Prof. Dr. I. Nasser Dec. 28, 2012
density_matrix

Properties of the density operator

Consider a general case of a system which can be in either one of a set of normalized, but not necessarily orthogonal, state $|\psi_i\rangle$. Suppose a quantum mechanical average or the expectation value of an operator A when the system is definitely in the state $|\psi_i\rangle$ is given by A_i , where

$$A_i = \langle \hat{A} \rangle_i = \langle \psi_i | \hat{A} | \psi_i \rangle .$$

The statistical or ensemble average which is seen to be a weighted average of $\langle \hat{A} \rangle_i$ taken over all the states that the system may occupy is defined by:

$$\langle \hat{A} \rangle = \sum_i p_i A_i = \sum_i p_i \langle \psi_i | \hat{A} | \psi_i \rangle .$$

In which p_i is the probability of the system being in the normalized state $|\psi_i\rangle$ and the sum is taken over all the states that are accessible to the system. The probability p_i evidently satisfies

$$0 \le p_i \le 1, \qquad \sum_i p_i = 1, \qquad \sum_i p_i^2 \le 1 .$$

We now introduce the density operator, which is in some sense the "optimal" specification of the system. The density operator is defined as:

$$\hat{\rho} = \sum_i p_i |\psi_i\rangle\langle\psi_i|$$

Suppose the set $|\varphi_n\rangle$ forms a basis, complete set, of the Hilbert space of the system under consideration. Then the expectation value of the operator $\hat{A}$ can be rewritten after inserting the unit operator $1 = \sum_n |\varphi_n\rangle\langle\varphi_n|$ as

$$\langle \hat{A} \rangle = \sum_i p_i \langle \psi_i | \hat{A} | \psi_i \rangle = \sum_i p_i \langle \psi_i | \sum_n |\varphi_n\rangle\langle\varphi_n | \hat{A} | \psi_i \rangle$$

$$= \sum_n \langle \varphi_n | \left[\sum_i p_i |\psi_i\rangle\langle\psi_i| \right] \hat{A} | \varphi_n \rangle = \sum_n \langle \varphi_n | \hat{\rho}\hat{A} | \varphi_n \rangle = \mathrm{Tr}(\hat{\rho}\hat{A})$$

Here we have used the trace operator, Tr which adds all diagonal terms of an operator. For a general operator

$$\mathrm{Tr}\,\hat{Q} = \sum_n \langle \varphi_n | \hat{Q} | \varphi_n \rangle$$

The trace is independent of the basis used- it is invariant under a basis transformation. Another property of the trace is:

$$\mathrm{Tr}|\eta\rangle\langle\chi| = \langle\eta|\chi\rangle$$

Which is easily verified by writing out the trace with respect to a basis φ_n .

In general the density operator is defined as:

$$\hat{\rho} = \sum_i |\psi_i\rangle p_i \langle\psi_i| .$$

If a system is in a well-defined quantum state $|\psi\rangle$, we say that the system is in a pure state. In pure state there is just one p_i which is equal to unity and all the rest are zero. In that case:

$$\hat{\rho} = |\psi\rangle\langle\psi| ,$$

Which is the projection operator into that state, and we will have the conditions:

$$\left\langle \hat{A} \right\rangle_i = \left\langle \hat{A} \right\rangle \qquad \text{for pure syatem}$$

$$\hat{\rho}^2 = \hat{\rho},$$
$$\hat{\rho}^\dagger = \hat{\rho},$$
$$\mathrm{Tr}(\hat{\rho}) = \mathrm{Tr}(\hat{\rho}^2) = 1,$$
$$\mathrm{Tr}(\hat{\rho}\hat{A}) = \left\langle \hat{A} \right\rangle,$$

Examples: check all the properties of the density operator in the following examples.

