

Chapter 8

Density Matrix Formalism

8.1 Density Matrix Description

So far we have limited all discussions to so-called *pure states*, i.e. states that can be described by a wave function. $|\psi\rangle$. However, there exist states which cannot be described by a wave function, such as thermal states of motion, unpolarized light, or states prepared through a decoherence process such as spontaneous emission. Here a more general description is needed.

8.1.1 Basic Formalism

The general form of the density matrix of a state can be written as

$$\rho = \sum_i p_i |\psi_i\rangle \langle\psi_i|. \quad (8.1)$$

where the p_i coefficients are the relative weight of being found in state $|\psi_i\rangle$. So-called *pure* states have a single $p_j = 1$, while all other $p_{i \neq j} = 0$, resulting in the density matrix $\rho = |\psi_j\rangle \langle\psi_j|$. States which have more than one non-zero p_i are commonly referred to as *mixed* states.

Normalization of density matrices is enforced by the requirement that its trace is unity, i.e. $\text{Tr}(\rho) = 1$. This means

$$\begin{aligned} \text{Tr}(\rho) &= \sum_j \langle\psi_j| \rho |\psi_j\rangle \\ &= \sum_j \langle\psi_j| \sum_i p_i |\psi_i\rangle \langle\psi_i| \psi_j\rangle \\ &= \sum_i p_i \equiv 1 \end{aligned} \quad (8.2)$$

We should therefore interpret the p_i coefficients as the probability of being in state $|\psi_i\rangle$. In fact, for a general operator \hat{O} we extend it's expectation value to mixed states:

$$\begin{aligned}
\langle \hat{O} \rangle &= \sum_i p_i \langle \psi_i | \hat{O} | \psi_i \rangle \\
&= \sum_j \sum_i p_i \langle \psi_i | \psi_j \rangle \langle \psi_j | \hat{O} | \psi_i \rangle \\
&= \sum_j \sum_i p_j \langle \psi_i | \psi_j \rangle \langle \psi_j | \hat{O} | \psi_i \rangle \\
&= \sum_i \langle \psi_i | \left(\sum_j p_j |\psi_j\rangle \langle \psi_j| \hat{O} \right) | \psi_i \rangle \\
&= \sum_i \langle \psi_i | \rho \hat{O} | \psi_i \rangle = \text{Tr}(\rho \hat{O})
\end{aligned} \tag{8.3}$$

where in the second line we have inserted the identity operator $\mathbb{1} = \sum_j |\psi_j\rangle \langle \psi_j|$. We could have inserted the identity on the other side of \hat{O} , and we would have obtained $\langle \hat{O} \rangle = \text{Tr}(\hat{O} \rho)$. Therefore we have

$$\langle \hat{O} \rangle = \text{Tr}(\rho \hat{O}) = \text{Tr}(\hat{O} \rho) \tag{8.4}$$

Note also that, if given a density matrix, it is easy to determine if it is a mixed or pure state by looking at $\text{Tr}(\rho^2)$:

$$\begin{aligned}
\text{Tr}(\rho^2) &= \sum_k \langle \psi_k | \sum_j p_j |\psi_j\rangle \langle \psi_j| \sum_i p_i |\psi_i\rangle \langle \psi_i| \psi_k \rangle \\
&= \sum_k \sum_j \sum_i \delta_{kj} \delta_{ji} \delta_{ik} p_j p_i \\
&= \sum_i p_i^2
\end{aligned} \tag{8.5}$$

$$= \sum_i p_i^2 \tag{8.6}$$

For a pure state, and *only* for a pure state, this expression equals unity, i.e. $\text{Tr}(\rho^2) = \text{Tr}(\rho) = 1$.

8.1.2 Matrix Representation

In any N -dimensional Hilbert space, we are free to choose a basis $\{|i\rangle\}_{i=1}^N$ which spans space. In this basis the density matrix can be written as:

$$\rho = \begin{pmatrix} \rho_{00} & \rho_{01} & \cdots & \rho_{0N} \\ \rho_{10} & \rho_{11} & \cdots & \rho_{1N} \\ \vdots & \vdots & \ddots & \vdots \\ \rho_{N0} & \rho_{N1} & \cdots & \rho_{NN} \end{pmatrix} \tag{8.7}$$

The diagonal terms $\rho_{ii} \in (\mathbb{R} \geq 0)$ are called the *populations*, and must obey $\sum_{i=1}^N \rho_{ii} = 1$. The off-diagonal terms $\rho_{ij} \in \mathbb{C}$ are called the *coherences*, and must obey $\rho_{ij} = \rho_{ji}^*$, since the density matrix is Hermitian.

