5.74 Introductory Quantum Mechanics II
Spring 2009

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.

$$\rho(t) \equiv |\psi(t)\rangle\langle\psi(t)|. \tag{1.1}$$

This implies that if you specify a state $|\chi\rangle$, the integral $\langle\chi|\rho|\chi\rangle$ 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:

$$\langle A \rangle = \int A\, P(A)\, dA \tag{1.2}$$

$$\langle A \rangle = \langle\psi|A|\psi\rangle = Tr[A\rho]. \tag{1.3}$$

where Tr[…] refers to tracing over the diagonal elements of the matrix.

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

$$|\psi(t)\rangle = \sum_n c_n(t)|n\rangle, \tag{1.4}$$

the expectation value of an operator is

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

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

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

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

$$\left\langle \hat{A}(t) \right\rangle = \sum_{n,m} A_{mn} \rho_{nm}(t)$$
$$= Tr\left[\hat{A}\rho(t) \right] \tag{1.7}$$

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 me 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 of occupying quantum state $\left| \psi_k \right\rangle$, with $\sum_k p_k = 1$, evaluation of expectation values is simplified with a density matrix:

$$\left\langle \hat{A}(t) \right\rangle = \sum_k p_k \left\langle \psi_k(t) \middle| \hat{A} \middle| \psi_k(t) \right\rangle \tag{1.8}$$

$$\rho(t) \equiv \sum_k p_k \left| \psi_k(t) \right\rangle \left\langle \psi_k(t) \right| \tag{1.9}$$

$$\left\langle \hat{A}(t) \right\rangle = Tr\left[\hat{A}\rho(t) \right]. \tag{1.10}$$

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) ρ is Hermetian: $\rho_{nm}^* = \rho_{mn}$ (1.11)

    2) Normalization: $Tr(\rho) = 1$ (1.12)

3) $Tr\left(\rho^2\right)\begin{cases} =1 & \text{for pure state} \\ <1 & \text{for mixed state} \end{cases}$ (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) Cyclic invariance: $\quad Tr\left(ABC\right) = Tr\left(CAB\right) = Tr\left(BCA\right)$ (1.14)

2) Invariance to unitary transformation: $\quad Tr\left(S^\dagger AS\right) = Tr\left(A\right)$ (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

$$|\psi_i\rangle = \sum_n c_n^i |n\rangle,$$ (1.16)

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

$$\begin{aligned} \rho_{nm} &= \langle n|\rho|m\rangle \\ &= \sum_i \langle n|\psi_i\rangle\langle\psi_i|m\rangle \\ &= \sum_i \sum_{n,m} c_n^i \left(c_m^i\right)^* \\ &= \overline{c_n c_m^*} \end{aligned}$$ (1.17)

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

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

$$\rho_{nn} = \overline{c_n c_n^*} = p_n \geq 0$$ (1.18)

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.

$$\rho_{nm} = \overline{c_n(t)c_m^*(t)} = \overline{c_n c_m^*}\, e^{-i\omega_{nm}t} ,\tag{1.19}$$

and are referred to as **coherences**.

Density matrix at thermal equilibrium

Our work with statistical mixtures will deal heavily with systems at thermal equilibrium. The density matrix at thermal equilibrium ρ_{eq} (or ρ_0) is characterized by thermally distributed populations in the quantum states:

$$\rho_{nn} = p_n = \frac{e^{-\beta E_n}}{Z}\tag{1.20}$$

where Z is the partition function. This follows naturally from the general definition of the equilibrium density matrix

$$\rho_{eq} = \frac{e^{-\beta \hat{H}}}{Z}\tag{1.21}$$

where the partition function

$$Z = Tr\left(e^{-\beta \hat{H}}\right)\tag{1.22}$$

We obtain eq. (1.20) using the specific case $\hat{H}|n\rangle = E_n|n\rangle$,

$$\begin{aligned}
\left(\rho_{eq}\right)_{nm} &= \frac{1}{Z}\langle n|e^{-\beta \hat{H}}|m\rangle \\
&= \frac{e^{-\beta E_n}}{Z}\delta_{nm} \\
&= p_n \delta_{nm}
\end{aligned}\tag{1.23}$$