1- A completely polarized beam with state $\alpha \equiv (S_z +)$

Ans: In the basis set of α and β, the density matrix is:

$$\hat{\rho} = |+\rangle\langle+| = \begin{pmatrix} 1 \\ 0 \end{pmatrix}\begin{pmatrix} 1 & 0 \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} \quad \Rightarrow \quad \mathrm{Tr}(\hat{\rho}) = \mathrm{Tr}(\hat{\rho}^2) = 1$$

Also:

$$\langle \hat{s}_x \rangle = \mathrm{Tr}\left(\hat{\rho}\,\hat{s}_x\right) = \mathrm{Tr}\left(\begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} \times \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\right) = \frac{\hbar}{2}\mathrm{Tr}\begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} = 0$$

$$\langle \hat{s}_y \rangle = \mathrm{Tr}\left(\hat{\rho}\,\hat{s}_y\right) = \mathrm{Tr}\left(\begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} \times \frac{\hbar}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}\right) = \frac{\hbar}{2}\mathrm{Tr}\begin{pmatrix} 0 & -i \\ 0 & 0 \end{pmatrix} = 0$$

$$\langle \hat{s}_z \rangle = \mathrm{Tr}\left(\hat{\rho}\,\hat{s}_z\right) = \mathrm{Tr}\left(\begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} \times \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\right) = \frac{\hbar}{2}$$

as one would expect.

H.W. Find $\hat{\rho}$ for a completely polarized beam with state $\beta \equiv (S_z -)$, and calculate $\langle \hat{s}_x \rangle$, $\langle \hat{s}_y \rangle$ and $\langle \hat{s}_z \rangle$.

Ans:

$$\hat{\rho} = |-\rangle\langle-| = \begin{pmatrix} 0 \\ 1 \end{pmatrix}\begin{pmatrix} 0 & 1 \end{pmatrix} = \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}$$

H.W. For the state $|\psi\rangle \equiv a_1|\alpha\rangle + a_2|\beta\rangle$, with $|a_1|^2 + |a_2|^2 = 1.$ prove that the density matrix can be given by:

$$\begin{aligned}\hat{\rho} &= \left(a_1|\alpha\rangle + a_2|\beta\rangle\right)\left(a_1^*\langle\alpha| + a_2^*\langle\beta|\right) \\ &= \begin{pmatrix} |a_1|^2 & a_1a_2^* \\ a_2a_1^* & |a_2|^2 \end{pmatrix}\end{aligned}$$

Which indicates that the diagonal elements $|a_1|^2$ and $|a_2|^2$ are just the probabilities that the electron is in the state α or β, respectively.

2- A completely polarized beam with state $(s_x \pm) \equiv \frac{1}{\sqrt{2}}(\alpha \pm \beta) = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ \pm 1 \end{pmatrix}$

Ans:

$$\hat{\rho} = \frac{1}{\sqrt{2}}(\alpha \pm \beta)\frac{1}{\sqrt{2}}(\alpha^\dagger \pm \beta^\dagger)$$

$$= \frac{1}{2}\begin{pmatrix} 1 \\ \pm 1 \end{pmatrix}\begin{pmatrix} 1 & \pm 1 \end{pmatrix} = \frac{1}{2}\begin{pmatrix} 1 & \pm 1 \\ \pm 1 & 1 \end{pmatrix} \Rightarrow \mathrm{Tr}(\hat{\rho}) = \mathrm{Tr}(\hat{\rho}^2) = 1$$

3- Un-polarized beam with state (50%) $\frac{1}{2}\alpha + \frac{1}{2}\beta = \frac{1}{2}\begin{pmatrix} 1 \\ 1 \end{pmatrix}$

Ans:

$$\hat{\rho} = \left(\tfrac{1}{2}|+\rangle\langle+|\right) + \left(\tfrac{1}{2}|-\rangle\langle-|\right) = \frac{1}{2}\begin{pmatrix} 1 \\ 0 \end{pmatrix}\begin{pmatrix} 1 & 0 \end{pmatrix} + \frac{1}{2}\begin{pmatrix} 0 \\ 1 \end{pmatrix}\begin{pmatrix} 0 & 1 \end{pmatrix}$$

$$= \frac{1}{2}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = \frac{1}{2}\hat{1} \Rightarrow \mathrm{Tr}(\hat{\rho}) \neq \mathrm{Tr}(\hat{\rho}^2)$$

Another way of calculating $\hat{\rho}_{mn}$

$$\hat{\rho}_{11} = \langle+|\hat{\rho}|+\rangle = \frac{1}{2}\langle+|+\rangle\langle+|+\rangle + \frac{1}{2}\langle+|-\rangle\langle-|+\rangle = \frac{1}{2};$$

$$\hat{\rho}_{12} = \langle+|\hat{\rho}|-\rangle = \frac{1}{2}\langle+|+\rangle\langle+|-\rangle + \frac{1}{2}\langle+|-\rangle\langle-|-\rangle = 0$$

