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Quick linear algebra refresher

$$\langle\phi|\psi\rangle = (\cdots)\begin{pmatrix}\vdots\end{pmatrix}$$ inner or scalar product.

$$\langle a|b\rangle = (a_1, a_2)\begin{pmatrix} b_1 \\ b_2 \end{pmatrix} = a_1 b_1 + a_2 b_2$$

$$|\psi\rangle\langle\phi| = \begin{pmatrix}\vdots\end{pmatrix}(\cdots)$$ outer product

$$|b\rangle\langle a| = \begin{pmatrix} b_1 \\ b_2 \end{pmatrix}(a_1 \ a_2) = \begin{pmatrix} b_1 a_1 & b_1 a_2 \\ b_2 a_1 & b_2 a_2 \end{pmatrix}$$

canonical basis: $(\hat{e}_1, \hat{e}_2)$ $\hat{e}_1 = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$ $\hat{e}_2 = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$

$$\sum_n |\phi_n\rangle\langle\phi_n| = \mathbb{I}$$

2D Example:

$$|e_1\rangle\langle e_1| + |e_2\rangle\langle e_2| = \begin{pmatrix} 1 \\ 0 \end{pmatrix}\begin{pmatrix} 1 & 0 \end{pmatrix} + \begin{pmatrix} 0 \\ 1 \end{pmatrix}\begin{pmatrix} 0 & 1 \end{pmatrix} =$$

$$= \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} + \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = \mathbb{I}$$

Also: for continuous basis elements

$$\mathbb{I} = \sum_n |\phi_n\rangle\langle\phi_n| \longrightarrow \int |x\rangle\langle x|\, dx = 1$$

Position basis (coordinate representation).

$|\bar{r}\rangle$ all possible position vectors (expand the Hilbert space).

$$\langle \bar{r}' | \bar{r} \rangle = \delta(\bar{r} - \bar{r}')$$

$$\psi(\bar{r}) \equiv \langle \bar{r} | \psi \rangle \qquad \langle \psi | \bar{r} \rangle = \psi^*(\bar{r})$$

$$A\psi(\bar{r}) \equiv \langle \bar{r} | A | \psi \rangle$$

Also since $\int |x\rangle\langle x| \, dx = 1$

$\therefore$

$$\langle \psi | \phi \rangle = \langle \psi | \int |x\rangle\langle x| dx \, |\phi\rangle = \int \langle \psi | x \rangle \langle x | \phi \rangle dx$$

$$= \int \psi^*(x) \, \phi(x) \, dx$$

Canonical Ensemble:

(N, V, T) defines the ensemble.

$$P_r \propto e^{-\beta E_r}$$

probability of an ensemble member found in state r.

In energy representation

$$\rho_{mn} = \rho_n \delta_{mn}$$

$$\therefore \quad \rho_n = C e^{-\beta E_n}$$

because it is the probability of finding an ensemble member in state n.

Since $\sum_r P_r = 1 \Rightarrow C = \dfrac{1}{\sum_n e^{-\beta \epsilon_n}} = \dfrac{1}{Z_N(\beta)}$

$$\therefore \quad \hat{\rho} = \sum_n |\phi_n\rangle \rho_n \langle \phi_n| = \sum_n |\phi_n\rangle \frac{e^{-\beta \epsilon_n}}{Z_N(\beta)} \langle \phi_n| =$$

$$= \frac{e^{-\beta \hat{H}}}{Z_N(\beta)} \underbrace{\sum_n |\phi_n\rangle\langle \phi_n|}_{\mathbb{1}} = \frac{e^{-\beta \hat{H}}}{\mathrm{Tr}\, e^{-\beta \hat{H}}}\, \mathbb{1} = \frac{e^{-\beta \hat{H}}}{\mathrm{Tr}\, e^{-\beta \hat{H}}}$$

