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WINTER COLLEGE ON LASERS, ATOMIC AND MOLECULAR PHYSICS

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ELEMENTS OF STATISTICAL QUANTUM MECHANICS

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QUANTUM SYSTEM Q

HILBERT SPACE $\mathcal{H}$

$\varphi, \psi \in \mathcal{H}$ SCALAR PRODUCT

(φ, ψ) LINEAR IN ψ

$$(\varphi, a\psi_1 + b\psi_2) = a(\varphi, \psi_1) + b(\varphi, \psi_2)$$

ANTILINEAR IN φ

$$(a\varphi_1 + b\varphi_2, \psi) = a^*(\varphi_1, \psi) + b^*(\varphi_2, \psi)$$

$\|\psi\|^2 = (\psi, \psi) = (\text{NORM})^2$ OF ψ

COMPLETE ORTHONORMAL BASIS IN $\mathcal{H}$

$\{u_n\}$ $n = 1, 2, \ldots$

SUCH THAT

$$(u_n, u_m) = \delta_{n,m}$$

AND $\forall\ \psi \in \mathcal{H}$

$$\psi = \sum_n c_n u_n \quad , \quad c_n = (u_n, \psi)$$

DIRAC'S NOTATION

$$\psi \longrightarrow |\psi\rangle$$

KET

LINEAR BOUNDED FUNCTIONALS ON $\mathcal{H}$

$$\psi \in \mathcal{H} \longrightarrow \text{C-NUMBER}$$

$$\mathfrak{F}(\psi).$$

LINEAR $\mathfrak{F}(\alpha\psi_1 + \beta\psi_2) = \alpha\mathfrak{F}(\psi_1) + \beta\mathfrak{F}(\psi_2)$

BOUNDED $|\mathfrak{F}(\psi)| \leq K\|\psi\| \quad \forall \psi \in \mathcal{H}$

EXAMPLE :

$\varphi \in \mathcal{H}$ $\mathfrak{F}_\varphi(\psi) = (\varphi, \psi)$

$|(\varphi, \psi)| \leq \|\varphi\| \cdot \|\psi\|$ SCHWARTZ'S INEQUALITY

RIESZ THEOREM : For any given bounded linear functional $\mathfrak{F}(\psi)$ on $\mathcal{H}$, one can identify an element $\varphi \in \mathcal{H}$ such that

$$\mathfrak{F}(\psi) = (\varphi, \psi)$$

CORRESPONDENCE BETWEEN VECTORS $\in \mathcal{H}$ AND FUNCTIONALS ON $\mathcal{H}$

$$\varphi \in \mathcal{H} \longrightarrow \text{FUNCTIONAL } \mathfrak{F}_\varphi(\cdots) = (\varphi, \cdots)$$

ANTILINEAR $c_1\varphi_1 + c_2\varphi_2 \longrightarrow (c_1\varphi + c_2\varphi \ \ldots\ldots)$

DIRAC'S NOTATION

$$\mathfrak{Z}_\varphi(\dots) = (\varphi, \dots) \longrightarrow \langle\varphi|$$

BRA

$\langle\varphi|$ = BRA CONJUGATE TO THE KET $|\varphi\rangle$

$$\mathfrak{Z}_\varphi(\psi) = (\varphi, \psi) \longrightarrow \langle\varphi|\psi\rangle$$

BRA(C)KET

$$(\psi, \varphi) = (\varphi, \psi)^* \longrightarrow \langle\psi|\varphi\rangle = \langle\varphi|\psi\rangle^*$$

LINEAR BOUNDED OPERATORS ON $\mathcal{H}$

$$|\psi\rangle \longrightarrow |\bar{\psi}\rangle = A|\psi\rangle$$

$$A\left(c_1|\psi_1\rangle + c_2|\psi_2\rangle\right) = c_1 A|\psi_1\rangle + c_2 A|\psi_2\rangle$$

$$\|A\psi\| \leq K\|\psi\| \qquad \forall \psi \in \mathcal{H}$$

LET US DEFINE THE APPLICATION OF THE OPERATOR A ON THE BRAS

$$\langle\varphi|A$$

$$(\langle\varphi|A)|\psi\rangle \stackrel{\text{def}}{=} \langle\varphi|(A|\psi\rangle)$$

HENCE WE CAN WRITE SIMPLY

$$\langle\varphi|A|\psi\rangle$$

IN CONCLUSION

$$(\varphi, A\psi) \longrightarrow \langle\varphi|A|\psi\rangle$$

a) MATRIX REPRESENTATION OF A

$\{u_n\}$ COMPLETE ORTHONORMAL BASIS IN $\mathcal{H}$

$$A_{mn} = (u_m, A u_n) = \langle u_m|A|u_n\rangle$$

b) OBSERVABLE $A \longrightarrow$ SELFADJOINT OPERATOR $\hat{A}$

MEAN VALUE $\langle A\rangle = (\psi, \hat{A}\psi)$

$$= \langle\psi|\hat{A}|\psi\rangle$$

ADJOINT OPERATOR

$$A \to A^+$$

$$(\psi, A^+\psi) = (A\psi, \psi) = (\psi, A\psi)^*$$

$$\langle\psi|A^+|\psi\rangle = \langle\psi|A|\psi\rangle^*$$

SELF-ADJOINTNESS $A^+ = A$

$$\langle\psi|A|\psi\rangle = \langle\psi|A|\psi\rangle^*$$

MATRIX $A_{mn} = \langle u_m|A|u_n\rangle$

$$A^+ = A \Rightarrow A_{nm} = \langle u_n|A|u_m\rangle = \langle u_m|A|u_n\rangle^*$$

