Reminders

1. Exam 1 Monday 10/18 STEM bldg.
   - will share with you a day or 2 before the list of formulas that will be provided
   - Covers material thru lecture 15 (last friday) and HW's 1–4
2. HW 4 due Friday 10/15 11:59 PM
3. Problem session thurs. 2:30–3:30
4. Fridays class – review session for exam

Recap from L15

* QM microstate $\equiv |\Psi(t)\rangle$

* Ensemble avg. over $\mathcal{N}$ mental copies of our system w/ specified macro properties

$$\Rightarrow \quad \overline{O}(t) = \sum_{\alpha=1}^{\mathcal{N}} P_\alpha \langle \Psi^{(\alpha)}(t) | \hat{O} | \Psi^{(\alpha)}(t) \rangle$$

$$= \sum_{n,m} \underbrace{\left(\sum_\alpha P_\alpha \, C^{*(t)}_{m\alpha} \, C^{(t)}_{n\alpha} \right)}_{= \, \rho_{nm}^{(t)} \text{ "Density Matrix"}} \langle m | \hat{O} | n \rangle$$

$$\Rightarrow \quad \boxed{\overline{O}(t) = \sum_{n,m} \rho_{nm}^{(t)} O_{mn} = \mathrm{Tr}\left(\hat{\rho}(t)\hat{O}\right)}$$

$$\hat{\rho}(t) \equiv \sum_{\alpha=1}^{n} p_\alpha \, |\Psi^{(\alpha)}(t)\rangle\langle\Psi^{(\alpha)}(t)| \qquad \text{"density operator"}$$

1. <u>Hermitian</u> $\hat{\rho}^\dagger = \hat{\rho} \implies \hat{\rho} = \sum_i w_i \, |\rho_i\rangle\langle\rho_i|$

   where $\hat{\rho}|\rho_i\rangle = w_i |\rho_i\rangle$

2. <u>Normalization</u> $\mathrm{Tr}\,\rho = 1 = \sum_i w_i$

3. <u>Positivity</u> $0 \le w_i \le 1$

4. <u>Equation of motion</u>; $i\hbar \frac{\partial}{\partial t}\hat{\rho}(t) = [\hat{H}, \hat{\rho}(t)]$

$$\Downarrow$$

$\hat{\rho} = \hat{\rho}(\hat{H})$ for equilibrium $\frac{\partial}{\partial t}\hat{\rho} = 0$

$$\Downarrow$$

$$\boxed{\hat{\rho} = \sum_n w_n \, |E_n\rangle\langle E_n| \quad \text{where } \hat{H}|E_n\rangle = E_n |E_n\rangle}$$

① Microcanonical Ensemble

$$\hat{\rho}_{MCE}(E) = \sum_i \frac{\delta_{E,E_i}}{\Omega(E)} |E_i\rangle\langle E_i| \Rightarrow W_i = \frac{1}{\Omega(E)}$$

② Canonical Ensemble

$$W_n = \frac{e^{-\beta E_n}}{\sum_n e^{-\beta E_n}} = \frac{e^{-\beta E_n}}{Tr\, e^{-\beta \hat{H}}}$$

$$\Rightarrow \boxed{\hat{\rho}_{CE} = \frac{e^{-\beta \hat{H}}}{Tr\, e^{-\beta \hat{H}}}}$$

③ Grand Canonical Ensemble

$$\hat{\rho}_{GCE} = \frac{e^{-\beta(\hat{H}-\mu\hat{N})}}{Tr\, e^{-\beta(\hat{H}-\mu\hat{N})}} \qquad W_{n_N} = \frac{e^{-\beta(E_n^N-\mu N)}}{Z_{GCE}}$$

Tr is over Fock Space (i.e., Hilbert spaces for $N=0,1,2,\ldots\infty$)

$$Tr\, e^{-\beta(\hat{H}-\mu\hat{N})} = \sum_N \sum_n \langle E_n^N | e^{-\beta(\hat{H}-\mu\hat{N})} | E_n^N \rangle$$

example: Find $\hat{\rho}_{CE}$ for a free particle in a box (periodic b.c.'s), and find $\langle \hat{H} \rangle$.