8.1.3 Density Matrix Time Evolution

We can see how the density matrix evolves in time by using the Schrödinger equation:

$$\begin{aligned}
\frac{d\rho}{dt} &= \sum_i p_i \left[\left(\frac{d}{dt} |\psi_i\rangle \right) \langle\psi_i| + |\psi_i\rangle \left(\frac{d}{dt} \langle\psi_i| \right) \right] \\
&= \sum_i p_i \left[\frac{H}{i\hbar} |\psi_i\rangle \langle\psi_i| + |\psi_i\rangle \langle\psi_i| \frac{H}{-i\hbar} \right] \\
&= -\frac{i}{\hbar} (H\rho - \rho H) = -\frac{i}{\hbar} [H, \rho]
\end{aligned} \tag{8.8}$$

This is known as the von Neumann equation, and it is a direct analogue of the Schrödinger equation for density matrices. If the Hamiltonian does not depend on time, this can be easily solved to give

$$\rho(t) = e^{-iHt/\hbar} \rho(0) e^{iHt/\hbar} \tag{8.9}$$

which makes sense, since consistency demands that:

$$\begin{aligned}
\rho(t) &= \sum_i p_i |\psi_i(t)\rangle \langle\psi_i(t)| \\
&= \sum_i p_i e^{-iHt/\hbar} |\psi_i(0)\rangle \langle\psi_i(0)| e^{iHt/\hbar} \\
&= e^{-iHt/\hbar} \rho(0) e^{iHt/\hbar}
\end{aligned} \tag{8.10}$$

8.1.4 Partial Trace

Consider a quantum mechanical system comprised of two coupled sub-systems A and B . The coupled system's state is given by the density matrix ρ_{AB} in the total Hilbert space \mathcal{H}_{AB} is made up of states in the tensor product $\mathcal{H}_A \otimes \mathcal{H}_B$ of the Hilbert spaces of the subsystems. The partial trace of the combined state with respect to subsystem B leaves us with the reduced density matrix of subsystem A , denoted by ρ_A . Mathematically, this means:

$$\text{Tr}_B(\rho_{AB}) = \rho_A \tag{8.11}$$

Suppose we have an operator X , which is defined in subspace A . In order for the partial trace to be a sensible operation, we must have the following:

$$\text{Tr}(X\rho_A) = \text{Tr}[(X \otimes \mathbb{1}_B)\rho_{AB}] \tag{8.12}$$

We can verify this is true by:

$$\begin{aligned}
\text{Tr}[(X \otimes \mathbb{1}_B)\rho_{AB}] &= \sum_a \sum_b (\langle a| \otimes \langle b|) (X \otimes \mathbb{1}_B) \rho_{AB} (|a\rangle \otimes |b\rangle) \\
&= \sum_a \sum_b \sum_{b'} (\langle a| \otimes \langle b|) (X \otimes |b'\rangle \langle b'|) \rho_{AB} (|a\rangle \otimes |b\rangle) \\
&= \sum_a \sum_b \langle a| X \langle b| \rho_{AB} |b\rangle (|a\rangle) \\
&= \sum_a \langle a| X \rho_A |a\rangle = \text{Tr}(X\rho_A)
\end{aligned} \tag{8.13}$$

In practice the partial trace is often used to "trace out" a system we have no knowledge of and/or we want to average over. In fact, it provides a way to uniquely describe subsystem A in the event we have no access to measurements in subsystem B .

8.2 Open Quantum Systems and Lindblad Master Equation

An *open quantum system* allows for coupling between the system of interest and the external environment, or *bath*. In general, the bath has an infinite number of degrees of freedom and is too complex to simulate or describe analytically, but with some simplifying assumptions we can obtain a powerful result known as the master equation in Lindblad form, also known as the Gorini–Kossakowski–Sudarshan–Lindblad equation (GKSL equation), or simply the Lindbladian. We present here a somewhat simplified derivation of the Lindblad master equation for a weakly interacting system and bath.

A general interaction between a system and bath can be described by the Hamiltonian

$$H_T = H + H_B + H_{SB} \quad (8.14)$$

where H describes the system dynamics, H_B the bath dynamics, and H_{SB} describes the system-bath interaction. We have implied the tensor multiplication of the system and bath's Hilbert space, and their respective Hamiltonians would be more accurately written as $H \otimes \mathbb{1}_B$ and $\mathbb{1} \otimes H_B$.

The total (system and bath) state is given by the total density matrix ρ_T , which evolves according to the von Neumann equation:

$$\dot{\rho}_T = -\frac{i}{\hbar} [H + H_B + H_{SB}, \rho_T] \quad (8.15)$$

Generally, we are only interested in the system dynamics, and therefore we want eliminate the bath's degrees of freedom by taking the partial trace over the bath: $\rho_S = \text{Tr}_B(\rho_T)$. We will first, however, need to determine how ρ_T evolves.

