Quantum Statistical Mechanics

Final topic in the course: can we derive a master equation for a quantum mechanical system, thereby importing the mathematical tools developed over the course into the quantum domain.

Prototypical system: qubit

\[ |1\rangle, |0\rangle \] eigenstates of \[ \hat{H} \] a Hamiltonian with energies \[ E_0, E_1 \]
Analogue of the classical ensemble $p_n(t)$: a quantum ensemble described by a density operator $\hat{\rho}(t) = \sum_n p_n |\psi_n\rangle\langle\psi_n|$

$p_n =$ fraction of the ensemble in state $|\psi_n\rangle$ at time $t$

$\{ |\psi_n\rangle \}$ set does not have to be a complete basis set, or orthogonal to each other.

However $\langle\psi_n | \psi_n\rangle = 1$ for each $n$

Example: $\hat{\rho} = \sum_i |i\rangle\langle i|$

i) $\hat{\rho} = |\psi_1\rangle\langle\psi_1|$, where $|\psi_1\rangle = \frac{1}{\sqrt{2}} (10\rangle + 11\rangle)$

[pure state: $p_n = 1$ for some $n$, all others zero]

ii) $\hat{\rho} = \frac{1}{4} |\psi_1\rangle\langle\psi_1| + \frac{3}{4} |\psi_2\rangle\langle\psi_2|$

[mixed state: $p_n < 1$ for all $n$]

$\hat{\rho}$ can be written as a matrix in some orthonormal basis, i.e. $\{10\rangle, 11\rangle\}$:

$p_{ij} = \langle i| \hat{\rho} |j\rangle \Rightarrow$

i) $\rho = \begin{pmatrix}
0 & \frac{1}{2} \\
\frac{1}{2} & \frac{1}{2}
\end{pmatrix}$

ii) $\rho = \begin{pmatrix}
0 & \frac{1}{8} \\
\frac{1}{8} & \frac{7}{8}
\end{pmatrix}$
If that basis is the set of e-vectors of an observable like $\hat{A}$, we can use it to calculate mean measured value of $\hat{A}$ in ensemble:

$$\langle H \rangle = \text{tr} (\hat{\rho} \hat{H})$$

$$= \sum_i \langle i | \hat{\rho} \hat{A} | i \rangle$$

$$= \sum_i E_i \frac{\langle i | \hat{\rho} | i \rangle}{\rho_{ii}}$$

$$= \sum_{i,n} E_i \ p_n \ |\langle i | \psi_n \rangle|^2$$

\[\text{prob. of measuring } E_i \text{ in state } |\psi_n \rangle\]

\[\text{prob. of state } |\psi_n \rangle \]

\[\text{two contributions to probability}\]

$$\rho_{ii} = \sum_n p_n |\langle i | \psi_n \rangle|^2 \geq 0 \text{ in any basis}$$

$$= \text{total prob. to observe } E_i \text{ in ensemble}$$

$$\sum_i \rho_{ii} = \text{tr}(\hat{\rho}) = \sum_{n,i} p_n \langle \psi_n | i \rangle \langle i | \psi_n \rangle$$

$$= \sum_n p_n = 1$$

Compare:

$$\bar{E} = \sum_n p_n E_n \Rightarrow \langle H \rangle = \sum_i \rho_{ii} E_i$$

Strange quirk of quantum ensembles:
There are usually many ensembles which give you the same \( \hat{\rho} \):

\[
\hat{\rho} = p |0\rangle \langle 0| + (1-p) |1\rangle \langle 1|
\]

\[
= \frac{1}{2} \left( |u\rangle \langle u| + \frac{1}{2} |v\rangle \langle v| \right)
\]

where \( |u\rangle = \sqrt{p} |0\rangle + \sqrt{1-p} |1\rangle \)

\( |v\rangle = \sqrt{p} |0\rangle - \sqrt{1-p} |1\rangle \)

We call these different decompositions of \( \hat{\rho} \): they are impossible to physically distinguish, b/c each will give same results for all experimental averages, i.e. \( \langle H \rangle = \text{tr}(\hat{\rho} \hat{H}) \).

Thus the operator \( \hat{\rho} \) is the true fundamental description of the ensemble, not the values \( \{ p_n \} \) in a particular decomposition

\[
\hat{\rho} = \sum_n p_n |\psi_n\rangle \langle \psi_n|
\]

which are generally not unique.