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

$$\psi_E(\vec{x}) = \frac{1}{L^{3/2}} e^{i\vec{k}\cdot\vec{x}} \quad ; \; E = \frac{\hbar^2\vec{k}^2}{2m}$$

$$\psi_E(x+L, y, z) = \psi_E(x, y+L, z) = \psi(x, y, z+L) = \psi_E(x, y, z)$$

$$\Rightarrow \vec{k}_{n_x n_y n_z} = \frac{2\pi}{L}(n_x, n_y, n_z) \qquad n = 0, \pm 1, \pm 2, \ldots$$

* Can use any basis to evaluate $\hat{\rho}_{CE}$ in

$$\Rightarrow \langle \vec{x} | e^{-\beta \hat{H}} | \vec{x}' \rangle = \sum_{n_x n_y n_z} \langle \vec{x} | E_{\vec{n}} \rangle \langle E_{\vec{n}} | \vec{x}' \rangle \, e^{-\beta \frac{\hbar^2 k_n^2}{2m}}$$

$$= \sum_{n_x n_y n_z} \frac{1}{L^3} e^{i\vec{k}_{\vec{n}}\cdot(\vec{x}-\vec{x}')} e^{-\frac{\beta\hbar^2 k_n^2}{2m}}$$

* Use $\frac{1}{L}\sum_{n_x} \xrightarrow{L \gg 1} \int \frac{dk_x}{2\pi}$

$$\Rightarrow \langle \vec{x} | e^{-\beta \hat{H}} | \vec{x}' \rangle = \int \frac{d^3k}{(2\pi)^3} e^{i\vec{k}\cdot(\vec{x}-\vec{x}')} e^{-\beta\frac{\hbar^2\vec{k}^2}{2m}}$$

$$\Rightarrow \langle \vec{x} | e^{-\beta \hat{H}} | \vec{x}' \rangle = \int \frac{d^3k}{(2\pi)^3} e^{i\vec{k}\cdot(\vec{x}-\vec{x}')} e^{-\beta \frac{\hbar^2 \vec{k}^2}{2m}}$$

For each cartesian component, have

$$\int \frac{dk_i}{(2\pi)} e^{i k_i \Delta x_i - \frac{\beta\hbar^2}{2m} k_i^2}$$

$$= \int \frac{dk_i}{(2\pi)} e^{-\frac{\beta\hbar^2}{2m}\left(k_i^2 - \frac{2m}{\beta\hbar^2} i k_i \Delta x_i\right)}$$

$$k_i^2 - \frac{i 2m k_i \Delta x_i}{\beta\hbar^2} = \left[\left(k_i - \frac{i m \Delta x_i}{\beta\hbar^2}\right)^2 + \frac{m^2 \Delta x_i^2}{\beta^2\hbar^4}\right]$$

$$= e^{-\frac{m\Delta x_i^2}{2\beta\hbar^2}} \underbrace{\int \frac{dk_i}{(2\pi)} e^{-\frac{\beta\hbar^2}{2m}\left(k_i - \frac{i m \Delta x}{\beta\hbar^2}\right)^2}}_{=\frac{1}{(2\pi)}\times\sqrt{\frac{\pi}{\alpha}}} \qquad \alpha = \frac{\beta\hbar^2}{2m}$$

$$\Rightarrow \boxed{\langle \vec{x} | e^{-\beta\hat{H}} | \vec{x}' \rangle = \left(\frac{m}{2\pi\beta\hbar^2}\right)^{3/2} e^{-\frac{m}{2\beta\hbar^2}|\vec{x}-\vec{x}'|^2}}$$

* lastly, $\hat{\rho} = \frac{1}{Z} e^{-\beta \hat{H}}$, so

$$Z = \mathrm{Tr}\, e^{-\beta \hat{H}} = \int_{L^3} d\vec{x}\, \langle \vec{x} | e^{-\beta \hat{H}} | \vec{x} \rangle$$

$$= L^3 \left(\frac{m}{2\pi \beta \hbar^2} \right)^{3/2}$$

$$\boxed{\langle \vec{x} | \hat{\rho}_{CE} | \vec{x}' \rangle = \frac{1}{V} e^{-\frac{m}{2\beta\hbar^2} |\vec{x} - \vec{x}'|^2}}$$

