Quantum Ensemble Dynamics

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October 18, 2019

Previously on CHM676...

System State: Abstract "vector" in Hilbert space

$$(x, p) \rightarrow |\psi\rangle = \begin{bmatrix} a_1 \\ a_2 \\ \vdots \end{bmatrix}$$

Physical "Observables": Hermitian operators

$$x, p, E, ... \rightarrow \hat{x}, \hat{p}, \hat{E} \sim \begin{bmatrix} A_{11} & A_{12} & ... \\ A_{21} & A_{22} & ... \\ \vdots & \vdots & \ddots \end{bmatrix}$$

Previously on CHM676...

Fourth Postulate: *In any experimental measurement of an observable a corresponding to Hermitian operator $\hat{A}$ with a purely discrete spectrum, the probability of obtaining the value λ is given by*

$$P(a == \lambda) = |\langle \phi_\lambda | \psi \rangle|^2$$

where ϕ_λ is the eigenvector corresponding to λ.

$$\begin{aligned} \langle a \rangle &= \sum_n \lambda_n P(a == \lambda_n) \\ &= \sum_n \langle \psi | \phi_n \rangle \lambda_n \langle \phi_n | \psi \rangle \\ &= \left\langle \psi \middle| \hat{A} \middle| \psi \right\rangle . \end{aligned}$$

Today: Observable dynamics in quantum ensembles.

Quantum Ensembles: The Density Matrix

Quantum Ensembles

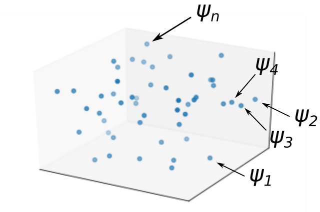
Two sources of uncertainty in quantum measurements:

Classical Uncertainty: What is the probability that the system has a given quantum state?

Quantum Uncertainty: What is the probability that a given quantum state will result in a given measured value?

Average values $\langle A \rangle$ incorporate both sources:

$$\langle A \rangle = \frac{1}{N} \sum_{n=1}^{N} \langle \psi_n | \hat{A} | \psi_n \rangle$$



The Density Matrix

Average values can be written more concisely

$$
\begin{aligned}
\langle A \rangle &= \frac{1}{N} \sum_{n=1}^{N} \langle \psi_n | \hat{A} | \psi_n \rangle \\
&= \frac{1}{N} \sum_{n=1}^{N} \sum_{j} \langle \psi_n | k \rangle \langle k | \hat{A} | \psi_n \rangle \\
&= \sum_{k} \langle k | \hat{A} \left(\frac{1}{N} \sum_{n=1}^{N} | \psi_n \rangle \langle \psi_n | \right) | k \rangle \\
&= \mathsf{Tr}\{\hat{A}\hat{\rho}\},
\end{aligned}
$$

in terms of the **density matrix** and the **trace**

$$\hat{\rho} \equiv \frac{1}{N} \sum_{n=1}^{N} | \psi_n \rangle \langle \psi_n |$$

$$\mathsf{Tr}\{\ldots\} \equiv \sum_{k} \langle k | \ldots | k \rangle .$$

What does the density matrix mean?

For any given Hermitian operator $\hat{A}$, there is always a basis of vectors $|n\rangle$ in which $\hat{A}$ is diagonal:

$$\hat{A} = \begin{bmatrix} A_{11} & 0 & \dots \\ 0 & A_{22} & \dots \\ \vdots & \vdots & \ddots \end{bmatrix}.$$

In this basis, the *diagonal elements* of $\hat{\rho}$ determines the statistics of $\hat{A}$ just like a classical probability distribution:

$$\begin{aligned} \langle A \rangle &= \mathrm{Tr}\{\hat{A}\hat{\rho}\} \\ &= \sum_n \left\langle n \middle| \hat{A}\hat{\rho} \middle| n \right\rangle \\ &= \sum_n A_{nn}\rho_{nn} \end{aligned}$$

However: It is **not** always possible to find a basis in which two *different* operators are *both* diagonal! $\Rightarrow$ Quantum uncertainty: $\sigma_x \sigma_p \geq \frac{\hbar}{2}$

Take-Home Points

Two sources of uncertainty in quantum systems:

- Statistical (classical) uncertainty: What is the state of the system?
- Quantum uncertainty: Given the state, what will be the measurement outcome?