$$= A^*_{mn} \quad \text{SELF-ADJOINT MATRIX}$$

a) THE BRA CONJUGATE TO $A|\psi\rangle$ IS $\langle\psi|A^+$

<u>PROOF</u>

CONJUGATION $|\varphi\rangle \to \langle\varphi|$

$$\langle\varphi| = \mathfrak{F}_\varphi(\cdots) = (\varphi, \cdots)$$

$$\mathfrak{F}_{A\varphi}(\psi) = (A\varphi, \psi) = (\varphi, A^+\psi)$$

$$= \langle\varphi|(A^+|\psi\rangle) = (\langle\varphi|A^+)|\psi\rangle$$

b) $A = |u\rangle\langle v|$ LINEAR OPERATOR ON $\mathcal{H}$

$A|\psi\rangle = |u\rangle\langle v|\psi\rangle$ DIADIC

NOW $(|u\rangle\langle v|)^+ = |v\rangle\langle u|$

IN FACT

$$\langle\varphi|A^+|\psi\rangle = \langle\varphi|(|u\rangle\langle v|)^+|\psi\rangle =$$

$$= \langle\varphi|v\rangle\langle u|\psi\rangle = \langle u|\psi\rangle\langle\varphi|v\rangle =$$

$$= \langle\psi|u\rangle^*\langle v|\varphi\rangle^* = (\langle\psi|u\rangle\langle v|\varphi\rangle)^*$$

$$= \langle\psi|(|u\rangle\langle v|)|\varphi\rangle^* = \langle\psi|A|\varphi\rangle^*$$

ORTHOGONAL PROJECTION OPERATORS

$\mathcal{S}$ AND $\mathcal{S}_\perp$ ORTHOGONAL SUBSPACES OF $\mathcal{H}$

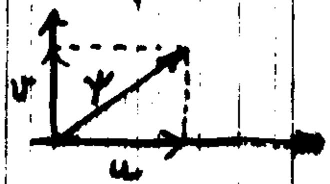
$u \in \mathcal{S}$, $v \in \mathcal{S}_\perp$ $\quad (u,v)=0$

$\langle u|v\rangle = 0$

$\forall\, |\psi\rangle \in \mathcal{H}$ $\quad |\psi\rangle = |u\rangle + |v\rangle$

$|u\rangle \in \mathcal{S}$

$|v\rangle \in \mathcal{S}_\perp$



CORRESPONDENCE $\quad |\psi\rangle \Longrightarrow |u\rangle$

LINEAR $\quad |u\rangle = P|\psi\rangle$

P ORTHOGONAL PROJECTION OPERATOR ONTO THE SUBSPACE $\mathcal{S}$

$P = P^+ \quad \langle\varphi|P|\psi\rangle = \langle\psi|P|\varphi\rangle^*$

$|\psi\rangle = |u\rangle + |v\rangle \quad \langle\psi| = \langle u| + \langle v|$

$|\varphi\rangle = |u'\rangle + |v'\rangle \quad \langle\varphi| = \langle u'| + \langle v'|$

$\langle\psi|P|\varphi\rangle^* = \langle\psi|u'\rangle^* = \langle u'|\psi\rangle$

$= \langle u'|u\rangle = \langle\varphi|u\rangle = \langle\varphi|P|\psi\rangle$

P IDEMPOTENT $\quad P^2 = P\cdot P = P$

EIGENVALUES OF $P = 0, 1$

$\lambda^2 = \lambda \Rightarrow \lambda = 1, 0$

YES – NO OBSERVABLES

LET $\{|u_n\rangle\}$ BE A COMPLETE ORTHONORMAL BASIS IN $\mathcal{H}$ SUCH THAT, FOR EACH n, EITHER $|u_n\rangle \in \mathcal{S}$ OR $|u_n\rangle \in \mathcal{S}_\perp$

s DIMENSION OF $\mathcal{S}$

$n = 1, 2, \dots, s \quad |u_n\rangle \in \mathcal{S}$

$n = s+1, \dots \quad |u_n\rangle \in \mathcal{S}_\perp$

$|\psi\rangle = \sum_n c_n |u_n\rangle \qquad c_n = \langle u_n|\psi\rangle$

$|\psi\rangle = \sum_{n=1}^{s} c_n |u_n\rangle + \sum_{n=s+1}^{\infty} c_n |u_n\rangle$

$P|\psi\rangle = \sum_{n=1}^{s} c_n |u_n\rangle \Rightarrow P = \sum_{n=1}^{s} |u_n\rangle\langle u_n|$

IN FACT

$P|\psi\rangle = \sum_{n=1}^{s} |u_n\rangle \underbrace{\langle u_n|\psi\rangle}_{c_n}$

