Density Matrix

Most times experiments do not prepare particles in a pure state in Hilbert space. For example in some cases the detectors are not "ideal". In these cases we need to introduce a more general treatment that can account for statistical mixtures of quantum states. This is possible by the introduction of density matrix methods.

Example: For the case of light (photons), linearly-polarized light is a pure state. Unpolarized light is a statistical mixture. Unpolarized light traveling along $\hat{z}$ can be viewed as "50%" probability to be in $|y\rangle = \frac{1+\hat{\sigma}_z}{\sqrt{2}}$ and "50%" probability to be in $|x\rangle$ here $|x\rangle = (1+i\hat{\sigma}_y)|y\rangle$.

Crucial Point: You must understand that this is very different to the pure state $|x\rangle + |y\rangle$ $\sqrt{2}$

Let's consider the simplest scenario when we have a statistical mixture that has probability $p_x$ to be in $|x\rangle$ and probability $p_y$ to be in $|y\rangle$, initially. Suppose only this two states are initially present, then $p_x + p_y = 1$ (unpolarized case $p_x = p_y = \frac{1}{2}$)

The rule for finding the probability for any outcome is:

Perform the entire calculation first using $|x\rangle$ with all usual postulates and methods for pure states in Hilbert space to get the $P_x$(result). Then repeat using an initial state $|y\rangle$ to get the $P_y$(result). Then the final answer is just the weighted average.
Probablility = \( p_x P_x(\text{result}) + p_y P_y(\text{result}) \)

General Formulation

We represent a statistical mixture of pure states \( |\psi^{(a)}\rangle \) (do not need to be orthogonal) through a set of probabilities \( p_a \) for the system to be in each of those states. The probabilities satisfy \( \sum_a p_a = 1 \).

Now write this in a chosen representation, i.e. using a complete orthonormal set of states \( |\alpha_n\rangle \) in the Hilbert space.

For a pure state, \( |\psi\rangle = \sum_n \alpha_n |\alpha_n\rangle \), an operator \( \hat{A} \) has a mean value written as

\[
\langle \hat{A} \rangle = \langle \psi | \hat{A} | \psi \rangle = \sum_{n,n'} \alpha_n^* \langle \alpha_{n'} | \hat{A} | \alpha_n \rangle \alpha_n
\]

Instead for a non pure state, we must take a weighted average, i.e.

\[
\langle \hat{A} \rangle = \sum_a p_a \langle \psi^{(a)} | \hat{A} | \psi^{(a)} \rangle
\]

\[
= \sum_n p_n \sum_{n'} \alpha_n^* \alpha_{n'} C_n^{(a)} C_{n'}^{(a)} \text{ with } |\psi^{(a)}\rangle = \sum_n \alpha_n |\alpha_n\rangle
\]

It is convenient to define the density matrix to describe this more general mixed state as:

\[
\rho_{nn'} = \sum_a p_a^{(a)} \alpha_n^{(a)} \alpha_{n'}^{(a)}
\]

With this definition, the mean value can be written as

\[
\langle \hat{A} \rangle = \sum_{n,n'} \alpha_n^* \alpha_n \rho_{nn'} = \text{Tr} [\hat{A} \rho] = \text{Tr} [\rho \hat{A}]
\]
We can also write the density matrix of the system as
\[ \hat{\varrho} = \sum p^{(m)}_{\psi} |\psi^{(m)}\rangle \langle \psi^{(m)}| \]
or in the \( |u_n\rangle \) basis as
\[ \hat{\varrho} = \sum_{n,n'} g_{nn'} |u_n\rangle \langle u_{n'}| = \sum_{n,n'} p^{(m)} c^{(m)*}_{n} c^{(m)}_{n'} |u_n\rangle \langle u_{n'}| \]

**Main Properties of the density matrix/operator**

1) \( \hat{\varrho} \) must be Hermitian \( \hat{\varrho} = \hat{\varrho}^\dagger \)

2) \( \text{Tr} (\hat{\varrho}) = \sum g_{nn} = 1 \) Interpret \( \text{Tr} \hat{\varrho} \) as the total probability to find the system in some state. It must equal 1.

