

4. THE DENSITY MATRIX

The density matrix or density operator is an alternate representation of the state of a quantum system for which we have previously used the wavefunction. Although describing a quantum system with the density matrix is equivalent to using the wavefunction, one gains significant practical advantages using the density matrix for certain time-dependent problems—particularly relaxation and nonlinear spectroscopy in the condensed phase.

The density matrix is defined as the outer product of the wavefunction with its conjugate.

$$\rho(t) \equiv |\psi(t)\rangle\langle\psi(t)| \quad (4.1)$$

This implies that if you specify a state $|\chi\rangle$, $\langle\chi|\rho|\chi\rangle$ gives the probability of finding a particle in the state $|\chi\rangle$. Its name derives from the observation that it plays the quantum role of a probability density. If you think of the statistical description of a classical observable obtained from moments of a probability distribution P , then ρ plays the role of P in the quantum case:

$$\langle A \rangle = \int A P(A) dA \quad (4.2)$$

$$\langle A \rangle = \langle\psi|A|\psi\rangle = Tr[A\rho] \quad (4.3)$$

where $Tr[\dots]$ refers to tracing over the diagonal elements of the matrix, $Tr[\dots] = \sum_a \langle a|\dots|a\rangle$.

The last expression is obtained as follows. If the wavefunction for the system is expanded as

$$|\psi(t)\rangle = \sum_n c_n(t)|n\rangle \quad (4.4)$$

the expectation value of an operator is

$$\langle\hat{A}(t)\rangle = \sum_{n,m} c_n(t)c_m^*(t)\langle m|\hat{A}|n\rangle \quad (4.5)$$

Also, from eq. (4.1) we obtain the elements of the density matrix as

$$\begin{aligned} \rho(t) &= \sum_{n,m} c_n(t)c_m^*(t)|n\rangle\langle m| \\ &\equiv \sum_{n,m} \rho_{nm}(t)|n\rangle\langle m| \end{aligned} \quad (4.6)$$

We see that ρ_{nm} , the density matrix elements, are made up of the time-evolving expansion coefficients. Substituting into eq. (4.5) we see that

$$\begin{aligned} \langle\hat{A}(t)\rangle &= \sum_{n,m} A_{mn}\rho_{nm}(t) \\ &= Tr[\hat{A}\rho(t)] \end{aligned} \quad (4.7)$$

In practice this makes evaluating expectation values as simple as tracing over a product of matrices.

What information is in the density matrix elements, ρ_{mn} ? The diagonal elements ($n = m$) give the probability of occupying a quantum state:

$$\rho_{nn} = c_n c_n^* = p_n \geq 0 \quad (4.8)$$

For this reason, diagonal elements are referred to as populations. The off-diagonal elements ($n \neq m$) are complex and have a time-dependent phase factor

$$\rho_{nm} = c_n(t) c_m^*(t) = c_n c_m^* e^{-i\omega_{nm}t} \quad (4.9)$$

Since these describe the coherent oscillatory behavior of coherent superpositions in the system, these are referred to as coherences.

So why would we need the density matrix? It becomes a particularly important tool when dealing with mixed states, which we take up later. Mixed states refer to statistical mixtures in which we have imperfect information about the system, for which we must perform statistical averages in order to describe quantum observables. For mixed states, calculations with the density matrix are greatly simplified. Given that you have a statistical mixture, and can describe p_k , the probability of occupying quantum state $|\psi_k\rangle$, evaluation of expectation values is simplified with a density matrix:

$$\langle \hat{A}(t) \rangle = \sum_k p_k \langle \psi_k(t) | \hat{A} | \psi_k(t) \rangle \quad (4.10)$$

$$\rho(t) \equiv \sum_k p_k |\psi_k(t)\rangle \langle \psi_k(t)| \quad (4.11)$$

$$\langle \hat{A}(t) \rangle = \text{Tr}[\hat{A}\rho(t)] \quad (4.12)$$

Evaluating expectation value is the same for pure or mixed states.

