Section 4.2) and the fact that a mixed state density operator is simply a linear combination of the pure state density operators.

1. \( \hat{\rho} \) is Hermitian,

\[
\rho_{nm} = \rho_{mn}^*
\]

2. The diagonal elements of \( \hat{\rho} \) are real nonnegative numbers

\[
\rho_{nn} = \langle \psi_n | \left( \sum_k P_k |\psi_k\rangle \langle \psi_k| \right) |\psi_n \rangle = P_n \geq 0
\]

since the probabilities \( P_k \) are real nonnegative by definition.

(This actually holds for \( \hat{\rho} \) expressed in any basis set \( \{|\varphi_n\rangle\} \), not only for basis set \( \{|\psi_n\rangle\} \): in the basis set \( \{|\varphi_n\rangle\} \).)
\[
\rho_{mn} = \langle \varphi_n | \left( \sum_k P_k | \psi_k \rangle \langle \psi_k | \right) | \varphi_n \rangle = \sum_k P_k \langle \varphi_n | \psi_k \rangle \langle \psi_k | \varphi_n \rangle = \sum_k P_k | \langle \varphi_n | \psi_k \rangle |^2 \geq 0 .
\]

3. Normalization:
(4.34) \[ \text{Tr}\rho = 1 \]
Indeed, \[ \text{Tr}\rho = \sum_k P_k \text{Tr} \hat{\rho}_k = \sum_k P_k = 1 \] since each \( \hat{\rho}_k \) describes a pure state and we already proved that \( \text{Tr} \hat{\rho}_k = 1 \) for any pure state.

4. Schwartz inequality (‘the triangle rule’): the off-diagonal element cannot be larger in amplitude than the geometric mean of the corresponding diagonal elements,
(4.35) \[ |\rho_{mn}|^2 \leq \rho_{mm} \rho_{nn} \]
(For proof, see Mukamel, Ch. 3).

This means that when the populations (the diagonal elements of \( \hat{\rho} \)) of two states \( |\psi_m\rangle \) and \( |\psi_m\rangle \) die out, the coherence between these two states must die out with them (or faster). This makes sense – there can be no coherence between the states with no population in them! The opposite situation, however, is possible: there can be population in two states \( |\psi_m\rangle \) and \( |\psi_m\rangle \), but no coherence between them, \( \rho_{mn} = 0 \).

5. A significant difference between pure and mixed states is the following. For a pure state \( \hat{\rho}_k = |\psi_k\rangle \langle \psi_k | \),
(4.36) \[ \hat{\rho}_k^2 = |\psi_k\rangle \langle \psi_k | \psi_k \rangle \langle \psi_k | = \hat{\rho}_k \]
Operators for which \( \hat{\rho}^2 = \hat{\rho} \) are called idempotent. As a consequence,
(4.37) \[ \text{Tr} \hat{\rho}_k^2 = 1 \] for pure state
For a mixed state, however, the density operation is not idempotent, \( \hat{\rho}^2 \neq \hat{\rho} \). We can also prove (Homework 4) that for a mixed state,
(4.38) \[ \text{Tr} \hat{\rho}^2 < 1 \]
In fact, this condition can be used as a definition of a mixed state.

4.4 Reduced density operator
An important advantage of the density operator is that we can use it to describe the following (physically relevant) situation: we have a chromophore molecule (“system”) surrounded by other molecules (“bath”, e.g. solvent molecules surrounding the chromophore solute) which are not spectroscopically active. We’d like to calculate some spectroscopic observable for this system (e.g., dipole moment at a resonant
frequency), which means an expectation value of some operator \( \hat{A} \) which acts *only on the system degrees of freedom* (since the bath molecules do not interact with light).

Let’s denote the system’s degrees of freedom, collectively, \( Q \), and the bath degrees of freedom \( q \). The Hamiltonian for the whole system-bath ensemble (the so-called *extended system*) consists of the system Hamiltonian, bath Hamiltonian, and the term describing the system-bath interaction:

\[
\hat{H} = \hat{H}^S(Q) + \hat{H}^b(q) + \hat{H}^\text{int}(Q,q)
\]

(here and below, the upper case letters refer to the system indices and coordinates and lower case letters – to the bath).