SPECIAL CASE : $\mathcal{S}$ ONEDIMENSIONAL, SPANNED BY THE VECTOR $|u\rangle$, $\langle u|u\rangle = 1$

$P_u = |u\rangle\langle u|$

LET US NOW REWRITE THE RELATIONS OF ORTHONORMALITY AND COMPLETENESS IN DIRAC'S NOTATIONS

ORTHONORMALITY

$(u_n, u_m) = \delta_{n,m}$ $\qquad$ $\langle u_n | u_m \rangle = \delta_{n,m}$

COMPLETENESS

$\psi = \sum_n c_n u_n$ $\qquad$ $c_n = (u_n, \psi)$

$\sum_n |u_n\rangle\langle u_n| = \mathbb{1}$ IDENTITY OPERATOR

IN FACT

$$\sum_n |u_n\rangle\langle u_n|\psi\rangle = \sum_n |u_n\rangle c_n = |\psi\rangle = \mathbb{1}|\psi\rangle$$

$$P_n = |u_n\rangle\langle u_n|$$

$$\sum_n P_n = \mathbb{1}$$

SPECTRAL DECOMPOSITION OF SELF-ADJOINT OPERATORS

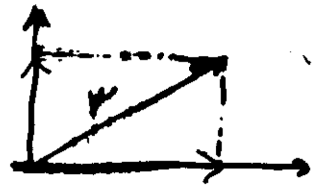
$A = A^+$ PURELY DISCRETE SPECTRUM

$$A = \sum_n a_n P_n \qquad a_1 \neq a_2 \neq a_3 \neq \dots$$

a_n = EIGENVALUES OF A

P_n = PROJECTION OPERATOR ONTO THE EIGENSPACE ASSOCIATED TO THE EIGENVALUE a_n

$P_n P_m = P_n \delta_{n,m}$ ORTHONORMALITY



$\sum_n P_n = \mathbb{1}$ COMPLETENESS

MAXIMAL (i.e. COMPLETE) OBSERVATION

SET OF OBSERVABLES $A^{(1)}, A^{(2)}, \dots, A^{(K)}$ THAT COMMUTE, SUCH THAT THE SIMULTANEOUS SPECTRAL DECOMPOSITION

$$\hat{A}^{(i)} = \sum_n a_n^{(i)} P_n \qquad i = 1, 2, \dots, K$$

HAS $P_n = |u_n\rangle\langle u_n|$, i.e. ONEDIMENSIONAL COMMON EIGENSPACES

IF THE RESULT OF THE SIMULTANEOUS OBSERVATION IS $\{a_{\Xi}^{(i)}\}$, THE STATE OF THE SYSTEM AFTER THE MEASUREMENT IS $|u_{\Xi}\rangle$

FLUCTUATIONS
NOISE
QUANTUM NOISE

QUANTUM SYSTEM Q, HILBERT SPACE $\mathcal{H}$

MAXIMAL (COMPLETE) OBSERVATION $\longrightarrow$ INITIAL STATE VECTOR $|\psi\rangle_0$

SCHRÖDINGER EQUATION

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

$\hat{H}$ HAMILTONIAN OPERATOR

COLLECTION OF N IDENTICAL SYSTEMS

OBSERVABLE $A \longrightarrow$ OPERATOR $A = A^{\dagger}$ IN $\mathcal{H}$

MEAN VALUE $\langle A\rangle(t) = {}_t\langle\psi|A|\psi\rangle_t$

OBSERVABLES YES–NO (1–0) ASSOCIATED WITH ORTHOGONAL PROJECTION OPERATORS $P = P^{\dagger} = P^2$; SUBSPACE $\mathcal{S}_P$ OF $\mathcal{H}$ SUCH THAT $P|\psi\rangle \in \mathcal{S}_P \quad \forall |\psi\rangle$

<u>REVERSIBILITY</u>: IF $|\psi\rangle_t$ IS A SOLUTION OF THE SCHR. EQ., ALSO $|\psi^*\rangle_{-t}$ IS A SOLUTION

n PARTICLES $\vec{x}_1, \vec{x}_2, \dots, \vec{x}_n$

$|\psi\rangle_t \longrightarrow$ WAVE FUNCTION $\psi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_n, t)$

$|\psi^*\rangle_{-t} \longrightarrow$ WAVE FUNCTION $\psi^*(\vec{x}_1, x_2, \dots, \vec{x}_n, -t)$

$$\langle\psi^*|\hat{\vec{x}}_i|\psi^*\rangle = \langle\psi|\hat{\vec{x}}_i|\psi\rangle$$

$$\langle\psi^*|\hat{\vec{p}}_i|\psi^*\rangle = -\langle\psi|\hat{\vec{p}}_i|\psi\rangle$$

