

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 formally defined as the outer product of the wavefunction and its conjugate.

$$\rho(\mathbf{t}) = |\Psi(\mathbf{t})\rangle\langle\Psi(\mathbf{t})| \quad (1.1)$$

This implies that if $|x\rangle$ specify a state, the integral $\langle\chi|P|\chi\rangle$ gives the probability of finding a particle in the state $|x\rangle$. 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:

$$\langle A \rangle = \int A P(A) dA \quad (1.2)$$

$$= \langle\Psi|A|\Psi\rangle = \text{Tr} [A\rho] \quad (1.3)$$

Where $\text{Tr} [\dots]$ refers to tracing over the diagonals of the matrix.

The last expression is obtained as follows. For a system described by a wavefunction

$$|\Psi(\mathbf{t})\rangle = \sum_n c_n(\mathbf{t}) |n\rangle \quad (1.4)$$

the expectation value of an operator is

$$\langle\hat{A}(\mathbf{t})\rangle = \sum_{n,m} c_n(\mathbf{t}) c_m^*(\mathbf{t}) \langle m|\hat{A}|n\rangle \quad (1.5)$$

Also, from eq. (1.1) we obtain the elements of the density matrix as

$$\begin{aligned} \rho(\mathbf{t}) &= \sum_{n,m} c_n(\mathbf{t}) c_m^*(\mathbf{t}) |n\rangle\langle m| \\ &\equiv \sum_{n,m} \rho_{n,m}(\mathbf{t}) |n\rangle\langle m| \end{aligned} \quad (1.6)$$

We see that ρ_{nm} , the density matrix elements, are made up of the time-evolving expansion coefficients. Substituting into eq. (1.5) we see that

$$\begin{aligned}\langle \hat{A}(t) \rangle &= \sum_{nm} A_{nm} \rho_{nm}(t) \\ &= \text{Tr} [\hat{A} \rho(t)]\end{aligned}\quad (1.7)$$

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

So why would we need the density matrix? It is a practical tool when dealing with mixed states. Pure states are those that are characterized by a single wavefunction. 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. A mixed state refers to any case in which we subdivide a microscopic or macroscopic system into an ensemble, for which there is initially no phase relationship between the elements of the mixture. Examples include an ensemble at thermal equilibrium, and independently prepared states.

Given that you have a statistical mixture, and can describe the probability p_k occupying quantum state with a density matrix:

$$\langle \hat{A}(t) \rangle = \sum_k p_k \langle \Psi_k(t) | \hat{A} | \Psi_k(t) \rangle \quad (1.8)$$

$$\rho(t) = \sum_k p_k | \Psi_k(t) \rangle \langle \Psi_k(t) | \quad (1.9)$$

$$\langle \hat{A}(t) \rangle = \text{Tr} [\hat{A} \rho(t)] \quad (1.10)$$

Evaluating expectation value is the same for pure or mixed states – these only differ in the way elements of ρ are obtained.

Properties of the density matrix

$$1) \quad \rho \text{ is Hermitian } \rho_{nm}^* = \rho_{mn} \quad (1.11)$$

$$2) \quad \text{Normalization: } \text{Tr}(\rho) = 1 \quad (1.12)$$

$$3) \quad \text{Tr}(\rho^2) = \begin{cases} = 1 & \text{for pure state} \\ > 1 & \text{mixed state} \end{cases} \quad (1.13)$$

The last expression reflects the fact that diagonal matrix elements can be 0 or 1 for pure states but lie between 0 and 1 for mixed states. In addition, when working with the density matrix it is convenient to make note of these trace properties:

$$1) \text{Cyclic invariance: } Tr(ABC) = Tr(CAB) = Tr(BCA) \quad (1.14)$$

$$2) \text{ Invariance to unitary transformation: } Tr(S^\dagger AS) = Tr(A) \quad (1.15)$$

Density matrix elements

Let's discuss the density matrix elements for a mixture. You can think about this as an ensemble in which the individual molecules ($i = 1$ to N) are described in terms of the same internal basis states $|n\rangle$, but the probability of occupying those states may vary from molecule to molecule.

We then expect that we can express the state of a certain molecule as

$$|\Psi_i\rangle = \sum_n c_n^i |n\rangle \quad (1.16)$$

Where c_n^i is the complex and time-dependent amplitude coefficient for the occupation of basis state n on molecule i . Then the density matrix elements are

$$\rho_{nm} = \langle n | \rho | m \rangle \quad (1.17)$$

$$= \sum_i \langle n | \Psi_i \rangle \langle \Psi_i | m \rangle$$

$$= \sum_i \sum_{nm} c_n^i (c_m^i)^*$$

$$\rho_{nm} = \overline{c_n c_m^*} \quad (1.18)$$

This expression states that the density matrix elements represent values of the eigenstate coefficients averaged over the mixture

Diagonal elements ($n = m$) give the probability of occupying a quantum state $|n\rangle$

$$\rho_{nn} = \overline{c_n c_n^*} = \rho_n \geq 0$$

(1.19)

For this reason, diagonal elements are referred to as populations

Off-Diagonal Elements ($n \neq m$) are complex and have a time-dependent phase factor that describes the evolution of coherent superpositions.

$$\rho_{nm} = \overline{c_n(t) c_m^*(t)} = \overline{c_n c_m^*} e^{-i\omega_{nm}t} \quad (1.20)$$

and are referred to as **coherences**.