* To get $\langle \hat{H} \rangle$, need to evaluate

$$\langle \hat{H} \rangle = \mathrm{Tr}\, \hat{H} \hat{\rho}_{CE}$$

This time, let's use $\{ |E_{\vec{n}}\rangle \}$ states to do the trace.

$$\langle \hat{H} \rangle = \frac{1}{Z} \sum_{n_x n_y n_z} \langle E_{\vec{n}} | \hat{H} e^{-\beta \hat{H}} | E_{\vec{n}} \rangle$$

$$= \frac{1}{Z} \sum_{n_x n_y n_z} e^{-\beta \frac{\hbar^2 \vec{k}_n^2}{2m}} \frac{\hbar^2 \vec{k}_n^2}{2m}$$

$$= \frac{1}{Z} \left(-\frac{\partial}{\partial \beta} \right) \sum_{\vec{n}} e^{-\beta \frac{\hbar^2 \vec{k}_n^2}{2m}} = -\frac{1}{Z} \frac{\partial}{\partial \beta} Z$$

* but $\quad Z = V \left(\dfrac{m}{2\pi\beta\hbar^2}\right)^{3/2}$

$$\therefore \quad \frac{\partial Z}{\partial \beta} = -\frac{3}{2}\left(\frac{Vm}{2\pi\beta\hbar^2}\right)^{3/2} \cdot \frac{1}{\beta} = -\frac{3}{2} Z \frac{1}{\beta}$$

$$\boxed{\therefore \quad \langle \hat{H} \rangle = \frac{3}{2}\frac{1}{\beta} = \frac{3}{2} k_B T \quad \checkmark}$$

N identical particles (non-interacting) in a box

* I claim that our fully QM formulation using the density operator $\hat{\rho}$ eliminates the need for ad-hoc $\frac{1}{N!}$ Gibbs correction factors $\left(Z_N = (Z_1)^N \longrightarrow \frac{1}{N!}(Z_1)^N \right)$ that only work at low density & high T where $\langle n_k \rangle \ll 1$,

* We can get an idea why this is since

$$\hat{\rho} = \sum_n W_n |E_n\rangle\langle E_n|$$

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

these are N-particle wf's, and we know how to treat identical particles by symmetrizing (Bosons) or Antisymmetrizing (Fermions) wf's.

* The detailed calculation of $\hat{\rho}$ for the canonical Ensemble is a bit tedious (next time we'll see the GCE offers technical simplifications)

* Therefore, I'd like to "preview" our end result so you know where we're going in the tedious derivation to follow

$$\Downarrow$$

We will find:

$$Z_N = \frac{1}{N!\, l_Q^{3N}} \int \prod_{\alpha=1}^{N} d^3\vec{x}_\alpha \sum_P \eta^P e^{-\frac{\pi}{l_Q^2} \sum_{\alpha=1}^{N} (\vec{x}_\alpha - \vec{x}_{P\alpha})^2}$$

$$l_Q = \sqrt{\frac{2\pi\hbar^2}{m k_B T}}$$

* Sum over $N!$ permutations of particle labels $(1\,2\,3\,..\,N) \rightarrow (P1\,P2\,...\,PN)$

* $\eta = \begin{cases} +1 & \text{bosons} \\ -1 & \text{fermions} \end{cases}$

* η^{P} — # of pairwise exchanges to go from $(1\,2\,..\,N) \longrightarrow (P1\,P2\,..\,PN)$

$$Z_N = \frac{1}{N!\, \ell_\alpha^{3N}} \int \prod_{a=1}^{N} d^3\vec{x}_a \sum_P \eta^P e^{-\frac{\pi}{\ell_\alpha^2}\sum_{\alpha=1}^{N}(\vec{x}_\alpha - \vec{x}_{P\alpha})^2} \quad (X)$$