Let’s work in the following basis set of wavefunctions:

\[
|\psi_{N,n}(q,Q)\rangle = |\Phi_N(Q)\rangle |\varphi_n(q)\rangle
\]

where \(|\Phi_N(Q)\rangle\) are eigenfunctions of the system Hamiltonian

\[
\hat{H}^S |\Phi_N(Q)\rangle = E^S_N |\Phi_N(Q)\rangle
\]

and \(|\varphi_n(q)\rangle\) are eigenfunctions of the bath Hamiltonian

\[
\hat{H}^b |\varphi_n(q)\rangle = E^b_n |\varphi_n(q)\rangle
\]

Note that, since the system and bath are coupled, \( \hat{H}^\text{int}(Q,q) \neq 0 \), our basis set wavefunctions are not the stationary states for the whole system. Nevertheless, they represent a complete basis set in the joint system-bath phase space.

Keep in mind that, by design, the system is “small” and the bath is “large”, so there are many more bath states \(|\varphi_n(q)\rangle\) than the system states \(|\Phi_N(Q)\rangle\). (For example, if we describe each molecule as a two-level system, the “system” will have only two states, but that bath will have \( 2 \times \) the number of bath molecules states.)

In this basis set, any quantum state \(|\Psi\rangle\) of the extended system (system+bath) is defined by a wavefunction (a vector)

\[
|\Psi(q,Q)\rangle = \sum_{N,n} \Theta_{N,n} |\psi_{N,n}(q,Q)\rangle = \sum_{N,n} C_N |\Phi_N(Q)\rangle c_n |\varphi_n(q)\rangle
\]

where \( C_N \) are amplitudes of the system states and \( c_n \) are amplitudes of the bath states in our superposition state \(|\Psi\rangle\). This is a *pure state for the extended system*. We can also write the density operator for this pure state:

\[
\hat{\rho}(Q,q) = |\Psi(q,Q)\rangle \langle \Psi(q,Q)| = \sum_{M,m} \Theta^*_{N,n} \Theta_{M,m} |\psi_{M,m}(q,Q)\rangle \langle \psi_{N,n}(q,Q) |=
\]

\[
= \sum_{M,m,N,n} C^*_{N,n} C_{M,m} |\Phi_M(Q)\rangle |\varphi_m(q)\rangle \langle \Phi_N(Q) |\varphi_n(q)\rangle
\]
Again, note that although this is the complete description of the system, it is very computationally expensive since we have to keep track of all of the bath amplitudes $c_n$, and the bath has a very large number of degrees of freedom.

Now let’s calculate the expectation value for an observable $A^S$ whose operator $\hat{A}^S(Q)$ acts only on the system coordinates $Q$:

$$\langle A^S(Q) \rangle = \langle \Psi(q,Q)|\hat{A}^S(Q)|\Psi(q,Q) \rangle = \text{Tr}\left(\hat{A}^S(Q)\hat{\mathcal{R}}(q,Q)\right)$$

using the definition of the trace,

$$\text{Tr}(ABC) = \sum_{m,n} \langle B_m | A | C \rangle$$

The matrix elements of $\hat{A}^S$ are

$$\langle \Psi_{N,n}(q,Q)|\hat{A}^S(Q)|\Psi_{M,m}(q,Q) \rangle = \langle \Phi_N(Q)|\langle \varphi_n(q)|\hat{A}^S(Q)|\Phi_M(Q)\rangle|\varphi_m(q) \rangle =$$

$$= \langle \Phi_N(Q)|\hat{A}^S(Q)|\Phi_M(Q)\rangle \langle \varphi_n(q)|\varphi_m(q) \rangle = \langle \Phi_N|\hat{A}^S|\Phi_M \rangle \delta_{nm}$$