Properties of the density matrix

We can now summarize some properties of the density matrix, which follow from the definitions above:

- 1) ρ is Hermitian since $\rho_{nm}^* = \rho_{mn}$
- 2) Since probability must be normalized, $\text{Tr}(\rho) = 1$
- 3) We can ascertain the degree of “pure-ness” of a quantum state from

$$\text{Tr}(\rho^2) \begin{cases} = 1 & \text{for pure state} \\ < 1 & \text{for mixed state} \end{cases}$$

In addition, when working with the density matrix it is convenient to make note of these trace properties:

- 1) The trace over a product of matrices is invariant to cyclic permutation of the matrices:

$$\text{Tr}(ABC) = \text{Tr}(CAB) = \text{Tr}(BCA)$$

- 2) From this result we see that the trace is invariant to unitary transformation:

$$\text{Tr}(S^\dagger AS) = \text{Tr}(S^{-1}AS) = \text{Tr}(A)$$

Time-evolution of the density matrix

The equation of motion for the density matrix follows naturally from the definition of ρ and the time-dependent Schrödinger equation.

$$\begin{aligned} \frac{\partial \rho}{\partial t} &= \frac{\partial}{\partial t} [|\psi\rangle\langle\psi|] \\ &= \left[\frac{\partial}{\partial t} |\psi\rangle \right] \langle\psi| + |\psi\rangle \frac{\partial}{\partial t} \langle\psi| \\ &= \frac{-i}{\hbar} H |\psi\rangle \langle\psi| + \frac{i}{\hbar} |\psi\rangle \langle\psi| H \end{aligned} \quad (4.13)$$

$$\frac{\partial \rho}{\partial t} = \frac{-i}{\hbar} [H, \rho] \quad (4.14)$$

Equation (4.14) is the Liouville-Von Neumann equation. It is isomorphic to the Heisenberg equation of motion, since ρ is also an operator. The solution to (4.14) is

$$\rho(t) = U \rho(0) U^\dagger \quad (4.15)$$

This can be demonstrated by first integrating eq. (4.14) to obtain

$$\rho(t) = \rho(0) - \frac{i}{\hbar} \int_0^t d\tau [H(\tau), \rho(\tau)] \quad (4.16)$$

If we expand eq. (4.16) by iteratively substituting into itself, the expression is the same as when we substitute

$$U = \exp_+ \left[-\frac{i}{\hbar} \int_0^t d\tau H(\tau) \right] \quad (4.17)$$

into eq. (4.15) and collect terms by orders of $H(\tau)$.

Note that eq. (4.15) and the cyclic invariance of the trace imply that the time-dependent expectation value of an operator can be calculated either by propagating the operator (Heisenberg) or the density matrix (Schrödinger or interaction picture):

$$\begin{aligned}\langle \hat{A}(t) \rangle &= \text{Tr} [\hat{A} \rho(t)] \\ &= \text{Tr} [\hat{A} U \rho_0 U^\dagger] \\ &= \text{Tr} [\hat{A}(t) \rho_0]\end{aligned}\quad (4.18)$$

For a time-independent Hamiltonian it is straightforward to show that the density matrix elements evolve as

$$\rho_{nm}(t) = \langle n | \rho(t) | m \rangle = \langle n | U | \psi_0 \rangle \langle \psi_0 | U^\dagger | m \rangle \quad (4.19)$$

$$\rho_{nm}(t) = e^{-i\omega_{nm}(t-t_0)} \rho_{nm}(t_0) \quad (4.20)$$

From this we see that populations, $\rho_{nn}(t) = \rho_{nn}(t_0)$, are time-invariant, and coherences oscillate at the energy splitting ω_{nm} .

The density matrix in the interaction picture

For the case in which we wish to describe a material Hamiltonian H_0 under the influence of an external potential $V(t)$,

$$H(t) = H_0 + V(t) \quad (4.21)$$

we can also formulate the density operator in the interaction picture, ρ_I . From our original definition of the interaction picture wavefunctions

$$|\psi_I\rangle = U_0^\dagger |\psi_S\rangle \quad (4.22)$$

We obtain ρ_I as

$$\rho_I = U_0^\dagger \rho_S U_0 \quad (4.23)$$

Similar to the discussion of the density operator in the Schrödinger equation, above, the equation of motion in the interaction picture is

$$\frac{\partial \rho_I}{\partial t} = -\frac{i}{\hbar} [V_I(t), \rho_I(t)] \quad (4.24)$$

where, as before, $V_I = U_0^\dagger V U_0$.