It is useful to move to the interaction picture, where we define $H_0 = H + H_B$ and $\tilde{\rho}_T = e^{-iH_0t/\hbar} \rho_T e^{iH_0t/\hbar}$ to see that

$$\begin{aligned} \dot{\tilde{\rho}}_T &= e^{iH_0t/\hbar} \left(i \frac{H_0}{\hbar} \rho_T + \dot{\rho}_T - i \rho_T \frac{H_0}{\hbar} \right) e^{-iH_0t/\hbar} \\ &= -\frac{i}{\hbar} e^{iH_0t/\hbar} (-H_0 \rho_T + [H_0 + H_{SB}, \rho_T] + \rho_T H_0) e^{-iH_0t/\hbar} \\ &= -\frac{i}{\hbar} e^{iH_0t/\hbar} (H_{SB} \rho_T - \rho_T H_{SB}) e^{-iH_0t/\hbar} \\ &= -\frac{i}{\hbar} e^{iH_0t/\hbar} (H_{SB} e^{-iH_0t/\hbar} e^{iH_0t/\hbar} \rho_T - \rho_T e^{-iH_0t/\hbar} e^{iH_0t/\hbar} H_{SB}) e^{-iH_0t/\hbar} \\ &= -\frac{i}{\hbar} \left[\tilde{H}_{SB}, \tilde{\rho}_T \right] \end{aligned} \quad (8.16)$$

where we have made the substitutions $\tilde{H}_{SB} = \exp(iH_0t/\hbar)H_{SB}\exp(-iH_0t/\hbar)$ to yield the effective interaction Hamiltonian, and $\tilde{\rho}_T = \exp(iH_0t/\hbar)\rho_T\exp(-iH_0t/\hbar)$.

Eq. 8.16 can be integrated to yield

$$\tilde{\rho}_T(t) = \tilde{\rho}_T(0) - \frac{i}{\hbar} \int_0^t dt' \left[\tilde{H}_{SB}(t'), \tilde{\rho}_T(t') \right] \quad (8.17)$$

which we can plug back into the von Neuman equation:

$$\dot{\tilde{\rho}}_T = -\frac{i}{\hbar} \left[\tilde{H}_{SB}, \tilde{\rho}_T(0) \right] - \frac{1}{\hbar^2} \int_0^t dt' \left[\tilde{H}_{SB}(t), \left[\tilde{H}_{SB}(t'), \tilde{\rho}_T(t') \right] \right] \quad (8.18)$$

We can safely assume that the system and bath were uncorrelated before the interaction was turned on, and therefore the first term on the right side of Eq. 8.18 vanishes. We now take the partial trace over the bath's degrees of freedom to arrive at an equation for $\tilde{\rho}_S = \text{Tr}_B(\tilde{\rho}_T) \equiv \tilde{\rho}$

$$\dot{\tilde{\rho}} = -\frac{1}{\hbar^2} \int_0^t \text{Tr}_B \left(\left[\tilde{H}_{SB}(t), \left[\tilde{H}_{SB}(t'), \tilde{\rho}_T(t') \right] \right] \right) \quad (8.19)$$

This equation for the dynamics of the system is exact, but it still requires knowledge of the bath's dynamics. To move past this point we make what is known as the *Born approximation*: The system and bath interact only weakly, and the bath is "large", and so the bath's eigenstates are not changed by the interaction. Since the system and bath were initially decoupled, this means that $\tilde{\rho}_T(t) = \tilde{\rho}(t) \otimes \tilde{\rho}_B(0)$. Eq. 8.19 then becomes

$$\dot{\tilde{\rho}} = -\frac{1}{\hbar^2} \int_0^t \text{Tr}_B \left(\left[\tilde{H}_{SB}(t), \left[\tilde{H}_{SB}(t'), \tilde{\rho}(t') \otimes \tilde{\rho}_B(0) \right] \right] \right) \quad (8.20)$$

We now make the assumption that the time derivative of the system's density matrix only depends on the density matrix at the current time, but not on the density matrix at any prior time, which also means that any correlations within the bath are quickly lost. This is the *Born-Markov approximation* and allows us to make the replacement $\tilde{\rho}(t') = \tilde{\rho}(t)$ in Eq. 8.20:

$$\dot{\tilde{\rho}} = -\frac{1}{\hbar^2} \int_0^t \text{Tr}_B \left(\left[\tilde{H}_{SB}(t), \left[\tilde{H}_{SB}(t'), \tilde{\rho}(t) \otimes \tilde{\rho}_B(0) \right] \right] \right) \quad (8.21)$$

A general form of the interaction Hamiltonian is given by:

$$\tilde{H}_{SB}(t) = \hbar \sum_i S_i(t) \otimes B_i(t) = \hbar \sum_i S_i^\dagger(t) \otimes B_i^\dagger(t) \quad (8.22)$$