(since $\hat{A}^S(Q)$ does not act on $|\varphi_m(q)\rangle$). Substituting into (4.46),

$$\langle A^S(Q) \rangle = \sum_{M,N,n} \langle \Phi_M(Q)|\langle \varphi_m(q)|\hat{R}(q,Q)|\varphi_n(q)\rangle|\Phi_N(Q)\rangle \langle \Phi_N|\hat{A}^S|\Phi_M \rangle \delta_{nm} =$$

the $\delta_{nm}$ term eliminates summation over $m$,

$$= \sum_{M,N,n} \langle \Phi_M(Q)|\langle \varphi_n(q)|\hat{R}(q,Q)|\varphi_n(q)\rangle|\Phi_N(Q)\rangle \langle \Phi_N|\hat{A}^S|\Phi_M \rangle =$$

$$= \sum_{M,N} \langle \Phi_M|\left\{\sum_n \langle \varphi_n(q)|\hat{R}(q,Q)|\varphi_n(q)\rangle\right\}|\Phi_N\rangle \langle \Phi_N|\hat{A}^S|\Phi_M \rangle$$

Now we introduce a new notation: the operator in the curly brackets $\{\ldots\}$ in (4.49),

$$\hat{\rho}(Q) = \sum_n \langle \varphi_n(q)|\hat{R}(q,Q)|\varphi_n(q)\rangle$$

is called the reduced density operator.

We can see that $\langle A^S \rangle$ is the trace of $\hat{A}^S$ times this reduced density operator $\hat{\rho}(Q)$:

$$\langle A^S(Q) \rangle = \text{Tr}_S\left(\hat{A}^S(Q)\hat{\rho}(Q)\right)$$

Tr$_S(\ldots)$ means that we are summing the diagonal elements only over the system states:

$$\text{Tr}_S\left(\hat{A}^S(Q)\hat{\rho}(Q)\right) = \sum_{M,N} \langle \Phi_M|\hat{\rho}|\Phi_N \rangle \langle \Phi_N|\hat{A}^S|\Phi_M \rangle$$

Let’s review our result. We started with a full description of the extended (system+bath), which existed in a pure state $|\Psi(q,Q)\rangle$. Calculating the evolution of such
pure state or the expectation values of physical observables is prohibitively expensive because of the large number of the bath degrees of freedom. However, we can simplify our description considerably if we are only interested in observable of the system (not bath). To do so, we do not need to know the full density matrix \( \hat{\mathcal{R}}(q, Q) \), but only the reduced density matrix \( \hat{\rho}(Q) \). If we know \( \hat{\rho}(Q) \), we can calculate the expectation value of any system observable via (4.51). You may say that in the reduced density matrix, we lose the information that we do not need. Indeed, as can be seen from the definition (4.50), the reduced density matrix \( \hat{\rho}(Q) \) is obtained by summing over the full density matrix \( \hat{\mathcal{R}}(q, Q) \) elements that are diagonal in the bath index \( n \). This procedure is sometimes called “tracing over the bath degrees of freedom”: in analogy to our notation in (4.51), we can write

\[
(4.53) \quad \hat{\rho}(Q) = \text{Tr}_b \hat{\mathcal{R}}(q, Q)
\]

where \( \text{Tr}_b (...) \) means that we are summing the diagonal elements only over the bath states.

\( \hat{\rho}(Q) \) thus contains some (ensemble averaged) information about the bath, but only “as seen” by the system. Information such as bath coherences (the off-diagonal matrix elements in the bath index) is lost. We, however, do not care since the spectroscopic observables of the system are not affected by these bath coherences.

Note that while we started with a pure state \( \hat{\mathcal{R}}(q, Q) \), the reduced density operator (4.50) in general is a mixed state. This is the price we pay for throwing away the unwanted information about the bath. This can be viewed in two ways. On one hand, we could write the rigorous first-principles equations of motion for the evolution of \( \hat{\mathcal{R}}(q, Q, t) \). However, they would be impossible to solve because of the large number of bath degrees of freedom. On the other hand, we can write approximate equations of motion for the reduced density operator \( \hat{\rho}(Q, t) \) (with various levels of approximations or phenomenological description of the system-bath relaxation phenomena, etc.), which are solvable and allow us to analyze the experimental data.