Equation (4.24) can be integrated to obtain

$$\rho_I(t) = \rho_I(t_0) - \frac{i}{\hbar} \int_{t_0}^t dt' [V_I(t'), \rho_I(t')] \quad (4.25)$$

Repeated substitution of $\rho_I(t)$ into itself in this expression gives a perturbation series expansion

$$\begin{aligned} \rho_I(t) = & \rho_0 - \frac{i}{\hbar} \int_{t_0}^t dt_1 [V_I(t_1), \rho_0] \\ & + \left(-\frac{i}{\hbar}\right)^2 \int_{t_0}^t dt_2 \int_{t_0}^{t_2} dt_1 [V_I(t_2), [V_I(t_1), \rho_0]] + \dots \\ & + \left(-\frac{i}{\hbar}\right)^n \int_{t_0}^t dt_n \int_{t_0}^{t_n} dt_{n-1} \dots \int_{t_0}^{t_2} dt_1 [V_I(t_n), [V_I(t_{n-1}), [\dots, [V_I(t_1), \rho_0] \dots]]] \\ & + \dots \end{aligned} \quad (4.26)$$

$$\rho_I(t) = \rho^{(0)} + \rho^{(1)} + \rho^{(2)} + \dots + \rho^{(n)} + \dots \quad (4.27)$$

Here $\rho_0 = \rho(t_0)$ and $\rho^{(n)}$ is the n^{th} -order expansion of the density matrix. This perturbative expansion will play an important role later in the description of nonlinear spectroscopy. An n^{th} order expansion term will be proportional to the observed polarization in an n^{th} order nonlinear spectroscopy, and the commutators observed in eq. (4.26) are proportional to nonlinear response functions. Similar to eq. (4.15), equation (4.26) can also be expressed as

$$\rho_I(t) = U_0 \rho_I(0) U_0^\dagger \quad (4.28)$$

This is the solution to the Liouville equation in the interaction picture.

In describing the time-evolution of the density matrix, particularly when describing relaxation processes later, it is useful to use a superoperator notation to simplify the expressions above. The Liouville equation can be written in shorthand in terms of the Liouvillian superoperator $\hat{\mathcal{L}}$

$$\frac{\partial \hat{\rho}_I}{\partial t} = \frac{-i}{\hbar} \hat{\mathcal{L}} \hat{\rho}_I \quad (4.29)$$

where $\hat{\mathcal{L}}$ is defined in the Schrödinger picture as

$$\hat{\mathcal{L}} \hat{A} \equiv [H, \hat{A}] \quad (4.30)$$

Similarly, the time propagation described by eq. (4.28) can also be written in terms of a superoperator \hat{G} , the time-propagator, as

$$\rho_I(t) = \hat{G}(t) \rho_I(0) \quad (4.31)$$

\hat{G} is defined in the interaction picture as

$$\hat{G} \hat{A}_I \equiv U_0 \hat{A}_I U_0^\dagger \quad (4.32)$$

Given the eigenstates of H_0 , the propagation for a particular density matrix element is

$$\begin{aligned} \hat{G}(t) \rho_{ab} &= e^{-iH_0 t/\hbar} |a\rangle \langle b| e^{iH_0 t/\hbar} \\ &= e^{-i\omega_{ab} t} |a\rangle \langle b| \end{aligned} \quad (4.33)$$

Using the Liouville space time-propagator, the evolution of the density matrix to arbitrary order in eq. (4.26) can be written as

$$\rho_I^{(n)} = \left(-\frac{i}{\hbar} \right)^n \int_{t_0}^t dt_n \int_{t_0}^{t_n} dt_{n-1} \dots \int_{t_0}^{t_2} dt_1 \hat{G}(t-t_n) V(t_n) \hat{G}(t_n-t_{n-1}) V(t_{n-1}) \dots \hat{G}(t_2-t_1) V(t_1) \rho_0 . \quad (4.34)$$