Compare vs our earlier result

$$Z_N = \left(\frac{V}{\ell_\alpha^3}\right)^N \rightarrow \frac{1}{N!}\left(\frac{V}{\ell_\alpha^3}\right)^N \quad \text{valid at high } T$$

$\Rightarrow$ This will correspond to $\ell_\alpha \to 0$, so the dominant term in (X) is when

$$\vec{x}_\alpha - \vec{x}_{P\alpha} = 0$$

(or P = the identity permutation

$(1\,2\,3 \cdots N) \longrightarrow (1\,2\,3 \cdots N]$)

$\therefore$ in that limit, we see eq. (X) has the correct $\frac{1}{N!}$ built in!

Symmetrization Postulate for N identical Particle Systems

* 2 types of particles $\left\langle \begin{array}{l} \text{Bosons (spin } 0,1,2,\ldots) \\ \text{Fermions (spin } \frac{1}{2}, \frac{3}{2}, \ldots) \end{array} \right.$ occur in Nature.

* Wf's for N-identical particles are either totally symmetric under exchanges (BOSONS) or totally Anti-Symmetric (FERMIONS) [Cf. Spin-Statistics thm. of QFT]

[Before the spin-Statistics thm in QFT, the founders of QM figured this need for Sym/Anti-Sym. wf's from Zeeman spectra (fermions) + Planck Radiation law (bosons)]

$$\hat{P}\,|\Psi(1,2,\ldots N)\rangle \equiv |\Psi(P1,P2,\ldots,PN)\rangle = \xi^{p}\,|\Psi(1,2,\ldots N)\rangle$$

Permutation operator

$\xi = +1$ Bosons
$\quad\;\; -1$ Fermions

$(P1,P2,\ldots PN)$ permutation of $(1,2,\ldots N)$

p = "parity of permutation"
= # of pairwise transpositions to bring $(P1,P2,\ldots PN)$ into $(1,2,\ldots N)$

* let $\mathcal{H}$ = Hilbert space of 1-particle systems

$\{|\alpha\rangle\}$ = orthonormal basis obeying $\langle\alpha|\beta\rangle = \delta_{\alpha\beta}$, $\sum_{\alpha} |\alpha\rangle\langle\alpha| = \mathbb{1}_{\text{1-body}}$

<u>* Extend to N-body system:</u> $\mathcal{H}_N = \underbrace{\mathcal{H}\otimes\mathcal{H}\otimes\cdots\otimes\mathcal{H}}_{N\text{-copies}}$

<u>orthonormal basis:</u> $|\alpha_1\alpha_2\cdots\alpha_N) \equiv |\alpha_1\rangle\otimes|\alpha_2\rangle\otimes\cdots\otimes|\alpha_N\rangle$ Note the curved bracket!

$$\sum_{\alpha_1\cdots\alpha_N} |\alpha_1\cdots\alpha_N)(\alpha_1\cdots\alpha_N| = \mathbb{1}_{\mathcal{H}_N}$$

$$(\alpha_1\alpha_2\cdots\alpha_N|\alpha_1'\alpha_2'\cdots\alpha_N') = \langle\alpha_1|\alpha_1'\rangle\langle\alpha_2|\alpha_2'\rangle\cdots\langle\alpha_N|\alpha_N'\rangle$$
$$= \delta_{\alpha_1\alpha_1'}\delta_{\alpha_2\alpha_2'}\cdots\delta_{\alpha_N\alpha_N'}$$

<u>Claim:</u> Un-symmetrized basis $|\alpha_1\cdots\alpha_N)$ OK for N-Distinguishable particles but <u>NOT</u> for identical particles

* For N-non-interacting particles,

$$\hat{H} = \sum_{a=1}^{N} \hat{H}_a = \sum_{a=1}^{N} -\frac{\hbar^2}{2m} \vec{\nabla}_a^{\,2}$$