— x —

TRACE OF AN OPERATOR

B BOUNDED OPERATOR IN $\mathcal{H}$

$\{|u_n\rangle\}$ = COMPLETE ORTHONORMAL SYSTEM IN $\mathcal{H}$

$\langle u_m|u_n\rangle = \delta_{n,m}$ (ORTHONORMALITY), $\quad \sum_n |u_n\rangle\langle u_n| = \mathbb{1}$ (COMPLETENESS)

$$\mathrm{Tr}\, B = \sum_n \langle u_n | B | u_n \rangle$$

INDEPENDENT OF THE CHOICE OF $\{|u_n\rangle\}$

$$\mathrm{Tr}(A+B) = \mathrm{Tr}\, A + \mathrm{Tr}\, B$$
$$\mathrm{Tr}(\lambda B) = \lambda\, \mathrm{Tr}\, B$$
$$\mathrm{Tr}(AB) = \mathrm{Tr}(BA)$$

CYCLIC PROPERTY: $\mathrm{Tr}(ABCD) = \mathrm{Tr}(BCDA) = \mathrm{Tr}(CDAB) = \ldots$

$P = P^+ = P^2$ $\quad \mathcal{S}_P$ = SUBSPACE OF $\mathcal{H}$ ONTO WHICH P PROJECTS ; s = DIMENSION OF $\mathcal{S}_P$

$\{|\varphi_j\rangle\}$ = ORTHONORMAL BASIS IN $\mathcal{S}_P$

$$\mathrm{Tr}(AP) = \sum_{j=1}^{s} \langle \varphi_j | A | \varphi_j \rangle$$

SPECIAL CASES

1) $\mathcal{S}_P$ ONEDIMENSIONAL $\longrightarrow$ $P_\psi = |\psi\rangle\langle\psi|$

$$\mathrm{Tr}(A P_\psi) = \langle \psi | A | \psi \rangle$$

HENCE $\langle A \rangle = \langle \psi | \hat{A} | \psi \rangle = \mathrm{Tr}(\hat{A} P_\psi)$

2) $A = \mathbb{1}$ $\quad \mathrm{Tr}\, P = \sum_{j=1}^{s} \langle \varphi_j | \mathbb{1} | \varphi_j \rangle = s$

QUANTUM STATISTICAL MECHANICS

MACROSCOPIC SYSTEM: COMPLETE OBSERVATION IMPOSSIBLE

$\{|\psi_n\rangle\}$ ORTHONORMAL BASIS IN $\mathcal{H}$

p_1	$\|\psi_1\rangle$
p_2	$\|\psi_2\rangle$
p_3	$\|\psi_3\rangle$
…	…

$$\sum_i p_i = 1$$

$\|\psi_1\rangle$	$\langle\psi_1\|\hat{A}\|\psi_1\rangle$	p_1
$\|\psi_2\rangle$	$\langle\psi_2\|\hat{A}\|\psi_2\rangle$	p_2
…	…	…
$\|\psi_i\rangle$	$\langle\psi_i\|\hat{A}\|\psi_i\rangle$	p_i
…	…	…

$$\langle A \rangle = \sum_i p_i \langle \psi_i | \hat{A} | \psi_i \rangle$$

ρ STATISTICAL OPERATOR $\quad \rho = \sum_i p_i |\psi_i\rangle\langle\psi_i| = \sum_i p_i P_{\psi_i}$

$$\langle A \rangle = \mathrm{Tr}(\hat{A}\rho)$$

$$\mathrm{Tr}(\hat{A}\rho) = \mathrm{Tr}\left(\sum_i p_i \hat{A} P_{\psi_i}\right) =$$

$$= \sum_i p_i \mathrm{Tr}(\hat{A} P_{\psi_i}) = \sum_i p_i \langle\psi_i|\hat{A}|\psi_i\rangle$$

COLLECTION OF N IDENTICAL SYSTEMS

$$N = N_1 + N_2 + \dots + N_i + \dots$$
$$|\psi_1\rangle \quad |\psi_2\rangle \quad |\psi_i\rangle$$

$$\frac{N_1}{N} = p_1, \quad \frac{N_2}{N} = p_2, \dots, \quad \frac{N_i}{N} = p_i, \dots$$

$p_i = \delta_{i,\bar{\imath}}$ "PURE STATE" $\rho = |\psi_{\bar{\imath}}\rangle\langle\psi_{\bar{\imath}}| = P_{\psi_{\bar{\imath}}}$

"MIXTURE OF STATES" $\rho = \sum_i p_i |\psi_i\rangle\langle\psi_i|$

$$|\psi\rangle = \sum_i c_i |\psi_i\rangle \qquad |c_i|^2 = p_i$$

$$c_i = r_i e^{i\theta_i} \qquad r_i = \sqrt{p_i}$$

$$|\psi\rangle = \sum_i r_i e^{i\theta_i} |\psi_i\rangle$$

IF WE KNEW θ_i: PURE STATE

$$\rho^{(\theta_1\theta_2\dots)} = |\psi\rangle\langle\psi| = \sum_{ij} r_i r_j e^{i(\theta_i-\theta_j)} |\psi_i\rangle\langle\psi_j|$$

θ_i ?

