

## 8.2: Density Matrix for a Mixed State

Based on the discussion of mixed state in [Section 7.1](#), we are led to define the expectation value of an operator for a mixed state as

$$\langle \hat{A}(t) \rangle = \sum_j p_j \langle \psi^{(j)}(t) | \hat{A} | \psi^{(j)}(t) \rangle \quad (8.2.1)$$

where  $p_j$  is the probability of finding a system in the state defined by the wavefunction  $|\psi^{(j)}\rangle$ . Correspondingly, the density matrix for a mixed state is defined as:

$$\rho(t) \equiv \sum_j p_j |\psi^{(j)}(t)\rangle \langle \psi^{(j)}(t)| \quad (8.2.2)$$

For the case of a pure state, only one wavefunction  $|\psi^{(k)}\rangle$  specifies the state of the system, and  $p_j = \delta_{jk}$ . Then the density matrix is as we described before,

$$\rho(t) = |\psi(t)\rangle \langle \psi(t)| \quad (8.2.3)$$

with the density matrix elements

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

For mixed states, using the separation of system ( $a$ ) and bath ( $\alpha$ ) degrees of freedom that we used above, the expectation value of an operator  $A$  can be expressed as

$$\begin{aligned} \langle A(t) \rangle &= \sum_{a,\alpha} c_{a,\alpha}^* c_{b,\beta} \langle a | A | b \rangle \delta_{\alpha,\beta} \\ &= \sum_{a,b} \left( \sum_{\alpha} c_{a,\alpha}^* c_{b,\alpha} \right) A_{ab} \\ &\equiv \sum_{a,b} (\rho_S)_{ba} A_{ab} \\ &= \text{Tr}[\rho_S A] \end{aligned}$$

Here, the density matrix elements are

$$\rho_{a,\alpha,b,\beta} = c_{a,\alpha}^* c_{b,\beta}, \quad (8.2.4)$$

We are now in a position, where we can average the system quantities over the bath configurations. If we consider that the operator  $A$  is only a function of the system coordinates, we can make further simplifications. An example is describing the dipole operator of a molecule dissolved in a liquid. Then we can average the expectation value of  $A$  over the bath degrees of freedom as

$$\begin{aligned} \langle A(t) \rangle &= \sum_{a,\alpha} c_{a,\alpha}^* c_{b,\beta} \langle a | A | b \rangle \delta_{\alpha,\beta} \\ &= \sum_{a,b} \left( \sum_{\alpha} c_{a,\alpha}^* c_{b,\alpha} \right) A_{ab} \\ &\equiv \sum_{a,b} (\rho_S)_{ba} A_{ab} \\ &= \text{Tr}[\rho_S A] \end{aligned}$$

Here we have defined a density matrix for the system degrees of freedom (also called the reduced density matrix,  $\sigma$ )

$$\rho_s = |\psi_s\rangle \langle \psi_s| \quad (8.2.5)$$

with density matrix elements that traced over the bath states:

$$|b\rangle \rho_s \langle a| = \sum_{\alpha} c_{a,\alpha}^* c_{b,\alpha} \quad (8.2.6)$$

The “s” subscript should not be confused with the Schrödinger picture wavefunctions. To relate this to our similar expression for  $\rho$ , Equation 8.2.3, it is useful to note that the density matrix of the system are obtained by tracing over the bath degrees of freedom:

$$\begin{aligned}\rho_S &= \text{Tr}_B(\rho) \\ &= \sum_{a,b} (\rho_S)_{ba} A_{ab}\end{aligned}$$

Also, note that

$$\text{Tr}(A \times B) = \text{Tr}(A) \text{Tr}(B) \quad (8.2.7)$$

To interpret what the system density matrix represents, let’s manipulate it a bit. Since  $\rho_S$  is Hermitian, it can be diagonalized by a unitary transformation  $T$ , where the new eigenbasis  $|m\rangle$  represents the mixed states of the original  $|\psi_S\rangle$  system.

$$\rho_S = \sum_m |m\rangle \rho_{mm} \langle m| \quad (8.2.8)$$

$$\sum_m \rho_{mm} = 1 \quad (8.2.9)$$

The density matrix elements represent the probability of occupying state  $|m\rangle$ , which includes the influence of the bath. To obtain these diagonalized elements, we apply the transformation  $T$  to the system density matrix:

$$\begin{aligned}(\rho_S)_{mn} &= \sum_{a,b} T_{mb} (\rho_S)_{ba} T_{an}^\dagger \\ &= \sum_{a,b,\alpha} c_{b,\alpha} T_{mb} c_{a,\alpha}^* T_{ma}^* \\ &= \sum_{\alpha} f_{m,\alpha} f_{m,\alpha}^* \\ &= |f_m|^2 = p_m \geq 0\end{aligned}$$

The quantum mechanical interaction of one system with another causes the system to be in a mixed state after the interaction. The mixed states, which are generally inseparable from the original states, are described by

$$|\psi_S\rangle = \sum_m f_m |m\rangle \quad (8.2.10)$$

If we only observe a few degrees of freedom, we can calculate observables by tracing over unobserved degrees of freedom. This forms the basis for treating relaxation phenomena.

## Readings

1. Blum, K., Density Matrix Theory and Applications. Plenum Press: New York, 1981.
2. Mukamel, S., Principles of Nonlinear Optical Spectroscopy. Oxford University Press: New York, 1995.

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