* If these were distinguishable, the $|E_i\rangle$ states would just be unsymmetrized product states

$$|E_i\rangle = |\vec{k}_1 \vec{k}_2 \cdots \vec{k}_N)$$

and

$$\hat{H}\,|\vec{k}_1 \vec{k}_2 \ldots \vec{k}_N) = \left(\sum_{a=1}^{N} \frac{\hbar^2 \vec{k}_a^{\,2}}{2m} \right) |\vec{k}_1 \cdots \vec{k}_N)$$

* We need to construct properly anti-symmetric (fermions) or symmetric (bosons) states

Fermionic Case

$$|\vec{k}_1 \vec{k}_2 \cdots \vec{k}_N\rangle_- = \frac{1}{\sqrt{N_-}} \sum_P (-1)^P \, \hat{P} \, |\vec{k}_1 \cdots \vec{k}_N)$$

Sum over all N! permutations

for normalization $N_- = N!$

e.g: $N=2$ $\quad |\vec{k}_1 \vec{k}_2\rangle_- = \frac{1}{\sqrt{2!}} \left[|\vec{k}_1 \vec{k}_2) - |\vec{k}_2 \vec{k}_1) \right]$

e.g. $N=3$ $\quad |\vec{k}_1\vec{k}_2\vec{k}_3\rangle_- = \frac{1}{\sqrt{3!}}\Big[|\vec{k}_1\vec{k}_2\vec{k}_3) + |\vec{k}_3\vec{k}_1\vec{k}_2) + |\vec{k}_2\vec{k}_3\vec{k}_1) - |\vec{k}_2\vec{k}_1\vec{k}_3) - |\vec{k}_3\vec{k}_2\vec{k}_1) - |\vec{k}_1\vec{k}_3\vec{k}_2) \Big]$

Note: 1. all the $\vec{k}_i$ in $|\vec{k}_1\vec{k}_2\cdots\vec{k}_N\rangle_-$ must be different or else you get 0 (Pauli Principle)

e.g. $|\vec{k}_1\vec{k}_1\vec{k}_3\rangle_-$ plug in to above + you'll get 0.

2. Since all $N!$ terms in $\sum_P (-1)^P \hat{P}|\vec{k}_1\cdots\vec{k}_N)$ are different, + since each term is normalized, we see why the overall normalization

$$\frac{1}{\sqrt{N_-}} = \frac{1}{\sqrt{N!}}$$

Bosonic Case

$$|\vec{k}_1\vec{k}_2\cdots\vec{k}_N\rangle_+ = \frac{1}{\sqrt{N_+}} \sum_P \hat{P}|\vec{k}_1\cdots\vec{k}_N)$$

Note: 1. no restriction on $\vec{k}_1 \neq \vec{k}_2 \neq \cdots \neq \vec{k}_N$

e.g., $\sum_P \hat{P}|\vec{k}\vec{k}) = |\vec{k}\vec{k}) + |\vec{k}\vec{k}) = 2|\vec{k}\vec{k})$

vs.

$\sum_P (-1)^P \hat{P}|\vec{k}\vec{k}) = |\vec{k}\vec{k}) - |\vec{k}\vec{k}) = 0$

$\therefore$ a certain $\vec{k}$ may be repeated $n_{\vec{k}}$-times and $\sum_{\vec{k}} n_{\vec{k}} = N$

(2) Normalization $N_+ = N! \prod_{\vec{k}} n_{\vec{k}}!$

e.g.: $|\vec{k}_1, \vec{k}_1, \vec{k}_2\rangle_+ = \frac{1}{\sqrt{3!\,2!\,1!}} \Big[|\vec{k}_1\vec{k}_1\vec{k}_2) + |\vec{k}_2\vec{k}_1\vec{k}_1) + |\vec{k}_1\vec{k}_2\vec{k}_1) + |\vec{k}_1\vec{k}_1\vec{k}_2) + |\vec{k}_2\vec{k}_1\vec{k}_1) + |\vec{k}_1\vec{k}_2\vec{k}_1) \Big]$

$$= \frac{1}{\sqrt{3}} \Big[|\vec{k}_1\vec{k}_2\vec{k}_2) + |\vec{k}_2\vec{k}_1\vec{k}_1) + |\vec{k}_1\vec{k}_2\vec{k}_1) \Big]$$