From this language one can also express a thermally averaged expectation value as:

$$\langle A \rangle = \frac{1}{Z}\sum_n e^{-\beta E_n}\langle n|A|n\rangle = \frac{1}{Z}Tr\left(A\rho_{eq}\right).\tag{1.24}$$

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. Using

$$\frac{\partial}{\partial t}|\psi\rangle = \frac{-i}{\hbar} H |\psi\rangle \qquad \frac{\partial}{\partial t}\langle\psi| = \frac{i}{\hbar}\langle\psi| H \tag{1.25}$$

$$\begin{aligned}
\frac{\partial\rho}{\partial t} &= \frac{\partial}{\partial t}\left[|\psi\rangle\langle\psi|\right] \\
&= \left[\frac{\partial}{\partial t}|\psi\rangle\right]\langle\psi| + |\psi\rangle\frac{\partial}{\partial t}\langle\psi| \\
&= \frac{-i}{\hbar} H |\psi\rangle\langle\psi| + \frac{i}{\hbar}|\psi\rangle\langle\psi| H
\end{aligned} \tag{1.26}$$

$$\frac{\partial\rho}{\partial t} = \frac{-i}{\hbar}\left[H, \rho\right] \tag{1.27}$$

Equation (1.27) is the Liouville-Von Neumann equation. It is isomorphic to the Heisenberg equation of motion for internal variables, since ρ is also an operator. The solution is

$$\rho(t) = U\rho(0)U^\dagger. \tag{1.28}$$

This can be demonstrated by first integrating eq. (1.27) to obtain

$$\rho(t) = \rho(0) - \frac{i}{\hbar}\int_0^t d\tau\left[H(\tau), \rho(\tau)\right] \tag{1.29}$$

If we expand eq. (1.29) by iteratively substituting into itself, the expression is the same as when we substitute

$$U = \exp_+\left[-\frac{i}{\hbar}\int_0^t d\tau H(\tau)\right] \tag{1.30}$$

into eq. (1.28) and collect terms by orders of $H(\tau)$.

Note that eq. (1.28) 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):

$$\left\langle \hat{A}(t)\right\rangle = Tr\left[\hat{A}\rho(t)\right]$$
$$= Tr\left[\hat{A}U\,\rho_0\,U^\dagger\right] \tag{1.31}$$
$$= Tr\left[\hat{A}(t)\rho_0\right]$$

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

$$\rho_{nm}(t) = \left\langle n|\rho(t)|m\right\rangle = \left\langle n|\psi(t)\right\rangle\left\langle \psi(t)|m\right\rangle = \left\langle n|U|\psi_0\right\rangle\left\langle \psi_0|U^\dagger|m\right\rangle \tag{1.32}$$

$$\rho_{nm}(t) = e^{-i\omega_{nm}(t-t_0)}\rho_{nm}(t_0) \tag{1.33}$$

From this we see that populations, $\rho_{nn}(t) = \rho_{nm}(t_0)$, 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 $V(t)$,

$$H(t) = H_0 + V(t) \tag{1.34}$$

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

$$\left|\psi_I\right\rangle = U_0^\dagger\left|\psi_S\right\rangle \tag{1.35}$$

We obtain ρ_I as

$$\rho_I = U_0^\dagger\rho_S U_0. \tag{1.36}$$

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

$$\frac{\partial\rho_I}{\partial t} = -\frac{i}{\hbar}\left[V_I(t),\rho_I(t)\right] \tag{1.37}$$

where, as before, $V_I = U_0^\dagger V U_0$. This expression can be written in shorthand in terms of the Liovillian superoperator $\hat{\hat{\mathcal{L}}}$

$$\frac{\partial \hat{\rho}_I}{\partial t} = \frac{-i}{\hbar} \hat{\hat{\mathcal{L}}} \hat{\rho}_I .$$ (1.38)

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

$$\hat{\hat{\mathcal{L}}} \hat{A} \equiv \left[H, \hat{A} \right]$$ (1.39)

Equation (1.37) can be integrated to obtain

$$\rho_I(t) = \rho_I(t_0) - \frac{i}{\hbar} \int_{t_0}^{t} dt' \left[V_I(t'), \rho_I(t') \right].$$ (1.40)