RANDOM PHASE ASSUMPTION (PURELY STATISTICAL)
(RPA)

$$\rho = \frac{1}{2\pi}\int_0^{2\pi} d\theta_1 \frac{1}{2\pi}\int_0^{2\pi} d\theta_2 \dots \rho^{(\theta_1\theta_2\dots)}$$

$$= \frac{1}{2\pi}\int_0^{2\pi} d\theta_1 \frac{1}{2\pi}\int_0^{2\pi} d\theta_2 \dots \sum_{ij} r_i r_j e^{i(\theta_i-\theta_j)} |\psi_i\rangle\langle\psi_j|$$

$$= \sum_i r_i^2 |\psi_i\rangle\langle\psi_i| = \sum_i p_i |\psi_i\rangle\langle\psi_i|$$

MIXTURE !

MACROSCOPIC OBSERVATION $\rightarrow$ SUBSPACE $\mathcal{S}$

$\{|\varphi_j\rangle\}$ COMPLETE BASIS IN $\mathcal{S}$
$j = 1, 2, \dots, s$

$$\rho = \sum_j p_j |\varphi_j\rangle\langle\varphi_j|$$

EQUAL PROBABILITY ASSUMPTION (PURELY STATISTICAL)
(EPA)

$$p_1 = p_2 = \dots = p_s \quad ; \quad \sum_{j=1}^{s} p_j = 1 \Rightarrow p_j = \frac{1}{s}$$

$$\rho = \frac{1}{s}\sum_j |\varphi_j\rangle\langle\varphi_j| = \frac{1}{s} P_{\mathcal{S}}$$

CHARACTERISTIC PROPERTIES OF ρ

$$\rho = \rho^+ \quad , \quad \rho \geq 0 \quad , \quad \mathrm{Tr}\, \rho = 1$$

PURE STATE $\rho^2 = \rho \quad , \quad \mathrm{Tr}\, \rho^2 = \mathrm{Tr}\, \rho = 1$

MIXTURE $\rho^2 \neq \rho \quad , \quad \mathrm{Tr}\, \rho^2 < 1$

$$\rho = \sum_i p_i \, |\psi_i\rangle\langle\psi_i|$$

$$\rho^2 = \sum_{i,j} p_i p_j \, |\psi_i\rangle\langle\psi_i|\psi_j\rangle\langle\psi_j|$$

$$= \sum_i p_i^2 \, |\psi_i\rangle\langle\psi_i| = \sum_i p_i^2 \, P_{\psi_i}$$

$$\mathrm{Tr}\, \rho^2 = \sum_i p_i^2 \, \mathrm{Tr}\, P_{\psi_i} = \sum_i p_i^2 < \left(\sum_i p_i\right)^2 = 1$$

DENSITY MATRIX

$\{|u_m\rangle\}$ COMPLETE BASIS IN $\mathcal{H}$

MATRIX ELEMENTS

$$\rho_{mm} = \langle u_m|\rho|u_m\rangle$$

OBSERVABLE A

MEAN VALUE $\langle A\rangle = \mathrm{Tr}\,(\hat{A}\rho)$

MEAN SQUARE VARIANCE = MEAN SQUARE FLUCTUATION $\Delta A^2 = \langle (A - \langle A\rangle)^2\rangle$

$$= \langle A^2\rangle - \langle A\rangle^2$$

PROBABILITY DISTRIBUTION OF A ?

$$\hat{A} = \sum_n a_n P_n$$

$$\langle A\rangle = \sum_n a_n \, \mathrm{Tr}\,(P_n \rho)$$

HENCE $p(a_n) = \mathrm{Tr}\,(P_n \rho) =$ PROBABILITY DISTRIBUTION

PURE STATE $\rho = P_\psi$

$$p(a_n) = \langle\psi|P_n|\psi\rangle$$

$P_n = \sum_j |\varphi_j\rangle\langle\varphi_j|$ $\quad \{|\varphi_j\rangle\}$ COMPLETE BASIS IN $\mathcal{S}_{P_n}$

$$p(a_n) = \sum_j \langle\psi|\varphi_j\rangle\langle\varphi_j|\psi\rangle$$

$$= \sum_j |\langle\varphi_j|\psi\rangle|^2$$

YES - NO OBSERVABLES

$$P \longrightarrow \mathcal{S}_P$$

$\langle P \rangle = \mathrm{Tr}(P\rho)$ PROBABILITY OF FINDING THE SYSTEM IN THE SUBSPACE $\mathcal{S}_P$

SPECIAL CASE : $P_\psi \longrightarrow |\psi\rangle$

$\langle P_\psi \rangle = \mathrm{Tr}(P_\psi \rho) = \langle \psi | \rho | \psi \rangle =$ PROBABILITY OF FINDING THE SYSTEM IN STATE $|\psi\rangle$

REMARKS

1) DIAGONAL ELEMENTS OF THE DENSITY MATRIX

$\rho_{mm} = \langle u_m | \rho | u_m \rangle =$ PROBABILITY OF FINDING THE SYSTEM IN THE STATE $|u_m\rangle$

2) $\rho = \frac{1}{s} P_{\mathcal{S}}$, $|\psi\rangle \in \mathcal{S}$

$$\langle \psi | \rho | \psi \rangle = \frac{1}{s} \langle \psi | P_{\mathcal{S}} | \psi \rangle = \frac{1}{s} \langle \psi | \psi \rangle = \frac{1}{s}$$