Due to the Hermiticity of the Hamiltonian, these two are equivalent and we can choose which version to insert. In the following we choose the non-daggered (daggered) form to replace $H_{SB}(t')$ ($H_{SB}(t)$) in the first and third terms, and opposite for the second and fourth term.

which can be plugged into Eq. 8.21 and expanded to yield:

$$\begin{aligned} \dot{\tilde{\rho}} = & - \sum_i \sum_j \int_0^t dt' \{ S_i^\dagger(t) S_j(t') \tilde{\rho}(t) \text{Tr} [B_i^\dagger(t) B_j(t') \tilde{\rho}_B(0)] \\ & - S_i(t) \tilde{\rho}(t) S_j^\dagger(t') \text{Tr} [B_i(t) \tilde{\rho}_B(0) B_j^\dagger(t')] \\ & - S_j(t') \tilde{\rho}(t) S_i^\dagger(t) \text{Tr} [B_j(t') \tilde{\rho}_B(0) B_i^\dagger(t)] \\ & + \tilde{\rho}(t) S_j^\dagger(t') S_i(t) \text{Tr} [\tilde{\rho}_B(0) B_j^\dagger(t') B_i(t)] \} \end{aligned} \quad (8.23)$$

We now use the cyclic property of traces to see that:

$$\text{Tr} [B_j(t') \tilde{\rho}_B B_i^\dagger(t)] = \text{Tr} [\tilde{\rho}_B B_i^\dagger(t) B_j(t')] = \text{Tr} [B_i^\dagger(t) B_j(t') \tilde{\rho}_B] \equiv \frac{h_{ij}}{2} \delta(t' - t) \quad (8.24)$$

$$\text{Tr} [B_i(t) \tilde{\rho}_B B_j^\dagger(t')] = \text{Tr} [\tilde{\rho}_B B_j^\dagger(t') B_i(t)] = \text{Tr} [B_j^\dagger(t') B_i(t) \tilde{\rho}_B] \equiv \frac{h_{ji}}{2} \delta(t' - t) \quad (8.25)$$

where the final equivalence is made assuming that correlations within the bath die out very quickly compared to the system's evolution. The h_{ij} factors are general numerical factors which result from performing the trace over the bath. This is another consequence of the weak system-bath interaction. Now Eq. 8.23 simplifies to

$$\dot{\tilde{\rho}} = - \sum_i \sum_j \left\{ \frac{h_{ij}}{2} [S_i^\dagger(t) S_j(t) \tilde{\rho}(t) - S_j(t) \tilde{\rho}(t) S_i^\dagger(t)] + \frac{h_{ji}}{2} [\tilde{\rho}(t) S_j^\dagger(t) S_i(t) - S_i(t) \tilde{\rho}(t) S_j^\dagger(t)] \right\} \quad (8.26)$$

Since i and j sum over the same operators we are free to swap the indices on the third and fourth terms to obtain (dropping the explicit time-dependent notation):

$$\begin{aligned} \dot{\tilde{\rho}} = & - \sum_i \sum_j \left\{ \frac{h_{ij}}{2} [S_i^\dagger S_j \tilde{\rho} - S_j \tilde{\rho} S_i^\dagger] + \frac{h_{ij}}{2} [\tilde{\rho} S_i^\dagger S_j - S_j \tilde{\rho} S_i^\dagger] \right\} \\ = & \sum_i \sum_j h_{ij} \left\{ S_j \tilde{\rho} S_i^\dagger - \frac{1}{2} (S_i^\dagger S_j \tilde{\rho} + \tilde{\rho} S_i^\dagger S_j) \right\} \end{aligned} \quad (8.27)$$

Finally, it is possible to diagonalize the matrix h using an appropriate unitary transformation $\Gamma = dh d^\dagger$, such that

$$\Gamma_i = \sum_k \sum_l d_{ik} h_{kl} d_{li}^* \quad (8.28)$$

$$L_i = \sum_k d_{ik} S_k \quad (8.29)$$

Using this, and moving back to the Schrödinger picture, Eq. 8.27 to the standard form of the quantum master equation in Lindblad form:

$$\dot{\rho} = -\frac{i}{\hbar} [H, \rho] + \sum_i \Gamma_i \left[L_i \rho L_i^\dagger - \frac{1}{2} (L_i^\dagger L_i \rho + \rho L_i^\dagger L_i) \right]. \quad (8.30)$$

Note that sometimes the jump operators are defined as $\tilde{L}_i = \sqrt{\Gamma_i} L_i$ to yield the Lindbladian:

$$\dot{\rho} = -\frac{i}{\hbar} [H, \rho] + \sum_i \left[\tilde{L}_i \rho \tilde{L}_i^\dagger - \frac{1}{2} \left(\tilde{L}_i^\dagger \tilde{L}_i \rho + \rho \tilde{L}_i^\dagger \tilde{L}_i \right) \right]. \quad (8.31)$$