### 4.5 Equation of motion for the density operator

We have seen already that density operator for a pure state \( \hat{\rho}_k \) obeys the Liouville-von Neumann equation (4.19),

\[
\left( \frac{i\hbar}{\tau} \hat{\rho}_k(t) \right) = \left[ \hat{H}_k, \hat{\rho}_k(t) \right].
\]

Consider an ensemble of such pure states (e.g., an ensemble of chromophore molecules) described by a mixed state

\[
\hat{\rho} = \sum_k P_k \hat{\rho}_k
\]
If the chromophores are the same, we can assume they are described by the same Hamiltonian \( \hat{H}_1 = \hat{H}_2 = \ldots = \hat{H} \). Then, due to the linearity of the Liouville-von Neumann equation, the mixed state density operator obeys the same equation,

\[
(4.54) \quad \frac{i\hbar}{\partial t} \frac{\partial}{\partial t} \hat{\rho}(t) = [\hat{H}, \hat{\rho}(t)]
\]

Note that this holds only if the probabilities \( P_k \) are themselves time-independent, i.e. if the chromophores do not interact with one another. If the molecules do interact with one another, we would need to re-define the pure states \( \hat{\rho}_k \) as, e.g. states of dimers of chromophores whose Hamiltonian explicitly includes the interaction term.

We also note that the density operator description allows, in principle, a more general form of the equation of motion than the Liouville-von Neumann equation:

\[
(4.55) \quad \frac{i\hbar}{\partial t} \frac{\partial}{\partial t} \hat{\rho}(t) = \hat{L} \hat{\rho}(t)
\]

known as the quantum Liouville equation. Here, \( \hat{L} \) is the Liouville operator.

The Liouville operator is a super-operator. An ordinary operator \( \hat{A} \) transforms one wavefunction into another wavefunction: \( \ket{\varphi} = \hat{A} \ket{\psi} \). Similarly, a super-operator \( \hat{B} \) transforms one operator into another operator: \( \hat{\beta} = \hat{B} \hat{\alpha} \). In the matrix representation, if the states \( \ket{\varphi} \) and \( \ket{\psi} \) are represented by an \( N \)-dimensional vector (column of \( N \)), then the operator \( \hat{A} \) is represented by an \( N \times N \) matrix (\( N^2 \) numbers). The super-operator \( \hat{B} \) that transforms an \( N \times N \) matrix \( \hat{\alpha} \) into an \( N \times N \) matrix \( \hat{\beta} \) is an \( N^2 \times N^2 \) object (strictly speaking, \( \hat{B} \) would be a \( N \times N \times N \times N \) \( 4^{th} \) rank tensor. However, we can write it as a \( N^2 \times N^2 \) matrix if we keep track of the indices when we do the matrix multiplication – if we write the \( N^2 \) elements of operator \( \hat{\alpha} \) in a single column).

The vector space populated by wavefunctions treated as \( N \)-dimensional vectors is referred to as the Hilbert space. The space populated by the density matrices treated as \( N^2 \) vectors is referred to as the Liouville space. Wavefunctions, which are vectors in the Hilbert space, are transformed one into another by operators. Similarly, operators such as density matrices “live” in Liouville space, and are transformed one into another by superoperators. Quantum dynamics, i.e. time-evolution of the quantum state of the system, can be represented as a unitary transformation (rotation) of a vector in Hilbert space, or as evolution of a density matrix in Liouville space.

For the situations described by the Liouville-von Neumann equation, the Liouville operator \( \hat{L} \) is defined by

\[
(4.56) \quad \hat{L} \hat{\rho} \equiv [\hat{H}, \hat{\rho}] = \hat{H} \hat{\rho} - \hat{\rho} \hat{H}
\]
However, the quantum Liouville equation (4.55) allows us to describe a more general situation, as we shall see in the following chapters, for example to phenomenologically include relaxation and dephasing in our equations of motion (by introducing the so-called relaxation super-operator) that cannot be described by the Hamiltonian.