HENCE RPA + EPA $\longrightarrow$ EQUIPROBABILITY OF ALL STATES IN $\mathcal{S}$

TIME EVOLUTION OF ρ

$$\rho(t) = \sum_i p_i \, |\psi_i\rangle_t \, {}_t\langle\psi_i| \qquad , \quad |\psi_i\rangle_t = e^{-\frac{i}{\hbar}\hat{H}t} |\psi_i\rangle$$

$$\rho(t) = \sum_i p_i \, e^{-\frac{i}{\hbar}\hat{H}t} |\psi_i\rangle\langle\psi_i| \, e^{\frac{i}{\hbar}\hat{H}t}$$

$$= e^{-\frac{i}{\hbar}\hat{H}t} \rho(0) \, e^{\frac{i}{\hbar}\hat{H}t}$$

$$\frac{d\rho}{dt} = -\frac{i}{\hbar}\hat{H} e^{-\frac{i}{\hbar}\hat{H}t} \rho(0) \, e^{\frac{i}{\hbar}\hat{H}t} + e^{-\frac{i}{\hbar}\hat{H}t} \rho(0) \, e^{\frac{i}{\hbar}\hat{H}t} \frac{i}{\hbar}\hat{H}$$

$$= -\frac{i}{\hbar}\hat{H}\rho(t) + \frac{i}{\hbar}\rho(t)\hat{H}$$

$$\frac{d\rho}{dt} = -\frac{i}{\hbar}\left[\hat{H}, \rho\right]$$ VON NEUMANN EQUATION

QUANTUM ANALOGUE OF THE CLASSICAL LIOUVILLE EQUATION

$$\rho_{nm} = \langle u_n | \rho | u_m \rangle$$

$$\frac{d\rho_{nm}}{dt} = -\frac{i}{\hbar}\left(\langle u_n | \hat{H}\rho | u_m \rangle - \langle u_n | \rho\hat{H} | u_m \rangle \right)$$

$$\sum_{n'} |u_{n'}\rangle\langle u_{n'}| = 1$$

$$\frac{d\rho_{nm}}{dt} = -\frac{i}{\hbar}\sum_{n'}\Big(\langle u_n|\hat{H}|u_{n'}\rangle\langle u_{n'}|\rho|u_m\rangle$$

$$-\langle u_n|\rho|u_{n'}\rangle\langle u_{n'}|\hat{H}|u_m\rangle\Big)$$

$$= -\frac{i}{\hbar}\sum_{n'}\left(\hat{H}_{nn'}\rho_{n'm} - \rho_{nn'}H_{n'm}\right)$$

SPECIAL CASE $\{|u_n\rangle\}$ = ENERGY BASIS

$$\hat{H}|u_n\rangle = E_n|u_n\rangle\,, \qquad \hat{H}_{nn'} = E_n\,\delta_{n,n'}$$

$$\frac{d\rho_{nm}}{dt} = -\frac{i}{\hbar}\left(E_n\rho_{nm} - E_m\rho_{nm}\right)$$

$$\frac{E_n - E_m}{\hbar} = \omega_{nm}$$

$$\frac{d\rho_{nm}}{dt} = -i\omega_{nm}\rho_{nm}$$

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

$$\rho_{nn}(t) = \rho_{nn}(0) \quad \text{ENERGY CONSERVATION}$$

SCHRÖDINGER PICTURE

$\hat{A}$ INDEPENDENT OF TIME

$\rho(t)$ VON NEUMANN EQUATION

$$\langle A\rangle(t) = \mathrm{Tr}\left(\hat{A}\rho(t)\right)$$

HEISEMBERG PICTURE

ρ INDEPENDENT OF TIME

$\hat{A}(t)$ HEISEMBERG EQUATION

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

$$A(t) = e^{\frac{i}{\hbar}\hat{H}t}\,\hat{A}\,e^{-\frac{i}{\hbar}\hat{H}t} \qquad A(0) = \hat{A}$$

$$\langle A\rangle(t) = \mathrm{Tr}\left(\hat{A}(t)\rho\right)$$

$$= \mathrm{Tr}\left(e^{\frac{i}{\hbar}\hat{H}t}\hat{A}\,e^{-\frac{i}{\hbar}\hat{H}t}\rho\right)$$

$$= \mathrm{Tr}\left(\hat{A}\,e^{-\frac{i}{\hbar}\hat{H}t}\rho\,e^{\frac{i}{\hbar}\hat{H}t}\right)$$

$$= \mathrm{Tr}\left(\hat{A}\,\rho(t)\right)$$

APPROACH TO EQUILIBRIUM

$$\langle A \rangle (t) \xrightarrow{t \to \infty} \langle A \rangle_{eq}$$

IRREVERSIBILITY

EQUILIBRIUM STATE : WHICH ρ REPRESENTS A SYSTEM IN THERMODYNAMIC EQUILIBRIUM AT TEMPERATURE T ?

