Pure and mixed states. Density matrix.

$|\psi\rangle$ - state of a system A - observable (self-adjoint op.)

Exp. value of A in $|\psi\rangle$: $\langle A\rangle = \langle\psi|A|\psi\rangle$

Observe that if we define $\varrho = |\psi\rangle\langle\psi|$, then $\langle A\rangle = \mathrm{Tr}(\varrho A)$

(where $\mathrm{Tr}X = \sum_n \langle n|X|n\rangle$,

$\{|n\rangle\}$ - orthonormal basis

$$\mathrm{Tr}(\varrho A) = \sum_n \langle n|\psi\rangle\langle\psi|A|n\rangle = \langle\psi|A\underbrace{\sum_n |n\rangle\langle n|}_{1}\psi\rangle = \langle\psi|A|\psi\rangle = \langle A\rangle$$

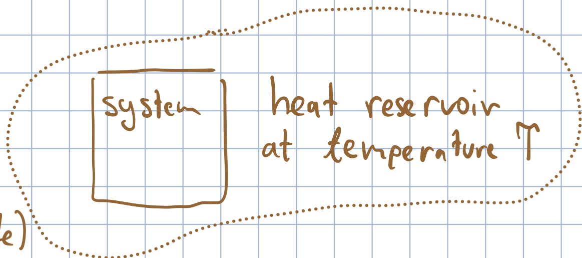
It often happens that we do not have full information about the system state.
We only have an ensemble of states $\{|\psi_i\rangle\}$ with probabilities p_i.

Assume: $\{|\psi_i\rangle\}$ - orthonormal basis, $\sum_i p_i = 1$ Then: $\langle A\rangle = \sum_i p_i \langle\psi_i|A|\psi_i\rangle$

If $p_i \neq \delta_{i,i_0}$ we say the system is in a mixed state.

Example:

(canonical ensemble)

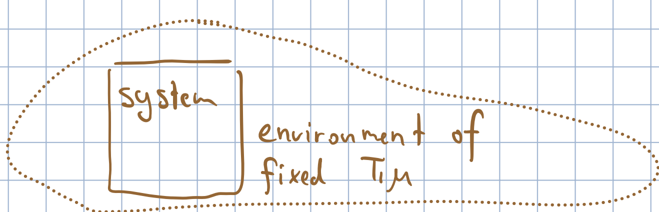


fixed (T, V, N)

$H|\psi_i\rangle = E_i|\psi_i\rangle \rightarrow p_i \sim e^{-\frac{E_i}{k_B T}}$

Example:

(grand canonical ensemble)



fixed (T, V, μ) $p_i \sim e^{-\frac{E_i - \mu N_i}{k_B T}}$

p_i - probability of finding a state of energy E_i and particle number N_i

Define $\varrho := \sum_i p_i |\psi_i\rangle\langle\psi_i|$ - density matrix

$\langle A\rangle = \mathrm{Tr}(\varrho A)$ $\left\{ \text{Because } \mathrm{Tr}(\varrho A) = \sum_n \sum_i \langle n|p_i|\psi_i\rangle\langle\psi_i|A|n\rangle = \sum_i \langle\psi_i|A\sum_n |n\rangle\langle n|\psi_i\rangle p_i = \sum_i p_i\langle\psi_i|A|\psi_i\rangle = \langle A\rangle \right\}$

$\varrho^\dagger = \varrho$, $\mathrm{Tr}\,\varrho = 1$ $\left\{ \sum_n\sum_i \langle n|p_i|\psi_i\rangle\langle\psi_i|n\rangle = \sum_i \langle\psi_i|\psi_i\rangle p_i = \sum_i p_i = 1. \right.$

Evolution of ϱ:

$$i\hbar\,\partial_t|\psi\rangle = H|\psi\rangle \qquad -i\hbar\,\partial_t\langle\psi| = \langle\psi|H$$

$$i\hbar\,\partial_t\varrho = i\hbar\sum_i p_i\left(|\dot\psi_i\rangle\langle\psi_i| + |\psi_i\rangle\langle\dot\psi_i|\right) = \sum_i p_i\left(H|\psi_i\rangle\langle\psi_i| - |\psi_i\rangle\langle\psi_i|H\right)$$

$$\underline{\partial_t\varrho = -\frac{i}{\hbar}[H,\varrho]} \qquad \text{(von Neumann eq.)}$$

(not to be confused with the evolution eq. for operators in the Heisenberg representation $\dot A(t) = \frac{i}{\hbar}[H, A(t)] + (\partial_t A)(t)$)

Linear response theory

External perturbation $\longrightarrow$ system's reaction
(time-dep. external field) (Response functions)

Linear response theory: response functions $\longrightarrow$ retarded Green's functions
(from equilibrium properties)

$H = H_0 + V_t$ $\rightarrow$ perturbation describing the interaction of the system with an external field
(sufficiently weak and slowly varying as function of t)

H_0: time indep., describes the system when the perturbation is inactive.

Assume that V_t can be written as

$V_t = B f_t$

f_t: scalar function of time.

B: op. describing an observable of the system

A - an observable (does not depend on time).