Now, case *B*: 50% in the state $|\uparrow\rangle$, 50% $|\downarrow\rangle$. The density matrix is

$$\hat{\rho} = \frac{1}{2}|\uparrow\rangle\langle\uparrow| + \frac{1}{2}|\downarrow\rangle\langle\downarrow|$$

$$= \frac{1}{2}\begin{pmatrix} 1 \\ 0 \end{pmatrix}\begin{pmatrix} 1 & 0 \end{pmatrix} + \frac{1}{2}\begin{pmatrix} 0 \\ 1 \end{pmatrix}\begin{pmatrix} 0 & 1 \end{pmatrix} = \frac{1}{2}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}.$$

This is proportional to the unit matrix, so $\mathrm{Tr}\,\hat{\rho}s_x = \frac{1}{2}\frac{\hbar}{2}\mathrm{Tr}\,\sigma_x = 0,$ and similarly for s_y and s_z, since the Pauli σ-matrices are all traceless. Note also that $\hat{\rho}^2 = \frac{1}{2}\hat{\rho} \neq \hat{\rho}$, as is true for all mixed states.

Finally, let us consider a 50%:50% mixed state of spins in $|\uparrow_x\rangle = \frac{1}{\sqrt{2}}\left(|\uparrow\rangle + |\downarrow\rangle\right)$, "up" along the *x*-axis, and $|\downarrow_x\rangle = \frac{1}{\sqrt{2}}\left(|\uparrow\rangle - |\downarrow\rangle\right)$, "down" in the *x*-direction.

It is easy to check that

$$\hat{\rho} = \frac{1}{2}\left|\uparrow_x\right\rangle\left\langle\uparrow_x\right| + \frac{1}{2}\left|\downarrow_x\right\rangle\left\langle\downarrow_x\right| = \frac{1}{2}\begin{pmatrix} 1/2 & 1/2 \\ 1/2 & 1/2 \end{pmatrix} + \frac{1}{2}\begin{pmatrix} 1/2 & -1/2 \\ -1/2 & 1/2 \end{pmatrix} = \frac{1}{2}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}.$$

Which is just the identity matrix divided by 2.
Check if we can put:

$$\tfrac{1}{2}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = \tfrac{1}{2}\begin{pmatrix} \frac{1}{2} & \frac{1}{2} \\ \frac{1}{2} & \frac{1}{2} \end{pmatrix} + \tfrac{1}{2}\begin{pmatrix} \frac{1}{2} & -\frac{1}{2} \\ -\frac{1}{2} & \frac{1}{2} \end{pmatrix} = \tfrac{1}{2}(S_x +) + \tfrac{1}{2}(S_x -)$$

Which is 50% of $(S_x +)$ and 50% of $(S_x -)$. What is this means to us? It means that both formulations describe a state about which we know nothing-we are in state of total ignorance, the spins are completely random, all directions are equally likely. The density matrix describing such a state can not depend on the direction we choose for our axis. Note that this is not the only representation.

This is exactly the same density matrix we found for 50% in the state $\left|\uparrow\right\rangle$, 50% $\left|\downarrow\right\rangle$! The reason is that both formulations describe a state about which we know nothing—we are in a state of total ignorance, the spins are completely random, all directions are equally likely. The density matrix describing such a state cannot depend on the direction we choose for our axes.

Another two-state quantum system that can be analyzed in the same way is the polarization state of a beam of light, the basis states being polarization in the *x*-direction and polarization in the *y*-direction, for a beam traveling parallel to the *z*-axis. Ordinary unpolarized light corresponds to the random mixed state, with the same density matrix as in the last example above.

4- A completely polarized beam with state $(S_X +) \equiv \frac{1}{\sqrt{2}}\left|\alpha+\beta\right\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix}$

$$\hat{\rho} = \frac{1}{\sqrt{2}}\left|\alpha+\beta\right\rangle \frac{1}{\sqrt{2}}\left\langle\alpha+\beta\right| = \frac{1}{2}\begin{pmatrix} 1 \\ 1 \end{pmatrix}\begin{pmatrix} 1 & 1 \end{pmatrix} = \frac{1}{2}\begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix}$$

$$\left\langle \hat{s}_x \right\rangle = \mathrm{Tr}\left(\hat{\rho}\,\hat{s}_x\right) = \mathrm{Tr}\left(\frac{1}{2}\begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix} \times \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\right) = \frac{\hbar}{2}$$

$$\left\langle \hat{s}_z \right\rangle = \mathrm{Tr}\left(\hat{\rho}\,\hat{s}_z\right) = \mathrm{Tr}\left(\frac{1}{2}\begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix} \times \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\right) = 0$$