However \( p_{ii} = \langle i | \hat{\rho} | i \rangle \) is unique, and plays the analogue of classical probability.

Time evolution:

I. Isolated system with time-indep. Hamiltonian \( \hat{H} \)

\[
t = 0: \quad \hat{\rho}(0) = \sum_n p_n |\psi_n\rangle \langle \psi_n|
\]

Later time: \( t > 0 \)

\[
|\psi_n\rangle \rightarrow e^{-i\hat{H}t/\hbar} |\psi_n\rangle = \hat{U}(t) |\psi_n\rangle
\]

where \( \hat{U}^\dagger \hat{U} = \hat{I} \) (\( \hat{U} \) is unitary)
\[ \hat{\rho}(t) = \sum_n p_n \hat{U}(t) |\psi_n\rangle \langle \psi_n| \hat{U}^+(t) \]

\[ = \hat{U}(t) \hat{\rho}(0) \hat{U}^+(t) \]

II. Isolated system w/ time-dep. \( \hat{A}(t) \):

- Same form since \( |\psi_n\rangle \Rightarrow \hat{U}(t) |\psi_n\rangle \)
  
  with \( \hat{U}(t) \) more complicated (but still unitary)

so:

\[ \hat{\rho}(t) = \hat{U}(t) \hat{\rho}(0) \hat{U}^+(t) \]

Since \( i\hbar \frac{\partial}{\partial t} |\psi_n(t)\rangle = \hat{A}(t) |\psi_n(t)\rangle \)

\[ \Rightarrow i\hbar \frac{\partial}{\partial t} \hat{U}(t) |\psi_n\rangle = \hat{A}(t) \hat{U}(t) |\psi_n\rangle \]

\[ \Rightarrow i\hbar \frac{\partial}{\partial t} \hat{U}(t) = \hat{A}(t) \hat{U}(t) \quad \text{or} \quad i\hbar \frac{\partial}{\partial t} \hat{U}^+(t) = \hat{U}^+ \hat{A} \quad \text{since} \quad \hat{A}^+ = \hat{A} \]

\[ \Rightarrow \frac{\partial}{\partial t} \hat{\rho}(t) = \frac{\partial}{\partial t} \hat{\rho}(0) \hat{U}^+ + \hat{U} \hat{\rho}(0) \frac{\partial}{\partial t} \hat{U}^+ \]

\[ = \hat{A} \hat{\rho} - \hat{\rho} \hat{A} = [\hat{A}(t), \hat{\rho}(t)] \cdot \frac{1}{i\hbar} \]

Von Neumann or "quantum Liouville" equation
When $\hat{H}(t) = \hat{H}$ constant + we choose $|i\rangle$ as e-vecs of $\hat{H}$

\[ \frac{d}{dt} \langle i | \hat{\rho} | i \rangle = \frac{i}{\hbar} \langle i | [\hat{H}, \hat{\rho}] | i \rangle = (E_i - E_i) \frac{\langle i | \hat{\rho} | i \rangle}{\hbar} \]

\[ \frac{dp_{ii}}{dt} = 0 \quad \text{very boring master equation (stationary state)} \]

III. System interacting w/ environment (open QM)

General theory beyond our scope, but there is one example known from elementary QM:
measuring an observable (for example $\hat{H}$) which by necessity requires interaction w/ outside "probe"

before measurement:

\[ \hat{\rho} = \sum_n p_n |\psi_n\rangle \langle \psi_n| \]

after measurement:

\[ \hat{\rho}' = \sum_n p_n |\psi_n\rangle \langle \psi_n| \]

\[ = \frac{\langle 0 | \hat{\rho} | 0 \rangle}{1} \quad \text{prob. of finding in ensemble} \]

\[ + \sum_n p_n |\langle 1 | \psi_n\rangle|^2 \]

\[ = \sum_{i=0}^{1} \langle i | \hat{\rho} | i \rangle \langle i | \rangle \]

\[ \Rightarrow \hat{\rho}' = \sum_{i=0}^{1} |i\rangle \langle i| \hat{\rho} |i\rangle \langle i| \]
call \( P_i \equiv |i\rangle \langle i| \) projection operator

\[ P_i^+ = P_i \]

\[ \hat{\rho}' = \frac{1}{\sum_i \hat{P}_i \hat{P}_i^+} \sum_i \hat{P}_i \hat{\rho} \hat{P}_i^+ \quad \text{note: } \sum_i \hat{P}_i \hat{P}_i^+ = 1 \]