### 4.6 Density operator for a ensemble at thermal equilibrium

A commonly encountered case is an ensemble of molecules at thermal equilibrium. In the basis set of the individual molecule’s stationary states \( \hat{H}|n\rangle = E_n|n\rangle \), the equilibrium density matrix is

\[
\rho_{\text{eq}} = \frac{1}{Z} \begin{pmatrix}
    e^{-\beta E_1} & 0 & 0 \\
    0 & e^{-\beta E_2} & 0 \\
    0 & 0 & \ldots
\end{pmatrix}
\]

where \( \beta = \frac{1}{k_B T} \) and \( Z = \sum_n e^{-\beta E_n} \) is the partition function. (Here we assume that the energy levels are non-degenerate. If they are, we need to add degeneracy factors \( g_n \) before each \( e^{-\beta E_n} \)).

That is, the diagonal elements of the equilibrium density matrix (the populations) are

\[
\rho_{nn} = \frac{1}{Z} e^{-\beta E_n}
\]

i.e. the Boltzmann population probabilities, and the off-diagonal elements (coherences) are all zero,

\[
\rho_{mn} = 0 \quad m \neq n
\]

It can be verified easily that the equilibrium density matrix obeys the Liouville-von Neumann equation yielding, as expected,

\[
\frac{\partial \hat{\rho}_{\text{eq}}(t)}{\partial t} = 0
\]

That is, the equilibrium state is stationary. Zero coherences ensure that there is no time evolution of any of the physical observables for this system.

More generally, we can write the density operator for an ensemble at thermal equilibrium as

\[
\hat{\rho}_{\text{eq}} = \frac{1}{Z} \exp(-\beta \hat{H})
\]

with the partition function

\[
Z = \text{Tr}[\exp(-\beta \hat{H})]
\]
These expressions work in any basis set. Also note that (4.61) immediately implies that the equilibrium density operator commutes with the Hamiltonian (since \( \hat{\rho}_{eq} \) operator only contains powers of \( \hat{H} \)). Therefore, \( \hat{\rho}_{eq} \) is time-independent (stationary) according to the Liouville-von Neumann equation.

4.7 Evolution of the density operator in the Interaction picture

Using the additivity of the density matrices of the ensemble components to form an ensemble density matrix, we can easily generalize the time evolution of the density matrix for a pure state, Eq. (4.18), to any mixed state:

\[
\hat{\rho}(t) = \hat{U}(t, t_0) \hat{\rho}(t_0) \hat{U}^\dagger(t, t_0)
\]

where \( \hat{U}(t, t_0) \) is the time evolution operator for the wavefunction: \( |\psi(t)\rangle = \hat{U}(t, t_0) |\psi(t_0)\rangle \). As we have seen in Chapter 3, it is convenient to work in the Interaction picture for calculation of spectroscopic signals, where we partition the Hamiltonian

\[
\hat{H} = \hat{H}_0 + \hat{H}'(t)
\]

into the unperturbed system’s Hamiltonian \( \hat{H}_0 \) (usually time-independent) and the perturbation by interaction with light \( \hat{H}'(t) \). We can then use Dyson series to expand the time-evolution operator in powers of the perturbation \( \hat{H}'(t) \), which will allow us to separate the different orders of linear and nonlinear optical response:

\[
\hat{U}(t, t_0) = \hat{U}_0(t, t_0) \exp \left[ -\frac{i}{\hbar} \int_{t_0}^t \hat{H}_1(\tau) d\tau \right] = \hat{U}_0(t, t_0) + \hat{U}_1(t, t_0) + \hat{U}_2(t, t_0) + ...
\]

where the nth order term is

\[
\hat{U}_n(t, t_0) = \left( -\frac{i}{\hbar} \right)^n \int_{t_0}^t d\tau_n \int_{t_0}^{\tau_n} d\tau_{n-1} \cdots \int_{t_0}^{\tau_{n-1}} d\tau_1 \hat{U}_0(t, \tau_n) \hat{H}'(\tau_n) \hat{U}_0(\tau_n, \tau_{n-1}) \hat{H}'(\tau_{n-1}) \cdots \hat{U}_0(\tau_2, \tau_1) \hat{H}'(\tau_1) \hat{U}_0(\tau_1, t_0)
\]