D/

$$e^{-\beta \hat{H}} = e^{-\beta \hat{H}} \sum_n |\phi_n\rangle\langle \phi_n| = \sum_{j=0}^{\infty} \frac{(-1)^j \beta^j \hat{H}^j}{j!} \sum_n |\phi_n\rangle\langle \phi_n| =$$

$$= \sum_n \sum_{j=0}^{\infty} \frac{(-1)^j \beta^j}{j!} \underbrace{\hat{H}^j |\phi_n\rangle}_{\epsilon_n^j |\phi_n\rangle} \langle \phi_n| = \sum_n |\phi_n\rangle e^{-\beta \epsilon_n} \langle \phi_n|$$

$$Z_N = \sum_n e^{-\beta E_n} = \sum_n e^{-\beta \hat{H}_n} = \operatorname{tr} e^{-\beta \hat{H}}$$

$$\begin{pmatrix} e^{-\beta E_1} & & \\ & \ddots & \\ & & e^{-\beta E_N} \end{pmatrix}$$

but if we were in a different basis (not energy basis)

$$e^{-\beta \hat{H}} = \sum_{j=0}^{\infty} \underbrace{\frac{(-1)^j \beta^j \hat{H}^j}{j!}}_{\text{not diagonal}}$$

but the trace is basis independent.

Now

$$\boxed{\langle \hat{G} \rangle_N} = Tr(\hat{\rho}\hat{G}) = Tr(\hat{G}\hat{\rho}) = \boxed{\frac{Tr(\hat{G}\, e^{-\beta \hat{H}})}{Tr\, e^{-\beta \hat{H}}}}$$

$$Tr\, AB = Tr\, BA$$

$$\sum_n (AB)_{nn} = \sum_{n,s} A_{ns} B_{sn} = \sum_{s,n} B_{sn} A_{ns} = \sum_s (BA)_{ss} =$$

$$= Tr\, B A$$

Grand - Canonical:

$$P_{r,s} = \frac{e^{-\beta(E_r - \mu N_s)}}{\mathcal{Z}(\mu, V, T)}$$

and in the energy representation

$\rho_{mn} = \rho_n \delta_{mn}$ diagonal.

$$\Rightarrow \hat{\rho} = \frac{e^{-\beta(\hat{H} - \mu \hat{N})}}{\mathcal{Z}(\mu, V, T)}$$

since ρ_n represents the probability of finding a member of the ensemble in the state n defined by (r, s).

$$\mathcal{Z}(\mu, V, T) = \sum_{r,s} e^{-\beta(E_r - \mu N_s)} = \operatorname{Tr} e^{-\beta(\hat{H} - \mu \hat{N})}$$

$$\therefore \quad \langle \hat{G} \rangle = \frac{\operatorname{Tr}\left(\hat{G}\, e^{-\beta \hat{H}} \underbrace{e^{\beta\mu\hat{N}}}^{e^{\beta\mu N}}\right)}{\mathcal{Z}(\mu, V, T)} =$$

$$= \frac{\sum_{N=0}^{\infty} z^N \langle G_N \rangle Z_N(\beta)}{\sum_{N=0}^{\infty} z^N Z_N(\beta)}$$

$$\langle \hat{G}_N \rangle = \frac{\operatorname{tr} G\, e^{-\beta \hat{H}}}{Z_N(\beta)} \Rightarrow \operatorname{tr} G\, e^{-\beta \hat{H}} = \langle \hat{G}_N \rangle Z_N(\beta)$$

Examples: e^- electron with $\hat{S} = \frac{\hbar}{2}\hat{\sigma}$ $\mu_B = \frac{e\hbar}{2mc}$

$\hat{\sigma} = (\sigma_x, \sigma_y, \sigma_z)$ Pauli matrices.

We'll work in the basis in which $\sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$ (diagonal)

$$\hat{H} = -\mu_B (\hat{\sigma}, \bar{B}) = -\mu_B B \hat{\sigma}_z = \begin{pmatrix} -\mu_B B & 0 \\ 0 & \mu_B B \end{pmatrix}$$

energy of the electron in a field $\bar{B}$.