H.W. If the density operator for the spin ½ particles is:

$$\hat{\rho} = c_o \hat{\mathrm{I}} + c_1 \hat{s}_x + c_2 \hat{s}_y + c_3 \hat{s}_z$$

with $\hat{\mathrm{I}}$ is the unit 2×2 matrix and c_i are constants, prove that:

$$\hat{\rho} = \begin{pmatrix} \frac{1}{2} + \langle \hat{s}_x \rangle & \langle \hat{s}_X \rangle - i \langle \hat{s}_y \rangle \\ \langle \hat{s}_x \rangle + i \langle \hat{s}_y \rangle & \frac{1}{2} - \langle \hat{s}_z \rangle \end{pmatrix}$$

$$= \frac{1}{2}\hat{\text{I}} + 2\langle \hat{\text{s}} \rangle . \hat{\text{s}} = \frac{1}{2}\left[\hat{\text{I}} + \langle \hat{\sigma} \rangle . \hat{\sigma}\right]$$

and $\hat{\sigma}$ are the Pauli's matrices.

Example: Consider a pure ensemble of spin ½ particles polarized along the vector $\vec{\text{P}} = (\frac{1}{2}, 0, \frac{1}{2}\sqrt{3})$

a- Calculate the density matrix for the ensemble and check that $\text{Tr}(\hat{\rho}) = \text{Tr}(\hat{\rho}^2) = 1$.

b- Calculate the ensemble average $\langle \hat{s}_z \rangle$ and $\langle \hat{s}_x \rangle$ using the density matrix.

Answer: for the polarization vector $\vec{\text{P}} = (\frac{1}{2}, 0, \frac{1}{2}\sqrt{3})$, we have

a- with $\hat{\rho} = \frac{1}{2}\left[\hat{\text{I}} + \hat{\sigma}.\vec{\text{P}}\right] = \frac{1}{2}\left[\hat{\text{I}} + \hat{\sigma}_x \text{P}_\text{x} + \hat{\sigma}_y \text{P}_\text{y} + \hat{\sigma}_z \text{P}_\text{z}\right]$, then

$$\hat{\rho} = \frac{1}{2}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \begin{pmatrix} \frac{1}{2} & 0 \\ 0 & \frac{1}{2} \end{pmatrix} + \begin{pmatrix} \frac{1}{2}\sqrt{3} & 0 \\ 0 & -\frac{1}{2}\sqrt{3} \end{pmatrix} = \frac{1}{2}\begin{pmatrix} 1 + \frac{1}{2}\sqrt{3} & \frac{1}{2} \\ \frac{1}{2} & 1 - \frac{1}{2}\sqrt{3} \end{pmatrix}$$

b- Will find $\hat{\rho} = \hat{\rho}^2 = \frac{1}{2}\begin{pmatrix} 1 + \frac{1}{2}\sqrt{3} & \frac{1}{2} \\ \frac{1}{2} & 1 - \frac{1}{2}\sqrt{3} \end{pmatrix}$ and $\text{Tr}(\hat{\rho}) = \text{Tr}(\hat{\rho}^2) = 1$.

Statistics of various ensembles

1- The microcanonical ensemble:- Systems with fixed N and V , and an energy lying within the interval $(E-\frac{1}{2}\Delta, E+\frac{1}{2}\Delta)$, where $\Delta << E$. The total number of distinct microstates accessible to a system is $\Gamma(E,V,N;\Delta)$. From the equal a priori probabilities

$$p_k = \frac{1}{\Gamma(E,V,N;\Delta)}$$

Thus all the states in the microcanonical ensemble appear with the same weight which implies that

$$\hat{\rho} = \sum_i p_i |\psi_i\rangle\langle\psi_i|$$

with the discrete eigenvalues (E_i) lying within the range $E-\frac{1}{2}\Delta < E_i < E+\frac{1}{2}\Delta$.