3) \( \hat{\varrho} \) must be a positive definite matrix

   i.e. ALL eigenvalues of \( \hat{\varrho} \) are non-negative
   and ALL diagonal elements \( g_{nn} > 0 \)

4) \( \text{Tr} (\hat{\varrho}^2) = \sum |g_{nn}|^2 \leq 1 \Rightarrow |g_{nn}|^2 \leq 1, \quad \forall \, n,n' \)

5) Time evolution: Suppose at time \( t=0 \) the density operator is \( \hat{\varrho}(0) = \sum p^{(m)} |\psi^{(m)}(0)\rangle \langle \psi^{(m)}(0)| \)

   This translates into an initial density matrix
\[ g_{nn'} (0) = \sum_{m} c^{(m)}_{n} (0) p^{(m)} c^{(m)*}_{n'} (0) \]

   where \( |\psi^{(m)}(0)\rangle = \sum_{n} |u_n\rangle c^{(m)}_{n} (0) \)

Then since the time-evolution (for a \( t \) independent \( H \)) is
\[ c^{(m)}_{n} (t) = \left( e^{-i H t / \hbar} \right)_{n'n} c^{(m)}_{n'} (0) \]

or simply \( |\psi^{(m)}(t)\rangle = e^{-i H t / \hbar} |\psi^{(m)}(0)\rangle \)
Then \( \hat{S}(t) = e^{-\frac{i}{\hbar} H t / h} \hat{S}(0) e^{\frac{i}{\hbar} H t / h} \).

An equivalent form obtained by differentiation is
\[
\frac{d\hat{S}}{dt} = -\frac{i}{\hbar} (\hat{H} \hat{S} - \hat{S} \hat{H}) = -\frac{i}{\hbar} [\hat{H}, \hat{S}]
\]

**Diagonal Representation of a density matrix**

Let \( (X)_{n,s} \) be a unitary transformation that diagonalizes the density matrix for some system.

Note that this unitary transformation is not unique unless no two of the corresponding eigenvalues are equal.

In this representation the density matrix is
\[
\hat{S} = \sum_{n,s} |V_n >= P_n <V_n|
\]

where \( |V_n >= \sum |U_{ns} > X_{ns} \) and \( |U_{ns} > \) was the original basis in which \( S_{nn'} \) was computed.

**Cases:**
- **Pure state case**: A pure density matrix has one eigenvalue equal to 1 and all others 0.
  
  \( S = |V_1> <V_1| \)
  
  and therefore \( S_{nn'} = <V_1 |V_1 > <V_1 |U_{1n'} > = X_{n1} (X^*)_{1,n'} \) is a separable matrix.

- **States at thermal equilibrium**

  Consider a system with a fixed number of particles, \( N \), in thermal contact an in equilibrium with a heat reservoir at temperature \( T \). (canonical ensemble)
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One finds in statistical mechanics that a system in thermodynamic equilibrium is an incoherent mixture of energy eigenstates \( |E_m\rangle \). The relative probabilities are \( \exp \left( -\frac{E_m}{k_B T} \right) \) there \( k_B \) is the Boltzmann constant.

The normalization constant corresponds to the Partition function

\[
Z(T) = \sum_m e^{-\frac{E_m}{k_B T}}
\]

i.e. \( \hat{g} \) is diagonal in the energy representation and the actual density matrix is explicitly given by:

\[
\hat{g}_{m,m'} = \frac{e^{-\frac{E_m}{k_B T}}}{Z(T)} \delta_{m,m'} \quad \text{and in an operator form}
\]

\[
\hat{g} = \frac{e^{-\hat{A}/k_B T}}{\text{Tr}[e^{-\hat{A}/k_B T}]} \quad \text{for } \hat{A} \text{-independent } \hat{A}
\]

The expectation value (thermal average) of any observable as usual is

\[
\langle \hat{A} \rangle = \text{Tr}[\hat{g} \hat{A}] = \frac{\sum_m \langle E_m | \hat{A} | E_m \rangle e^{-\frac{E_m}{k_B T}}}{\sum_m e^{-\frac{E_m}{k_B T}}}
\]

for example, the average energy is:

\[
\langle \hat{A} \rangle = -\frac{1}{2B} \ln Z \quad B = \frac{1}{k_B T}
\]

Also the quantum mechanical entropy in terms of \( \hat{g} \) is

\[
\sigma = -\text{Tr}[\hat{g} \ln \hat{g}]
\]

Two-level systems

The 3 Pauli matrices \( \{\sigma_x, \sigma_y, \sigma_z\} \) plus the 2x2 identity matrix \( I = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \), with

\[
\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad \text{and} \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}
\]
are a complete set of 2x2 matrices, and thus can be used to represent an arbitrary state in a two-level system. Therefore

\[
\hat{\mathbf{S}} = \frac{1}{2} \left( \mathbb{1} p_0 + p_x \sigma_x + p_y \sigma_y + p_z \sigma_z \right)
\]