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

$$\begin{aligned}
\rho_I(t) = \rho_0 &- \frac{i}{\hbar} \int_{t_0}^{t} dt_1 \left[V_I(t_1), \rho_0 \right] \\
&+ \left(-\frac{i}{\hbar} \right)^2 \int_{t_0}^{t} dt_2 \int_{t_0}^{t_2} dt_1 \left[V_I(t_2), \left[V_I(t_1), \rho_0 \right] \right] + \cdots \\
&+ \left(-\frac{i}{\hbar} \right)^n \int_{t_0}^{t} dt_n \int_{t_0}^{t_n} dt_{n-1} \cdots \int_{t_0}^{t_2} dt_1 \left[V_I(t_n), \left[V_I(t_{n-1}), \left[\ldots, \left[V_I(t_1), \rho_0 \right] \ldots \right] \right] \right] \\
&+ \cdots
\end{aligned}$$ (1.41)

$$\rho_I(t) = \rho^{(0)} + \rho^{(1)} + \rho^{(2)} + \cdots + \rho^{(n)} + \cdots$$ (1.42)

Here $\rho_0 = \rho(t_0)$ and $\rho^{(n)}$ is the nth-order expansion of the density matrix. Similar to eq. (1.28), equation (1.41) can also be expressed as

$$\rho_I(t) = U_0 \, \rho_I(0) U_0^{\dagger} .$$ (1.43)

This is the solution to the Liouville equation in the interaction picture. It can also be written in terms of a superoperator $\hat{\hat{G}}$, the time-propagator:

$$\rho_I(t) = \hat{\hat{G}}(t) \rho_I(0)$$ (1.44)

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

$$\hat{\hat{G}} \hat{A}_I \equiv U_0 \, \hat{A}_I \, U_0^{\dagger}$$ (1.45)

For the case where the eigenstates of H_0 are known (no relaxation), the propagation for a particular element of density matrix

$$\hat{\hat{G}}(t)\rho_{ab} = e^{-iH_0 t/\hbar}|a\rangle\langle b|e^{+iH_0 t/\hbar}$$
$$= e^{-i\omega_{ab}t}|a\rangle\langle b| \tag{1.46}$$

Using the Liouville space time-propagator, the evolution of the density matrix to arbitrary order in eq. (1.41) can be written as

$$\rho_I^{(n)} = \left(-\frac{i}{\hbar}\right)^n \int_{t_0}^t dt_n \int_{t_0}^{t_n} dt_{n-1}\dots\int_{t_0}^{t_2} dt_1 \hat{G}(t-t_n)V(t_n)\hat{G}(t_n-t_{n-1})V(t_{n-1})\cdots\hat{G}(t_2-t_1)V(t_1)\rho_0. \tag{1.47}$$

Correlation Functions and Response Functions

We have previously defined the correlation function as an equilibrium average of the expectation value in a product of operators:

$$C_{AA}(t) = \langle A(t)A(0)\rangle$$
$$= \sum_n p_n \langle n|A(t)A(0)|n\rangle. \tag{1.48}$$

Since $p_n = \langle n|\rho_{eq}|n\rangle$,

$$C_{AA} = Tr(\rho_{eq} A(t)A(0))$$
$$= Tr(A(t)A(0)\rho_{eq}) \tag{1.49}$$

Correlation functions can be expressed in terms of a time-propagator as

$$C_{AA}(t) = Tr(A(t)A(0)\rho_{eq})$$
$$= Tr(U_0^\dagger A U_0 A\rho_{eq})$$
$$= Tr(A U_0 A\rho_{eq} U_0^\dagger) \tag{1.50}$$
$$= Tr(A\hat{G}(t)A\rho_{eq})$$

Since the linear response function is related to the imaginary part of correlation function

$$R(\tau) = -\frac{i}{\hbar}\left(C_{AA}(\tau) - C_{AA}^*(\tau)\right)$$
$$= -\frac{i}{\hbar}\left\{Tr(A(\tau)A(0)\rho_{eq}) - Tr(A(0)A(\tau)\rho_{eq})\right\} \tag{1.51}$$
$$= -\frac{i}{\hbar}Tr([A(\tau),A(0)]\rho_{eq})$$