$\therefore \; {}_+\langle \vec{k}_1, \vec{k}_1, \vec{k}_2 | \vec{k}_1, \vec{k}_1, \vec{k}_2 \rangle_+ = 1$

Unified notation

$$|\{\vec{k}\}\rangle_\eta = \frac{1}{\sqrt{N! \prod_{\vec{k}} n_{\vec{k}}!}} \sum_P \eta^P \hat{P} |\{\vec{k}\})$$

$\eta = +1$ Bosons

$\quad = -1$ Fermions

where $n_{\vec{k}} = \{ 0$ or 1 (Fermions)

$n_{\vec{k}} = 0, 1, 2, \ldots$ (Bosons

and $\sum_{\vec{k}} n_{\vec{k}} = N$

Completeness:

* If $\sum_{\vec{k}} |\vec{k}\rangle\langle\vec{k}| = \mathbb{1}_1$, then for N <u>distinguishable</u> particles

$$\mathbb{1}_N = \sum_{\vec{k}_1 \cdots \vec{k}_N} |\vec{k}_1 \cdots \vec{k}_N)(\vec{k}_1 \cdots \vec{k}_N|$$

* For N identical particles,

$$\mathbb{1}_{N,\eta} = \sum_{\{\vec{k}\}}{}' \, |\{\vec{k}\}\rangle_\eta \, {}_\eta\langle\{\vec{k}\}|$$

<u>Where</u> $\sum_{\{\vec{k}\}}'$ means only summing

over <u>distinct</u> N-particle states

<u>e.g.</u> N=2 for fermions

$$\mathbb{1}_{2,-} = \sum_{\vec{k}<\vec{k}'} |\vec{k}\vec{k}'\rangle_- \, {}_-\langle\vec{k}\vec{k}'|$$

Since $\vec{k} > \vec{k}'$ is gotten from

$$\hat{P}_{12} |\vec{k}'\vec{k}\rangle = (-1) |\vec{k}\vec{k}'\rangle$$

i.e., $|\vec{k}\vec{k}'\rangle$ & $|\vec{k}'\vec{k}\rangle$ are
the same physical state
(just differ by a phase)
& shouldn't be counted twice.

Claim: You can use unrestricted sums for $\mathbb{1}_{N,\eta}$ if you add the correction factor for overcounting

$$\sum_{\{\vec{k}\}}{}' \, |\{\vec{k}\}\rangle_\eta \, {}_\eta\langle\{\vec{k}\}| = \sum_{\{\vec{k}\}} \frac{\prod_{\vec{k}} n_{\vec{k}}!}{N!} \, |\{\vec{k}\}\rangle_\eta \, {}_\eta\langle\{\vec{k}\}|$$

Evaluation in Canonical Ensemble for ideal Gas

$$\hat{\rho} = \sum_i w_i \, |E_i\rangle\langle E_i| \qquad w_i = \frac{e^{-\beta E_i}}{Z_N}$$

$$|E_i\rangle = |\{\vec{k}\}\rangle_\eta$$

$$\therefore \hat{\rho} = \sum_{\{\vec{k}\}}{}' \frac{e^{-\beta \hat{H}}}{Z_N} \, |\{\vec{k}\}\rangle_\eta \, {}_\eta\langle\{\vec{k}\}|$$

$$\boxed{\begin{aligned} \hat{\rho} &= \sum_{\{\vec{k}\}}{}' \frac{1}{Z_N} e^{-\beta \sum_{a=1}^{N} \frac{\hbar^2 k_a^2}{2m}} \, |\{\vec{k}\}\rangle_\eta \, {}_\eta\langle\{\vec{k}\}| \\ &= \sum_{\{\vec{k}\}} \frac{1}{Z_N} e^{-\beta \sum_{a=1}^{N} \frac{\hbar^2 \vec{k}_a^2}{2m}} \frac{\prod_{\vec{k}} n_{\vec{k}}!}{N!} \, |\{\vec{k}\}\rangle_\eta \, {}_\eta\langle\{\vec{k}\}| \end{aligned}}$$