THE EQUILIBRIUM STATE IS A STATIONARY STATE $\frac{d\rho_{eq}}{dt} = 0$. HENCE $[\hat{H}, \rho_{eq}] = 0$

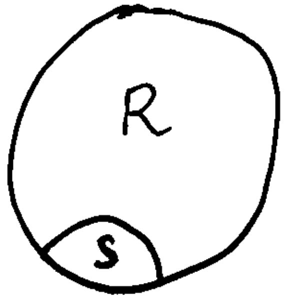
$\Rightarrow \rho_{eq}$ IS A FUNCTION OF THE CONSTANTS OF MOTION OF THE SYSTEM

ZEROTH LAW OF THERMODYNAMICS

$$\rho_{eq} = \frac{1}{Z} e^{-\beta \hat{H}}$$ CANONICAL STATISTICAL OPERATOR

$\beta = \frac{1}{\kappa T}$ κ = BOLTZMANN CONSTANT

$Z = \mathrm{Tr}\, e^{-\beta \hat{H}}$ PARTITION FUNCTION



R = RESERVOIR

S = SUBSYSTEM

RESERVOIR $\frac{e^{-\beta \hat{H}_R}}{Z_R}$

$$\rho_s(t) \xrightarrow{t \to \infty} \rho_{s,eq} = \frac{e^{-\beta \hat{H}_s}}{Z_s}$$

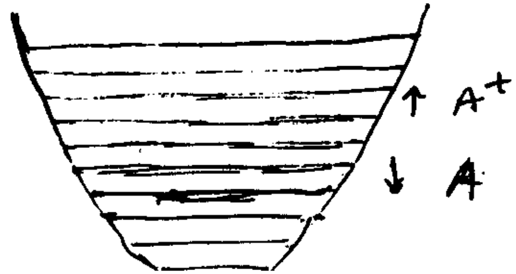
SPECIFIC EXAMPLE : S = HARMONIC OSCILLATOR

$$\hat{H}_s = (A^+A + \tfrac{1}{2})\hbar\omega$$

$A^+A\,|m\rangle = m\,|m\rangle$ $m = 0, 1, 2, \ldots$

$A\,|m\rangle = \sqrt{m}\,|m-1\rangle$ lowering

$A^+\,|m\rangle = \sqrt{m+1}\,|m+1\rangle$ raising



$$\rho_{eq} = \frac{e^{-\beta\hbar\omega A^+A}}{Z} = \frac{e^{-xA^+A}}{Z}$$

$$x = \beta\hbar\omega = \hbar\omega/KT$$

$$Z = \mathrm{Tr}\, e^{-xA^+A} = \sum_{n=0}^{\infty} \langle n| e^{-xA^+A} |n\rangle$$

$$= \sum_{n=0}^{\infty} e^{-xn} \langle n|n\rangle = \sum_{n=0}^{\infty} \left(e^{-x}\right)^n = \frac{1}{1-e^{-x}}$$

PROBABILITY DISTRIBUTION OF ENERGY

$$p_n = \rho_{nn} = \langle n|\rho|n\rangle = \frac{1}{Z}\langle n| e^{-xA^+A} |n\rangle$$

$$= \frac{e^{-xn}}{Z}$$

$$\langle n\rangle = \sum_{n=0}^{\infty} n\, p_n = \frac{1}{Z}\sum_{n=0}^{\infty} n\, e^{-xn}$$

$$= -\frac{1}{Z}\frac{\partial}{\partial x} Z = \frac{\partial}{\partial x}\ln Z$$

$$\langle n\rangle = \frac{1}{e^x-1}$$

$$\langle n^2\rangle = \frac{1}{Z}\frac{\partial^2}{\partial x^2} Z, \quad \text{etc.}$$

$$\Delta n^2 = \langle n^2\rangle - \langle n\rangle^2 = \langle n\rangle\left(\langle n\rangle + 1\right)$$

$$\frac{\Delta n^2}{\langle n\rangle^2} = 1 + \frac{1}{\langle n\rangle}$$

$$\frac{\Delta n}{\langle n\rangle} = \sqrt{1+\frac{1}{\langle n\rangle}} = \sqrt{1+e^x-1} = e^{+\frac{x}{2}}$$

LARGE T $\quad x = \frac{\hbar\omega}{KT} \ll 1 \quad \frac{}{\langle n\rangle} \simeq 1$

$T \to 0$ $\quad x = \frac{\hbar\omega}{KT} \gg 1 \quad \frac{}{\langle n\rangle} \to \infty$

——— x ———

CORRELATIONS

A, B

CLASSICAL CORRELATION :

$$\langle AB\rangle - \langle A\rangle\langle B\rangle$$

QM CORRELATION

$$\left\langle \frac{AB+BA}{2} \right\rangle - \langle A\rangle\langle B\rangle$$