The **density matrix** $\hat{\rho}$ is a quantum operator that **represents the system state**

$\hat{\rho}$ captures **both quantum and classical uncertainty** in measurements: $\langle A \rangle = \text{Tr}\{\hat{A}\hat{\rho}\}$.

The **trace** of an operator is the sum of its diagonal elements.

Quantum Ensemble Dynamics

Dynamics of Quantum Ensembles

How does $\hat{\rho}$ change with time?

$$\begin{aligned}
\frac{d\hat{\rho}}{dt} &= \frac{1}{N}\sum_{n=1}^{N}\frac{d}{dt}\left|\psi_n\right\rangle\left\langle\psi_n\right| \\
&= \frac{1}{N}\sum_{n=1}^{N}\left[\left(\frac{d}{dt}\left|\psi_n\right\rangle\right)\left\langle\psi_n\right| + \left|\psi_n\right\rangle\left(\frac{d}{dt}\left\langle\psi_n\right|\right)\right] \\
&= \frac{1}{N}\sum_{n=1}^{N}\left[\frac{1}{i\hbar}\hat{H}\left|\psi_n\right\rangle\left\langle\psi_n\right| - \frac{1}{i\hbar}\left|\psi_n\right\rangle\left\langle\psi_n\right|\hat{H}\right] \\
&= -\frac{i}{\hbar}\left(\hat{H}\hat{\rho} - \hat{\rho}\hat{H}\right) \equiv -\frac{i}{\hbar}\left[\hat{H},\hat{\rho}\right].
\end{aligned}$$

The Quantum Liouville Equation

The result is the quantum **Liouville Equation:**

$$i\hbar \frac{d}{dt}\hat{\rho} = \left[\hat{H}, \hat{\rho}\right].$$

This is the **quantum ensemble** equivalent of the Schrödinger equation. Compare:

Pure State:

$$i\hbar \frac{d\psi}{dt} = \hat{H}\psi$$

Mixed state (ensemble):

$$i\hbar \frac{d\rho}{dt} = \left[\hat{H}, \rho\right].$$

Big Idea: The *Hamiltonian commutator* $[\hat{H}, \quad]$ is to the *density matrix* what the the bare *Hamiltonian* is to the *wavefunction*!

Static Hamiltonian: Eigenbasis Solution

If the Hamiltonian is static in time: Let $\{|m\rangle\}$ be the eigenvector basis for $\hat{H}$.

$$\hat{\rho} = \sum_{m,n} |m\rangle \langle m |\hat{\rho}| n\rangle \langle n| = \sum_{m,n} \rho_{mn} |m\rangle \langle n| .$$

Applying the Liouville equation:

$$\frac{d\rho_{mn}}{dt} = \left\langle m \left| \frac{d\hat{\rho}}{dt} \right| n \right\rangle = \frac{1}{i\hbar} \left\langle m \left| \left(\hat{H}\hat{\rho} - \hat{\rho}\hat{H} \right) \right| n \right\rangle$$
$$= \frac{\varepsilon_m - \varepsilon_n}{i\hbar} \rho_{mn}.$$

The solution is:

$$\rho_{mn}(t) = e^{-i\omega_{mn} t} \rho_{mn}(0)$$

where

$$\omega_{mn} = \frac{\varepsilon_m - \varepsilon_n}{\hbar}.$$

Take-Home Points

The density matrix evolves under the **Quantum Liouville Equation:**

$$i\hbar \frac{d\hat{\rho}}{dt} = \left[\hat{H}, \hat{\rho}\right].$$

The **Liouville equation** is the mixed-state (ensemble) equivalent of the Schrödinger equation.

In the eigenbasis of a static Hamiltonian:

- **Populations:** Diagonal elements ρ_{nn} are static
- **Coherences:** Off-diagonal elements ρ_{mn} oscillate in time with frequency $\omega_{mn} = \frac{\varepsilon_m - \varepsilon_n}{\hbar}$.