$$(\hat{\rho})_{mn} = \sum_i \langle\psi_m|\psi_i\rangle p_i \langle\psi_i|\psi_n\rangle = \sum_i \frac{1}{\Gamma(E)}\delta_{mi}\delta_{in} = p_n\delta_{mn}$$

with

$$p_n = \begin{cases} \frac{1}{\Gamma(E)}, & \text{for each of the accessible states} \\ 0 & \text{for all other states} \end{cases}$$

The entropy

$$S = k_B \ln\Gamma(E)$$

where $\Gamma(E)$ is now calculated quantum mechanically, taking into account the indistinguishability of the particles, which implies no paradox, such as Gibbs' paradox. Also, as $T \to 0$, system goes to the ground state which gives $\Gamma(E)=1$ i.e. $S=0$ (third law of thermodynamics)

$$\Gamma(E) = \begin{cases} 1 & \text{pure case, } p = p^2 \\ >1 & \text{mixed case (degenrate), } p \neq p^2,\ S \neq 0 \end{cases}$$

2- The microcanonical ensemble:- Systems with fixed N , V and T and different energy E . The probability that a system, chosen at random from the ensemble, possesses an energy E_n is determined by Boltzmaan factor $e^{-\beta E_n}$, and the density matrix in the energy representation is therefore taken as

$$(\hat{\rho})_{mn} = p_n\delta_{mn}$$

with

$$p_n = \frac{e^{-\beta E_n}}{Z}, \qquad n = 0,1,2,\cdots$$

Thus density operator in the canonical ensemble could be written as:

$$\hat{\rho} = \sum_i |\psi_i\rangle p_i \langle\psi_i| = \sum_i |\psi_i\rangle \frac{e^{-\beta E_i}}{Z}\langle\psi_i| = \frac{e^{-\beta\hat{H}}}{Z}\sum_i |\psi_i\rangle\langle\psi_i|$$

$$= \frac{e^{-\beta\hat{H}}}{\mathrm{Tr}\left(e^{-\beta\hat{H}}\right)}$$

The expectation value $\left\langle \hat{A} \right\rangle_N$ of a physical quantity A is now given by

$$\left\langle \hat{A} \right\rangle_N = \mathrm{Tr}\left(\hat{A}\hat{\rho}\right) = \frac{\mathrm{Tr}\left(\hat{A}e^{-\beta\hat{H}}\right)}{\mathrm{Tr}\left(e^{-\beta\hat{H}}\right)}$$

the suffix N here emphasizes he fact that the averaging has been done over an ensemble with N fixed.

Example: If $\hat{H} = -\boldsymbol{\mu}\cdot\boldsymbol{B} = -\mu B\,\hat{\sigma}_z = -\mu B\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$ find $\left\langle \hat{\sigma}_z \right\rangle$.

Answer:

$$\begin{aligned}
e^{-\beta\hat{H}} = e^{-\mu B\hat{\sigma}_z} &= \hat{1} + (\beta\mu B)\hat{\sigma}_z + \frac{1}{2!}(\beta\mu B)^2\hat{\sigma}_z^2 + \frac{1}{3!}(\beta\mu B)^3\hat{\sigma}_z^3 + \cdots \\
&= \hat{1}\left(1 + \frac{1}{2!}(\beta\mu B)^2 + \cdots\right) + \hat{\sigma}_z\left((\beta\mu B) + \frac{1}{3!}(\beta\mu B)^3 + \cdots\right) \\
&= \hat{1}\cosh(\beta\mu B) + \hat{\sigma}_z \sinh(\beta\mu B) \\
&= \begin{pmatrix} \cosh(\beta\mu B) & 0 \\ 0 & \cosh(\beta\mu B) \end{pmatrix} + \begin{pmatrix} \sinh(\beta\mu B) & 0 \\ 0 & -\sinh(\beta\mu B) \end{pmatrix} = \begin{pmatrix} e^{\beta\mu B} & 0 \\ 0 & e^{-\beta\mu B} \end{pmatrix}
\end{aligned}$$