If V_t is off – equilibrium situation

$$\langle A \rangle = \langle A \rangle_0 = Tr(\varrho_0 A)$$

with (for example) $\varrho_0 = \dfrac{e^{-\frac{H_0}{k_B T}}}{Tr\, e^{-\beta H_0}}$

Upon switching V_t on $\varrho_0 \longrightarrow \varrho_t$ $\langle A \rangle_t = Tr(\varrho_t A)$

ϱ_t is given by $i\hbar \dot{\varrho}_t = [H, \varrho_t] = [H_0, \varrho_t] + (V_t, \varrho_t]$ $\lim_{t \to -\infty} \varrho_t = \varrho_0$

Use interaction rep. $\hat{\varrho}_t = e^{\frac{iH_0 t}{\hbar}} \varrho_t e^{-\frac{iH_0 t}{\hbar}}$ ⊛ ϱ_t

What is the time evolution of $\hat{\varrho}_t$

Recall $i\hbar \partial_t |\hat{\psi}(t)\rangle = \hat{V}(t) |\hat{\psi}(t)\rangle$

Take derivative of ⊛ + simple transformations (homework)

$$\dot{\hat{\varrho}}_t = \frac{i}{\hbar}[\hat{\varrho}_t, \hat{V}_t]$$

$$\dot{\hat{\varrho}}_t = \frac{i}{\hbar}[\hat{\varrho}_t, \hat{V}_t] \Big/ \xrightarrow{\text{integrate}} \int_{-\infty}^{t} dt'$$

$$\hat{\varrho}_t = \varrho_0 + \frac{i}{\hbar}\int_{-\infty}^{t} dt' [\hat{\varrho}_{t'}, \hat{V}_{t'}] = \varrho_0 - \frac{i}{\hbar}\int_{-\infty}^{t} dt' [\hat{V}_{t'}, \hat{\varrho}_{t'}]$$

Iterate this...

$$\hat{\varrho}_t = \varrho_0 - \frac{i}{\hbar}\int_{-\infty}^{t} dt_1 [\hat{V}_{t_1}, \varrho_0] + \left(\frac{-i}{\hbar}\right)^2 \int_{-\infty}^{t} dt_1 \int_{-\infty}^{t_1} dt_2 [\hat{V}_{t_1}, [\hat{V}_{t_2}, \varrho_0]] + \ldots =$$

$$= \varrho_0 + \sum_{i=1}^{\infty} \left(\frac{-i}{\hbar}\right)^n \int_{-\infty}^{t} dt_1 \int_{-\infty}^{t_1} dt_2 \ldots \int_{-\infty}^{t_{n-1}} dt_n \left[\hat{V}_{t_1}, [\hat{V}_{t_2}, [\hat{V}_{t_3} \ldots [V_{t_n}, \varrho_0] \ldots \right]\right]$$

In linear response theory we truncate at terms linear in $\hat{V}$.

In Schrödinger picture we obtain:

$$\varrho_t \simeq \varrho_0 - \frac{i}{\hbar}\int_{-\infty}^{t} dt_1\, e^{-i\frac{H_0 t}{\hbar}}\left[\hat{V}_{t_1}, \hat{\varrho}_0\right] e^{i\frac{H_0 t}{\hbar}}$$

$$\langle A\rangle_t = \mathrm{Tr}(\varrho_t A) \simeq \langle A\rangle_0 - \frac{i}{\hbar}\int_{-\infty}^{t} dt_1\, \mathrm{Tr}\left\{e^{-i\frac{H_0 t}{\hbar}}\left[\hat{V}_{t_1}, \varrho_0\right] e^{i\frac{H_0 t}{\hbar}} A\right\}$$

$$V_t = B f_t$$

$$\mathrm{Tr}(ABC) = \mathrm{Tr}(CAB)$$

$$\langle A\rangle_t \simeq \langle A\rangle_0 - \frac{i}{\hbar}\int_{-\infty}^{t} dt_1\, f_{t_1}\, \mathrm{Tr}\left\{e^{-\frac{iH_0 t}{\hbar}}\left[\hat{B}_{t_1}, \varrho_0\right] e^{\frac{iH_0 t}{\hbar}} A\right\} =$$

$$= \langle A\rangle_0 - \frac{i}{\hbar}\int_{-\infty}^{t} dt_1\, f_{t_1}\, \mathrm{Tr}\left\{\left[\hat{B}_{t_1}, \varrho_0\right]\hat{A}_t\right\} = \circledast$$

$$= \left\{ \mathrm{Tr}\{\ldots\} = \mathrm{Tr}\{B\varrho_0 A - \varrho_0 BA\} = \mathrm{Tr}\{\varrho_0 AB - \varrho_0 BA\} = \mathrm{Tr}\{\varrho_0 [A, B]\} \right\} =$$

$$\circledast \cdot \langle A\rangle_0 - \frac{i}{\hbar}\int_{-\infty}^{t} dt_1\, f_{t_1}\, \mathrm{Tr}\left\{\varrho_0\left[\hat{A}_t, \hat{B}_{t_1}\right]\right\}$$

$$\left\{ \mathrm{Tr}\{\varrho_0 C\} = \langle C\rangle_0 \right\}$$

$$\Delta A_t = \langle A\rangle_t - \langle A\rangle_0 = -\frac{i}{\hbar}\int_{-\infty}^{t} dt_1\, f_{t_1}\left\langle\left[\hat{A}_t, \hat{B}_{t_1}\right]\right\rangle_0$$

Average over unperturbed states ($V_t = 0$)

In this situation interaction and Heisenberg pictures are the same!

Reaction of the system is determined by expectation value of the unperturbed system. The interaction representation of the operators corresponds to the Heisenberg representation when the field is off.

Introduce $G^{Ret}_{AB}(t,t') := -i\theta(t-t')\langle[A(t), B(t')]\rangle_0$

Retarded Green's function

Heisenberg op.

$$\boxed{\Delta A_t = \frac{1}{\hbar}\int_{-\infty}^{\infty} dt'\, f_{t'}\, G^{Ret}_{AB}(t,t')}$$

Kubo formula

Alternative notation: $G^{Ret}_{AB}(t,t') = \langle\langle A(t), B(t')\rangle\rangle^{Ret}$