We define the $\hat{z}$ direction parallel to the direction of $\bar{B}$.

$$\bar{\sigma} \cdot \bar{B} = \hat{\sigma}_z B = \begin{pmatrix} B & 0 \\ 0 & -B \end{pmatrix}$$

$$\boxed{\hat{\rho} = \frac{e^{-\beta \hat{H}}}{\operatorname{Tr} e^{-\beta H}}} = \boxed{\frac{\begin{pmatrix} e^{+\mu_B B\beta} & 0 \\ 0 & e^{-\mu_B B \beta} \end{pmatrix}}{2\cosh(\beta \mu_B B)}}$$

$$\langle \sigma_z \rangle = \mathrm{Tr}\,(\hat\rho\,\hat\sigma_z) = \frac{2\sinh(\beta\mu_B B)}{2\cosh(\beta\mu_B B)} = \tanh(\beta\mu_B B)$$

As we knew.

$$\hat\rho\;\hat\sigma_z = \frac{\begin{pmatrix} e^{\beta\mu_B B} & 0 \\ 0 & e^{-\beta\mu_B B} \end{pmatrix}}{2\cosh(\beta\mu_B B)} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = \frac{\begin{pmatrix} e^{\beta\mu_B B} & 0 \\ 0 & -e^{-\beta\mu_B B} \end{pmatrix}}{2\cosh(\beta\mu_B B)}$$

Free particle in a box: $m, \; L^3 = V$

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)$$

PBC:
$$E = \frac{\hbar^2 k^2}{2m} \qquad k = \frac{2\pi}{L}(n_x, n_y, n_z)$$

$$n_i = 0, \pm 1, \pm 2, \ldots$$

$$\phi_E(r) = \frac{1}{L^{3/2}} e^{i\vec{k}\cdot\vec{r}} = |E\rangle \qquad 1$$

eigenfunctions in energy representation.

$$\hat{H}\phi_E(r) = E\,\phi_E(r)$$

Canonical ensemble in coordinate representation:

$\hat{\rho} = ?$

$$\langle r | e^{-\beta \hat{H}} | r' \rangle = \sum_E \underbrace{\langle r | E \rangle}_{\phi_E(\bar{r})} e^{-\beta E} \underbrace{\langle E | r' \rangle}_{\phi^*(\bar{r}')} =$$

$$= \sum_E e^{-\beta E} \phi_E(\bar{r}) \phi_E^*(\bar{r}') =$$

$$E = \frac{\hbar^2 k^2}{2m}$$

$$= \sum_k e^{-\beta \frac{\hbar^2 k^2}{2m}} \frac{1}{L^3 = V} e^{i \bar{k} \cdot \bar{r}} e^{-i \bar{k} \cdot \bar{r}'} =$$

1

$$= \frac{1}{V} \sum_k e^{-\beta \frac{\hbar^2 k^2}{2m}} e^{i \bar{k} \cdot (\bar{r} - \bar{r}')} \qquad \frac{1}{V} \sum_k \longrightarrow \frac{1}{(2\pi)^3} \int dk$$

$$= \frac{1}{(2\pi)^3} \int e^{-\frac{\beta \hbar^2 k^2}{2m} + i \bar{k} \cdot (\bar{r} - \bar{r}')} d^3k =$$

$$= \frac{1}{(2\pi)^3} \int e^{-\frac{\beta \hbar^2 k^2}{2m} + i\left[k_x (x-x') + k_y (y-y') + k_z (z-z')\right]} d^3k =$$

$$e^{ik_x(x-x')} = \cos(k_x(x-x')) + i \sin(k_x(x-x'))$$

$$= \left(\frac{m}{2\pi\beta\hbar^2}\right)^{3/2} e^{-\frac{m}{2\beta\hbar^2} |\bar{r}-\bar{r}'|^2} = \frac{e^{-\frac{m}{2\beta\hbar^2} |\bar{r}-\bar{r}'|^2}}{\lambda^3}$$

$$\lambda = \frac{h}{\sqrt{2\pi m k T}}$$

Next time: we will evaluate for $e^{-\beta H}$ to complete $\hat{\rho}$.

$$\mathrm{tr}\, e^{-\beta \hat{H}} = \int \langle r | \hat{\rho} | r \rangle \, d^3 r = \frac{1}{\lambda^3} \int d^3 r = \frac{V}{\lambda^3}$$

$$\therefore \boxed{\hat{\rho} = \frac{e^{-\frac{m}{2\beta\hbar^2} |\bar{r} - \bar{r}'|^2}}{V}}$$ non-diagonal.

$\rho_{r,r'} = \rho_{r'r}$ symmetric.

$\rho_{rr} = \frac{1}{V}$ $\forall r$ uniform density.