23/1/06

Quantum Statistical Mechanics

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

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

Expectation value of F

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

normalised

We'll assume $|\psi(t)\rangle$ is 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. $F = e^{t} q^2 + e^{-t} p^2$ $\rightarrow$ 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 Q. Mech.

identical copies with same initial state

→ Quantum statistical ensemble
= Collection of states $\{|\psi(t_i)\rangle, i=1,\dots,K\}$

General definition of quantum statistical ensemble :-

→ A collection of states $\{|\psi(t_i)\rangle, i=1,\dots,K\}$ with weight factors ω_i.

not necessarily orthogonal to each other

Ensemble average of an ~~observable~~ $\hat{F}$ is

$$\bar{F} = \sum_{i=1}^{K} \omega_i \langle \psi_{(i)} | \hat{F} | \psi_{(i)} \rangle \Big/ \sum_{i=1}^{K} \omega_i$$

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

Microcanonical ~~ensble~~ ensemble

Consider a basis of energy eigenstates:

$|n\rangle$

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

Microcanonical ensemble:

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

$$\omega_n = 1 \quad \text{if } E \le E_n \le E+\delta E$$
$$= 0 \quad \text{if } E_n > E+\Delta E \text{ or } < E$$

Why do q. stat. mech works?

bcs there are energy e. states for which $\langle\psi|F|\psi\rangle$ doesn't change at all

Why does quantum stat. mech. work?

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

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

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