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TIME CORRELATION FUNCTIONS

CLASSICAL

$$\langle A(t)\,B(t')\rangle - \langle A(t)\rangle\langle B(t')\rangle$$

$$\langle A(t)\rangle = \langle A\rangle(t)$$

QM (HEISENBERG PICTURE)

$$\left\langle \frac{A(t)B(t') + B(t')A(t)}{2} \right\rangle - \langle A(t)\rangle\langle B(t')\rangle$$

$$\langle \ldots\ldots \rangle = \mathrm{Tr}\,(\ldots\ldots\ \rho)$$

CASE OF EQUILIBRIUM STATE $\rho = \rho_{eq}$

$$\langle A(t)\rangle = \langle A\rangle_{eq} \qquad \langle B(t')\rangle = \langle B\rangle_{eq}$$

$$\langle A(t)\,B(t')\rangle_{eq} = \langle A(t-t')\,B(0)\rangle_{eq}$$
$$= \langle A(0)\,B(t'-t)\rangle_{eq}$$

$$\langle A(t)\,B(t')\rangle_{eq} = \mathrm{Tr}\,\{A(t)\,B(t')\,\rho_{eq}\}$$

$$= \mathrm{Tr}\,\{e^{\frac{i}{\hbar}\hat{H}t} A\, e^{-\frac{i}{\hbar}\hat{H}t}\, e^{\frac{i}{\hbar}\hat{H}t'} B\, e^{-\frac{i}{\hbar}\hat{H}t'}\,\rho_{eq}\}$$

$$= \mathrm{Tr}\,\{e^{-\frac{i}{\hbar}\hat{H}t'}\, e^{\frac{i}{\hbar}\hat{H}t} A\, e^{-\frac{i}{\hbar}\hat{H}(t-t')} B\rho_{eq}\}$$

$$= \mathrm{Tr}\,\{e^{\frac{i}{\hbar}\hat{H}(t-t')} A\, e^{-\frac{i}{\hbar}\hat{H}(t-t')} B\,\rho_{eq}\}$$

$$= \mathrm{Tr}\,\{A(t-t')\,B(0)\,\rho_{eq}\} = \langle A(t-t')B(0)\rangle_{eq}$$

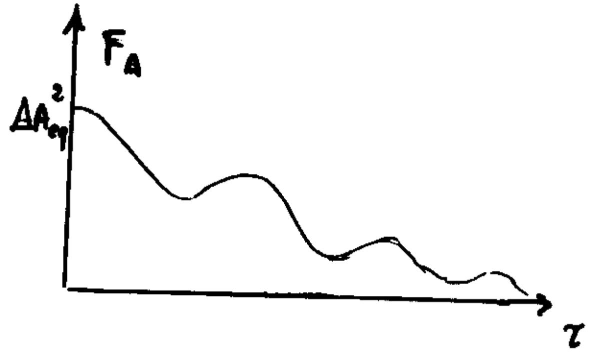
SPECIAL CASE : EQUILIBRIUM STATE AND $B = A$ (SELF-CORRELATION FUNCTION)

$$t - t' = \tau$$

$$F_A(\tau) = \frac{1}{2}\langle A(\tau)A(0) + A(0)A(\tau)\rangle_{eq} - \langle A\rangle_{eq}^2$$

$$\tau = 0 \qquad \langle A^2\rangle_{eq} - \langle A\rangle_{eq}^2 = (\Delta A^2)_{eq}$$

$$F_A(\tau) \xrightarrow{\tau\to\infty} 0$$



FLUCTUATIONS

INTENSIVE OBSERVABLE $\quad A = \frac{1}{n} \sum_{i=1}^{n} a_i$

$$\langle A \rangle = \frac{1}{n} \sum_{i=1}^{n} \langle a_i \rangle = \mathcal{O}(n^0)$$

NORMAL FLUCTUATIONS $\quad \Delta A \propto \frac{1}{n^{1/2}}$

$\langle a_i \rangle = a \qquad \langle a_i^2 \rangle - \langle a_i \rangle^2 = \Delta a^2$

$\langle a_i a_j \rangle - \langle a_i \rangle \langle a_j \rangle = 0$ for $i \neq j$

uncorrelation!

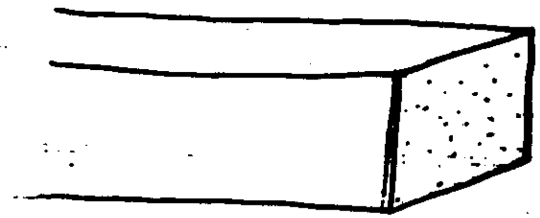
$$\langle A \rangle = \frac{1}{n} \sum_{i=1}^{n} \langle a_i \rangle = \langle a \rangle$$

$$\Delta A^2 = \langle A^2 \rangle - \langle A \rangle^2 = \frac{1}{n^2} \sum_{i,j} \left(\langle a_i a_j \rangle - \langle a_i \rangle \langle a_j \rangle \right)$$

$$= \frac{1}{n^2} \left\{ \sum_i \left(\langle a_i^2 \rangle - \langle a_i \rangle^2 \right) + \sum_{i \neq j} \left(\langle a_i a_j \rangle - \langle a_i \rangle \langle a_j \rangle \right) \right\}$$

$$= \frac{1}{n^2} \cdot n \, \Delta a^2 = \frac{1}{n} \Delta a^2 \implies \Delta A = \frac{1}{\sqrt{n}} \Delta a$$

EXAMPLE : AVERAGE POSITION OF A SURFACE



$$X = \frac{1}{n} \sum_{i=1}^{n} x_i$$

$$\Delta x = \frac{1}{\sqrt{n}} \delta x$$