Now observe since \( \text{Tr} \sigma_i = 0 = \text{Tr} (\sigma_i \sigma_j) \) for \( i \neq j \) and since \( \text{Tr} (\mathbb{1}) = \text{Tr} (\sigma_i^2) = 2 \) (i.e. \( \text{Tr} (\sigma_i \sigma_j) = 2 \delta_{ij} \)) then we get

\[
\text{Tr} (\hat{\mathbf{S}}) = 1 \Rightarrow p_0 = 1
\]

\[
\text{Tr} (\hat{\mathbf{S}} \sigma_i) = \langle \sigma_i \rangle \Rightarrow p_i = \langle \sigma_i \rangle
\]

The density matrix in its most general form can thus be written as

\[
\hat{\mathbf{S}} = \frac{1}{2} \left( \mathbf{1} + \langle \sigma \rangle \cdot \vec{\sigma} \right) \quad \langle \sigma \rangle \text{ are real numbers}
\]

\[
= \frac{1}{2} \begin{pmatrix}
1 + \langle \sigma_x \rangle & \langle \sigma_y \rangle - i \langle \sigma_z \rangle \\
\langle \sigma_y \rangle + i \langle \sigma_z \rangle & 1 - \langle \sigma_x \rangle
\end{pmatrix}
= \begin{pmatrix}
g_{11} & g_{12} \\
g_{21} & g_{22}
\end{pmatrix}
\]

In general terms \( g_{12} \) are referred to as quantum coherences and \( g_{11} \) as populations.

Example: If my system is in the state

\[
\hat{\mathbf{S}} = \frac{1}{2} \left( \left\langle \psi \right| \left\langle \psi \right| + 1 b \left| \psi \rightangle \left\langle \psi \right| \right)
\]

what is the probability to find it in state \( \left| x \right> = \frac{1 0 + 1 b}{\sqrt{2}} \)

\[
\left\langle x | \hat{\mathbf{S}} | x \right> = \frac{1}{2} \left\langle x | \left( \left| \psi \right> \left\langle \psi \right| + 1 0 \left| \psi \rightangle \left\langle \psi \right| \right) | x \right>
\]

\[
= \frac{1}{2} \left( \frac{1}{2} + \frac{1}{2} \right) = \frac{1}{2}
\]

In fact if you look at this case \( \hat{\mathbf{S}} \) is trivial \( \hat{\mathbf{S}} = \mathbb{1}/2 \)

So there is no coherence in all basis. Maximally mixed state

Mixed states naturally occur in open systems: A quantum system interacting with other system whose degrees of freedom can not be tracked of.
Example 2: Imagine \( |\Psi\rangle = C_{\phi} |\Psi_{1}\rangle + C_{\phi}^* |\Psi_{2}\rangle \)

But imagine we do not know the phase so we need to do an statistical average

\[
\hat{\mathbf{S}} = \int d\phi \, p(\phi) \left( C_{\phi} e^{i\phi} |\Psi_{1}\rangle + C_{\phi}^* |\Psi_{2}\rangle \right) \left( C_{\phi}^* e^{-i\phi} |\Psi_{1}\rangle + C_{\phi} |\Psi_{2}\rangle \right)
\]

\[
= \int d\phi \, p(\phi) \left( 1 |\Psi_{1}\rangle \langle \Psi_{1}| + |\Psi_{2}\rangle \langle \Psi_{2}| + e^{i\phi} |\Psi_{1}\rangle \langle \Psi_{2}| + e^{-i\phi} |\Psi_{2}\rangle \langle \Psi_{1}| \right)
\]

If \( p(\phi) \) is uniformly distributed between \((0, 2\pi)\) then

\[
\hat{\mathbf{S}} = 1 |\Psi_{1}\rangle \langle \Psi_{1}| + |\Psi_{2}\rangle \langle \Psi_{2}| \quad \Rightarrow \quad \text{Loss of phase coherence}
\]

Finally regarding the Bloch vector representation note that

\[
\text{Tr}[\hat{S}_{z}] = \frac{1}{2} \left( 1 + \frac{\langle \sigma_{x}^2 + \langle \sigma_{y}^2 + \langle \sigma_{z}^2 \rangle \rangle \rangle}{\langle \sigma \rangle^2} \right)
\]

\[
0 \leq r \leq 1
\]

\[
\frac{1}{2} \leq \text{Tr}[\hat{S}_{z}] \leq 1
\]

\[\downarrow\]

pure state

\[\downarrow\]

maximally mixed

The set of Bloch vectors live \( r \leq 1 \) live in the Bloch ball. States at the surface are pure state.