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Quantum Statistical Mechanics

Describe the state of a system ~~to~~ at a given time t by a vector $|\psi(t)\rangle$ in a Hilbert space & not as a point in the phase space.

Observable $F \leftrightarrow$ operator \hat{F} acting on states in the Hilbert space

Expectation value of F
 $\langle F \rangle(t) = \langle \psi(t) | \hat{F} | \psi(t) \rangle$

We'll assume $|\psi(t)\rangle$ is normalised

↳ normalised

Macroscopic observables

are those whose expectation values become time independent if we wait long enough for the system to come to equilibrium.

$\langle F \rangle = \frac{1}{K} \sum_{i=1}^K \langle \psi(t_i) | \hat{F} | \psi(t_i) \rangle$ when the system is in equilibrium

We are not proving the system reaches eqm. it is observed that if we wait long enough

F may be having an intrinsic time dependence - for e.g.
 $F = e^{\gamma} q^2 + e^{-\gamma} p^2$
→ in Schr. picture

Prepare identical system - Measure $\langle \psi | \hat{F} | \psi \rangle$ for diff. systems at diff. time - Can't think that you ^{first} measure & then let the same system evolve - violates ψ -mech -

identical copies with same initial state

⇒ Quantum Statistical ensemble
 = collection of states $\{ |\psi(x_i)\rangle, i=1, \dots, K \}$

General definition of quantum statistical ensemble :-

→ A collection of states $\{ |\psi(x_i)\rangle, i=1, \dots, K \}$
 with weight factors w_i . ↘ not necessarily orthogonal to each other

Ensemble average of an observable \hat{F} is

$$\bar{F} = \frac{\sum_{i=1}^K w_i \langle \psi(x_i) | \hat{F} | \psi(x_i) \rangle}{\sum_{i=1}^K w_i}$$

Microcanonical ~~ensemble~~ ensemble

consider a basis of energy eigenstates:

$$|n\rangle$$

$$\hat{H} |n\rangle = E_n |n\rangle$$

Microcanonical ensemble:

$$\{ |n\rangle, n=1, 2, \dots, \infty \text{ with}$$

$$w_n = 1 \quad \text{if } E \leq E_n \leq E + \Delta E$$

$$= 0 \quad \text{if } E_n > E + \Delta E \text{ or } < E$$

On order that \bar{F} describes something physical, you must average over infinite no. of time slices

Why do q. stat. mech works?
 ↓
 because there are energy e. states for which $\langle \psi | \hat{F} | \psi \rangle$ doesn't change at all

Why does quantum stat. mech. work?

If $|\psi(t)\rangle$ is energy eigenstate then

$$|\psi(t)\rangle = e^{-iEt/\hbar} |\psi(t=0)\rangle$$

$$\langle \hat{F} \rangle(t) = \langle \psi(0) | \hat{F} | \psi(0) \rangle \rightarrow \text{time independent}$$