\( \hat{U}_0(t, t_0) \) is the time-evolution operator for the unperturbed system (under the Hamiltonian \( \hat{H}_0 \)). For time-independent \( \hat{H}_0 \),

\[
\hat{U}_0(t, t_0) = \exp \left[ -\frac{i}{\hbar} \hat{H}_0 t \right]
\]

If the work in the basis set of the stationary states of \( \hat{H}_0, \hat{H}_0 |n\rangle = E_n |n\rangle \), then

\[
\hat{U}_0(t, t_0) = \sum_n |n\rangle \exp \left[ -\frac{i}{\hbar} E_n t \right] \langle n|
\]
Under the time-independent $\hat{H}_0$, the elements of the density matrix will evolve as

$$\rho_{mn}(t) = \langle m | \hat{\rho}(t) | n \rangle = \langle m | \hat{U}_0(t,t_0) \hat{\rho}(t_0) \hat{U}_0^\dagger(t,t_0) | n \rangle$$

$$= \langle m | \sum_i |i\rangle \exp \left[ -\frac{i}{\hbar} E_i(t-t_0) \right] \langle i | \hat{\rho}(t_0) \sum_j |j\rangle \exp \left[ \frac{i}{\hbar} E_j(t-t_0) \right] \langle j | n \rangle =$$

$$= \sum_{i,j} \langle m | i \rangle \langle i | \hat{\rho}(t_0) | j \rangle \langle j | n \rangle \exp \left[ -i\omega_{ij}(t-t_0) \right] =$$

$$= \rho_{mn}(t_0) \exp \left[ -i\omega_{mn}(t-t_0) \right]$$

(4.68)

That is, the populations (diagonal elements) are stationary ($\omega_{nn}=0$), and the coherences (off-diagonal elements) oscillate with the transition frequencies.

If we simply plug in the expression (4.65) for $\hat{U}(t,t_0)$ into (4.63), we will get a series for $\hat{\rho}(t)$ (with $\hat{\rho}(t_0)$ as the initial condition) in powers of $\hat{H}'(t)$:

$$\hat{\rho}(t) = \left( \hat{U}_0(t,t_0) + \hat{U}_1(t,t_0) + \hat{U}_2(t,t_0) + \ldots \right) \hat{\rho}(t_0) \left( \hat{U}_0^\dagger(t,t_0) + \hat{U}_1^\dagger(t,t_0) + \hat{U}_2^\dagger(t,t_0) + \ldots \right) =$$

$$= \hat{\rho}_0(t) + \hat{\rho}_1(t) + \hat{\rho}_2(t) + \ldots$$

Note that since we’ll have to multiply through two series (for $\hat{U}(t,t_0)$ and for $\hat{U}_0^\dagger(t,t_0)$), there will be two first-order terms in $\hat{H}'(t)$, three second-order terms, four 3rd order terms, etc.:

$$\hat{\rho}_0(t) = \hat{U}_0(t,t_0) \hat{\rho}(t_0) \hat{U}_0^\dagger(t,t_0)$$

$$\hat{\rho}_1(t) = \hat{U}_0(t,t_0) \hat{\rho}(t_0) \hat{U}_1^\dagger(t,t_0) + \hat{U}_1(t,t_0) \hat{\rho}(t_0) \hat{U}_0^\dagger(t,t_0)$$

$$\hat{\rho}_2(t) = \hat{U}_0(t,t_0) \hat{\rho}(t_0) \hat{U}_2^\dagger(t,t_0) + \hat{U}_1(t,t_0) \hat{\rho}(t_0) \hat{U}_1^\dagger(t,t_0) + \hat{U}_2(t,t_0) \hat{\rho}(t_0) \hat{U}_0^\dagger(t,t_0)$$

... Doing it this way, however, has two significant disadvantages: (1) this limits us to using the Liouville – von Neumann equation which is less general than the quantum Liouville equation (e.g., cannot describe relaxation); (2) more importantly, this way we would have to keep track of the time ordering in the integrals in terms like $\hat{U}_m(t,t_0) \hat{\rho}(t_0) \hat{U}_n^\dagger(t,t_0)$, for higher order terms ($m,n \geq 1$), since the $\hat{H}'(t_i)$ at different moments of time $t_i$ do not commute with one another! This is a very tedious task (see S. Mukamel, “Principles of Nonlinear Optical Spectroscopy, Appendix 5A).

