As an example of a density matrix, we can apply it to an ensemble of spin $\frac{1}{2}$ particles. The density matrix is defined as

$$\rho \equiv \sum_i p_i |i\rangle \langle i|$$

where $p_i$ is the probability of a single system being state $|i\rangle$. For a spin $\frac{1}{2}$ particle, there are only 2 states, so the density matrix can be written as a $2 \times 2$ matrix, once we define a basis for the states (for example, the basis of $S_z$ states where $S_z = \pm \frac{\hbar}{2}$). Since any $2 \times 2$ matrix can be written as a linear combination of the Pauli matrices and the identity matrix, the density matrix can be written as

$$\rho = a_0 I + A \cdot \sigma$$

Since the trace of each of the Pauli matrices is zero, and $\text{Tr} I = 2$, we have

$$\text{Tr} \rho = 2a_0$$

However, we know that $\text{Tr} \rho = 1$, so we must have $a_0 = \frac{1}{2}$, so we can write

$$\rho = \frac{1}{2} (I + a \cdot \sigma)$$

for some vector $a$ whose elements are complex numbers.

To find the average value $\langle \hat{\Omega} \rangle$ of an observable $\Omega$ in an ensemble, we can use the density matrix in the form

$$\langle \hat{\Omega} \rangle = \text{Tr} (\Omega \rho)$$

To find $\langle \sigma_x \rangle$, we can work out each component separately. For $\sigma_x$ we have, using the properties of the $\sigma_i$:  

\begin{align*}
\langle \bar{\sigma}_x \rangle &= \text{Tr} (\sigma_x \rho) \\
&= \frac{1}{2} \text{Tr} (\sigma_x I + a_x \sigma_x^2 + a_y \sigma_x \sigma_y + a_z \sigma_x \sigma_z) \\
&= \frac{1}{2} \text{Tr} (\sigma_x + a_x \sigma_x + ia_y \sigma_z - ia_z \sigma_y) \\
&= \frac{1}{2} (0 + 2a_x + 0 + 0) \\
&= a_x \tag{7}
\end{align*}

We can do similar calculations to get the other two components, with the result

\begin{equation}
\langle \bar{\sigma} \rangle = a \tag{11}
\end{equation}

Finally, suppose we have an ensemble of electrons in a constant magnetic field \( \mathbf{B} = B\hat{z} \), and that this ensemble is in thermal equilibrium at temperature \( T \). A central result of statistical mechanics (which we haven’t covered yet) is that particles in thermal equilibrium obey the Boltzmann distribution, which states that the probability of finding a particle with energy \( E \) in the ensemble is

\begin{equation}
p_E \propto e^{-E/kT} \tag{12}
\end{equation}

where \( k \) is the Boltzmann constant. In this case, the energy is that of a magnetic moment \( \mu \) in a constant magnetic field \( \mathbf{B} \), which is

\begin{equation}
H = -\mu \cdot \mathbf{B} = -\gamma \mathbf{S} \cdot \mathbf{B} = -\gamma S_z B \tag{13}
\end{equation}

There are only two states \( (S_z = \pm \frac{1}{2}) \), so the probabilities are

\begin{align*}
p_\uparrow &= \frac{1}{P} e^{\gamma B h/2kT} \tag{14} \\
p_\downarrow &= \frac{1}{P} e^{-\gamma B h/2kT} \tag{15} \\
P &= e^{\gamma B h/2kT} + e^{-\gamma B h/2kT} \tag{16}
\end{align*}

The density matrix is therefore

\begin{equation}
\rho = \frac{1}{P} \left( e^{\gamma B h/2kT} |\uparrow\rangle \langle \uparrow | + e^{-\gamma B h/2kT} |\downarrow\rangle \langle \downarrow | \right) \tag{17}
\end{equation}

In the \( S_z \) basis, this is
\[
\rho = \frac{1}{P} \begin{bmatrix} e^{\gamma B h/2kT} & 0 \\ 0 & e^{-\gamma B h/2kT} \end{bmatrix}
\]  

(18)

We can work out the average magnetic moment for the ensemble as

\[
\langle \vec{\mu} \rangle = \text{Tr}(\vec{\mu} \rho)
\]

(19)

\[
= \frac{\hat{\vec{z}}}{P} \left[ \frac{\gamma \hbar}{2} e^{\gamma B h/2kT} - \frac{\gamma \hbar}{2} e^{-\gamma B h/2kT} \right]
\]

(20)

\[
= \frac{\gamma \hbar}{e^{\gamma B h/2kT} + e^{-\gamma B h/2kT}} \frac{\gamma \hbar}{2} \hat{\vec{z}}
\]

(21)

\[
= \frac{\gamma \hbar}{2} \text{tanh} \left( \frac{\gamma B h}{2kT} \right) \hat{\vec{z}}
\]

(22)

\[
= -\frac{e \hbar}{2mc} \text{tanh} \left( -\frac{e B h}{2mckT} \right) \hat{\vec{z}}
\]

(23)

\[
= \frac{e \hbar}{2mc} \text{tanh} \left( \frac{e B h}{2mckT} \right) \hat{\vec{z}}
\]

(24)