What about an "imperfect" measuring error apparatus, that yields state \(|11\rangle\) w/ prob. \(\epsilon_{10}\) when should have collapsed to \(|10\rangle\), and yields \(|10\rangle\) w/ prob. \(\epsilon_{01}\) when should have collapsed to \(|11\rangle\).

\[ \hat{\rho}' = |10\rangle \langle 01| \langle 01| \hat{\rho} |10\rangle \langle 10| (1 - \epsilon_{10}) \]

\[ + |11\rangle \langle 11| \langle 01| \hat{\rho} |10\rangle \langle 10| \epsilon_{10} \]

\[ + |11\rangle \langle 11| \langle 11| \hat{\rho} |11\rangle \langle 11| (1 - \epsilon_{01}) \]

\[ + |10\rangle \langle 01| \langle 11| \hat{\rho} |11\rangle \langle 11| \epsilon_{01} \]

\[ = \sum_{k=1}^{4} \hat{M}_k \hat{\rho} \hat{M}_k^+ \quad \text{where} \quad \hat{M}_1 = \sqrt{1 - \epsilon_{10}} |10\rangle \langle 01| \]

\[ \hat{M}_2 = \sqrt{\epsilon_{10}} |11\rangle \langle 01| \]

\[ \hat{M}_3 = \sqrt{1 - \epsilon_{01}} |11\rangle \langle 11| \]

\[ \hat{M}_4 = \sqrt{\epsilon_{01}} |10\rangle \langle 11| \]

\[ \sum_i \hat{M}_i^+ \hat{M}_i = 1 \]

Most general physically reasonable mapping of \(\hat{\rho} \rightarrow \hat{\rho}'\) where \(\hat{\rho}\) and \(\hat{\rho}'\) are density operators can be expressed in this form:

\[ \hat{\rho}' = \sum_k \hat{M}_k^+ \hat{\rho} \hat{M}_k^+ \quad \text{with} \quad \sum_k \hat{M}_k^+ \hat{M}_k = 1 \]

[Krns representation theorem]
Imagine our qubit interacting with imperfect apparatus measuring \( \hat{H} \) over time interval \( \Delta t \):
\[
\hat{\rho}(t + \Delta t) = \sum_{k=1}^{4} \hat{M}_k \hat{\rho}(t) \hat{M}_k^\dagger
\]

In the \( |10\rangle, |11\rangle \) basis:

\[
\begin{pmatrix}
\rho_{00}(t + \Delta t) & \rho_{01}(t + \Delta t) \\
\rho_{10}(t + \Delta t) & \rho_{11}(t + \Delta t)
\end{pmatrix} =
\begin{pmatrix}
\rho_{00}(t) - \varepsilon_{10} \rho_{00}(t) + \varepsilon_{01} \rho_{11}(t) \\
0
\end{pmatrix}
\]

Note equation for \( 0,0 \) component

\[
\Rightarrow \quad \frac{\rho_{00}(t + \Delta t) - \rho_{00}(t)}{\Delta t} = \frac{\varepsilon_{01}}{\Delta t} \rho_{11}(t) - \frac{\varepsilon_{10}}{\Delta t} \rho_{00}(t)
\]

\[\varepsilon_{01} \equiv W_{01}, \quad \varepsilon_{10} \equiv W_{10}\]

\[
\frac{\partial \rho_{00}}{\partial t} = W_{01} \rho_{10}(t) - W_{10} \rho_{00}(t)
\]

\( \Rightarrow \) a classical master equation for diagonal matrix elements

\[\text{note: } \rho_{10}(t + \Delta t) = 0 \Rightarrow \text{off-diagonal elements of } \hat{\rho} \text{ go to zero ("decoherence")}\]

Though this is one specific example, the general trend holds: environmental interactions impose a "special basis" where off-diag. elements of \( \hat{\rho} \) go to zero, & diag. elements obey classical master equation.
Because $W_{01}$, $W_{10}$ involve energy exchange w/ environment, satisfy detailed balance:

$$\frac{W_{10}}{W_{01}} = e^{-\beta(E_1 - E_0)}$$

and hence stat. state in equilibrium means

$$\rho_{ii} = \frac{e^{-\beta E_i}}{Z}$$

⇒ starting point of quantum stat. mech i.e. all definitions work w/ $\rho_n$ replaced by $\rho_{ii}$, for example:

entropy $S(t) = -k_B \sum_i \rho_{ii} \ln \rho_{ii}$