A better strategy is to use the formal analogy between the time-dependent Schrödinger equation

$$i\hbar \frac{\partial |\psi(t)\rangle}{\partial t} = \hat{H} |\psi(t)\rangle$$

(4.1)
and the quantum Liouville equation

\[ i\hbar \frac{\partial \hat{\rho}(t)}{\partial t} = \hat{L} \hat{\rho}(t), \]

Just like in Hilbert space, we can introduce the interaction picture by breaking up the Liouville operator

\[ \hat{L} = \hat{L}_0 + \hat{L}'(t) \]

where the unperturbed system’s Liouville operator is

\[ \hat{L}_0 \hat{\rho} \equiv \left[ \hat{H}_0, \hat{\rho} \right] = \hat{H}_0 \hat{\rho} - \hat{\rho} \hat{H}_0 \]

And the (time-dependent) perturbation is

\[ \hat{L}' \hat{\rho} \equiv \left[ \hat{H}', \hat{\rho} \right] = \hat{H}' \hat{\rho} - \hat{\rho} \hat{H}' \]

We define the **Liouville space time-evolution operator** - a superoperator which propagates the density operator from time \( t_0 \) to time \( t \):

\[ \hat{\rho}(t) = \hat{U}(t, t_0) \hat{\rho}(t_0) \]

Note that for the unperturbed system, we have

\[ \hat{U}_0(t, t_0) \hat{\rho}(t_0) = \hat{U}_0(t, t_0) \hat{\rho}(t_0) \hat{U}_0^\dagger(t, t_0) \]

and in the case of time-independent \( \hat{H}_0 \),

\[ \hat{U}_0(t, t_0) \hat{\rho}(t_0) = \exp \left[ -\frac{i}{\hbar} \hat{H}_0 t \right] \hat{\rho}(t_0) \exp \left[ \frac{i}{\hbar} \hat{H}_0 t \right] \]

Now we can write a series in powers of \( \hat{L}' \) for \( \hat{U}(t, t_0) \) for Liouville space dynamics, in complete analogy to (4.65) for Hilbert space dynamics:

\[ \hat{U}(t, t_0) = \hat{U}_0(t, t_0) + \hat{U}_1(t, t_0) + \hat{U}_2(t, t_0) + \ldots \]

where the \( n \)-th order term is

\[ \hat{U}_n(t, t_0) = \left( -\frac{i}{\hbar} \right)^n \int_{t_0}^{t} \int_{t_{n-1}}^{t} \ldots \int_{t_0}^{t} d\tau_n d\tau_{n-1} \ldots d\tau_1 \hat{U}_0(t, \tau_n) \hat{L}'(\tau_n) \hat{U}_0(\tau_n, \tau_{n-1}) \hat{L}'(\tau_{n-1}) \ldots \hat{U}_0(\tau_2, \tau_1) \hat{L}'(\tau_1) \hat{U}_0(\tau_1, t_0) \]

We just have to keep in mind that every time we have \( \hat{U}_0(t, t_0) \) superoperator acting on the density operator, it means acting from right with \( \hat{U}_0^\dagger(t, t_0) \) and from left.
with $\hat{U}_0(t,t_0)$ as per Eq. (4.73), while every time $\hat{L}'$ acts on $\hat{\rho}$, this means taking commutator $[\hat{H}',\hat{\rho}]$, per Eq. (4.71).

We can now calculate the density operator at any moment in time, and use it to calculate physical observables for our system, e.g. the time-dependent polarization $P(t)$ that gives rise to the spectroscopic signals.