Note that: With the definition $\hat{\sigma}_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$, one finds

$$\hat{\sigma}_z^2 = \hat{\sigma}_z^4 = \hat{\sigma}_z^6 = \cdots = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = \hat{1},$$

$$\hat{\sigma}_z^3 = \hat{\sigma}_z^5 = \hat{\sigma}_z^7 = \cdots = \hat{\sigma}_z\,,$$

then

$$\mathrm{Tr}(e^{-\beta\hat{H}}) = e^{\beta\mu B} + e^{-\beta\mu B} = 2\cosh(\beta\mu B)$$

$$\Rightarrow \hat{\rho} = \frac{e^{-\beta\hat{H}}}{\mathrm{Tr}(e^{-\beta\hat{H}})} = \frac{1}{2\cosh(\beta\mu B)}\begin{pmatrix} e^{\beta\mu B} & 0 \\ 0 & e^{-\beta\mu B} \end{pmatrix}$$

$$\begin{aligned}
\left\langle \hat{\sigma}_z \right\rangle = \mathrm{Tr}\left(\hat{\rho}\hat{\sigma}_z\right) &= \frac{1}{2\cosh(\beta\mu B)}\mathrm{Tr}\left(\begin{pmatrix} e^{\beta\mu B} & 0 \\ 0 & e^{-\beta\mu B} \end{pmatrix} \times \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\right) \\
&= \frac{1}{2\cosh(\beta\mu B)}\mathrm{Tr}\begin{pmatrix} e^{\beta\mu B} & 0 \\ 0 & -e^{-\beta\mu B} \end{pmatrix} \\
&= \frac{e^{\beta\mu B} - e^{-\beta\mu B}}{2\cosh(\beta\mu B)} = \frac{2\sinh(\beta\mu B)}{2\cosh(\beta\mu B)} = \tanh(\beta\mu B)
\end{aligned}$$

- Examples in spin-1/2 system:

$$\rho = |\uparrow\rangle\langle\uparrow|$$

$$\rho = \frac{\left(|\uparrow\rangle + |\downarrow\rangle\right)}{\sqrt{2}}\frac{\left(\langle\uparrow| + \langle\downarrow|\right)}{\sqrt{2}}$$

$$\rho == \frac{3}{4}|\uparrow\rangle\langle\uparrow| + \frac{1}{4}|\uparrow\rangle\langle\downarrow| + \frac{1}{4}|\downarrow\rangle\langle\uparrow| + \frac{1}{4}|\downarrow\rangle\langle\downarrow|$$

$$\rho == \frac{3}{4}|\uparrow\rangle\langle\uparrow| + \frac{1}{4}|\downarrow\rangle\langle\downarrow|$$

$$\begin{pmatrix} \frac{1}{2} & \frac{1}{2} \\ \frac{1}{2} & \frac{1}{2} \end{pmatrix}$$ pure

$$\begin{pmatrix} \frac{3}{4} & 0 \\ 0 & \frac{1}{4} \end{pmatrix}$$ totally mixed

$$\begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}$$ pure

$$\begin{pmatrix} \frac{3}{4} & \frac{1}{4} \\ \frac{1}{4} & \frac{1}{4} \end{pmatrix}$$ partially mixed

- In a given basis, the diagonal elements are always the probabilities to be in the corresponding states:

- The off diagonals are a measure of the 'coherence' between any two of the basis states.

$$\begin{pmatrix} \frac{1}{2} & \frac{1}{2} \\ \frac{1}{2} & \frac{1}{2} \end{pmatrix} \quad \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} \quad \begin{pmatrix} \frac{3}{4} & \frac{1}{4} \\ \frac{1}{4} & \frac{1}{4} \end{pmatrix} \quad \begin{pmatrix} \frac{3}{4} & 0 \\ 0 & \frac{1}{4} \end{pmatrix}$$

pure — pure — partially mixed — totally mixed

  - Coherence is maximized when:

$$\rho_{mn}\rho_{nm} = \rho_{mm}\rho_{nn}$$

As an example consider the wavefunction for a spin that is oriented at an angle θ and φ in polar coordinates: $\Psi = \cos(\frac{\theta}{2})e^{-i\phi/2}|u_{+1/2}> + \sin(\frac{\theta}{2})e^{i\phi/2}|u_{-1/2}>$

The density matrix for this state is: $\rho = \begin{bmatrix} cos^2(\theta/2) & cos(\theta/2)sin(\theta/2)e^{-i\phi} \\ cos(\theta/2)sin(\theta/2)e^{+i\phi} & sin^2(\theta/2) \end{bmatrix}$

The expectation value for S_x is: $< S_x >= \text{Trace}(\rho S_x)$

$$\begin{aligned} \rho S_x &= \begin{bmatrix} cos^2(\theta/2) & cos(\theta/2)sin(\theta/2)e^{-i\phi} \\ cos(\theta/2)sin(\theta/2)e^{+i\phi} & sin^2(\theta/2) \end{bmatrix} \frac{\hbar}{2} \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \\ &= \frac{\hbar}{2} \begin{bmatrix} cos(\theta/2)sin(\theta/2)e^{-i\phi} & cos^2(\theta/2) \\ sin^2(\theta/2) & cos(\theta/2)sin(\theta/2)e^{+i\phi} \end{bmatrix} \\ < S_x > &= \text{Trace}(\rho S_x) = \frac{\hbar}{2} \left[cos\frac{\theta}{2} sin\frac{\theta}{2} e^{-i\phi} + cos\frac{\theta}{2} sin\frac{\theta}{2} e^{+i\phi} \right] \\ &= \frac{\hbar}{2}\, 2\, cos\frac{\theta}{2} sin\frac{\theta}{2} \left[\frac{e^{i\phi} + e^{-i\phi}}{2} \right] = \frac{\hbar}{2}\, 2\, cos\frac{\theta}{2} sin\frac{\theta}{2} cos\phi \end{aligned}$$

If the spin is oriented such that its magnetic moment is along the x-axis, then θ = 90, and φ = 0. The expectation value of S_x is then, $< S_x >= \frac{\hbar}{2}\, 2\, \frac{1}{\sqrt{2}} \frac{1}{\sqrt{2}} = \frac{\hbar}{2}$ as expected:

Calculation of the expectation value of S_y for this example yields <Sy >= 0.

The population difference at thermal equilibrium is given by the Boltzmann distribution:

$$\frac{e^{-E/kT}}{Z}$$

Using the Boltzmann distribution as an operator gives the desired form of the density matrix. A single element of the density matrix is:

$$\rho_{pn} =< u_p|\frac{e^{-\mathcal{H}/kT}}{Z}|u_n >$$

And the entire density matrix is:

$$\rho = \frac{1}{Z}\begin{bmatrix} < u_1|e^{-\mathcal{H}/kT}|u_1 > & < u_1|e^{-\mathcal{H}/kT}|u_2 > \\ < u_2|e^{-\mathcal{H}/kT}|u_1 > & < u_2|e^{-\mathcal{H}/kT}|u_2 > \end{bmatrix} = \frac{1}{Z}\begin{bmatrix} e^{-E_1/kT} < u_1|u_1 > & e^{-E_2/kT} < u_1|u_2 > \\ e^{-E_1/kT} < u_2|u_1 > & e^{-E_2/kT} < u_2|u_2 > \end{bmatrix}$$

$$= \frac{1}{Z}\begin{bmatrix} e^{-E_1/kT} & 0 \\ 0 & e^{-E_2/kT} \end{bmatrix} = \frac{1}{Z}\begin{bmatrix} e^{+\hbar\omega_o/2kT} & 0 \\ 0 & e^{-\hbar\omega_o/2kT} \end{bmatrix}$$

Expanding the exponential as a series and taking only the first term ($e^a \approx 1 + a$) we find:

$$\rho = \frac{1}{Z}\begin{bmatrix} 1+\gamma & 0 \\ 0 & 1-\gamma \end{bmatrix} = \frac{1}{Z}\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} + \frac{1}{Z}\frac{\omega_o}{kT}\frac{\hbar}{2}\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \qquad (6.28)$$

Where $\gamma = \hbar\omega_o/2kT.$

One can see that this matrix is composed of the unit matrix plus S_z. Since the unit matrix has no effect on any of the common observables we can ignore it 1. Furthermore, since we are only interested in the changes in the amplitudes and the time evolution of the individual elements of the density matrix, we can also ignore constants. Therefore, the density operator for a system under thermal equilibrium can be written:

$$\rho_0 = \frac{\hbar}{2}\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} = S_z$$

To simplify the calculations even further, can be removed from the expression using the following representation of angular momentum operators: Thus, ρ_o is equal to the matrix I_z.

$$I_x = \frac{S_x}{\hbar} = \frac{1}{2}\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \quad I_y = \frac{S_y}{\hbar} = \frac{1}{2}\begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} \quad I_z = \frac{S_z}{\hbar} = \frac{1}{2}\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \quad (6.30)$$