4/2/23

(1)

I) Review:

- Origins of $q_{atom} = q_n q_e q_t$ and $\frac{Q_{classical}}{N!}$ $= \frac{(q_{ATOM})^N}{N!}$
FOR N ATOMS IN 1-STATE BOX IN HIGH TEMP/LOW N/V CLASSICAL LIMIT (WHERE $\frac{Q_{CLASSICAL}}{N!}$ ACCOUNTS FOR PARTICLE INDISTINGUISHABILITY)

A) a) $\hat{H}_{sys}|\psi_s\rangle = E_{sys}|\psi_{sys}\rangle$

b) N non-interacting ptcls:

(1.1a) $\boxed{\hat{H}_{sys} = \hat{H}_{ptcl_1} + \hat{H}_{ptcl_2} + \dots}$

(1.1b) $\boxed{|\psi_{sys}\rangle = |\psi_{ptcl_1}\rangle|\psi_{ptcl_2}\rangle \dots}$

(1.1c) $\boxed{E_{sys} = \epsilon_{p_1} + \epsilon_{p_2} + \epsilon_{p_3} + \dots}$

c) $\Rightarrow \hat{H}_{sys}|\psi_{sys}\rangle = [\hat{H}_{ptcl_1} + \dots]|\psi_{p_1}\rangle|\psi_{p_2}\rangle \dots$

d) $\Rightarrow [\hat{H}_{sys}]|\psi_{p_1}\rangle|\psi_{p_2}\rangle \dots = (\epsilon_{p_1} + \epsilon_{p_2} + \epsilon_{p_3} \dots)|\psi_{p_1}\rangle|\psi_{p_2}\rangle \dots$

e) d) $\Rightarrow$

(1.2)
$$\boxed{\begin{aligned} &\hat{H}_{p_1}|\psi_{p_1}\rangle[|\psi_{p_2}\rangle|\psi_{p_3}\rangle \dots] + \\ &+ \hat{H}_{p_2}|\psi_{p_2}\rangle[|\psi_{p_1}\rangle|\psi_{p_2}\rangle|\psi_{p_3}\rangle \dots] \\ &+ \hat{H}_{p_3}|\psi_{p_3}\rangle[|\psi_{p_1}\rangle|\psi_2\rangle|\psi_{p_4}\rangle \dots] + \dots \\ &= (\epsilon_1 + \epsilon_2 + \epsilon_3 + \dots)|\psi_{p_1}\rangle|\psi_{p_2}\rangle|\psi_{p_3}\rangle \dots \end{aligned}}$$

f) e) $\Rightarrow$

(1.3)
$$\boxed{\begin{aligned} &(\hat{H}_{p_1}|\psi_{p_1}\rangle - \epsilon_{p_1}|\psi_{p_1}\rangle) \cdot \left[\frac{\cancel{\psi_{p_2} \cdot \psi_{p_3} \cdot \psi_{p_4} \dots}}{\cancel{\psi_{p_2} \cdot \psi_{p_3} \cdot \psi_{p_4} \dots}}\right] + \\ &+ (\hat{H}_{p_2}\psi_{p_2} - \epsilon_{p_2}\psi_{p_2}) \cdot \left[\frac{\cancel{\psi_{p_1} \psi_{p_3} \psi_{p_4} \dots}}{[\psi_{p_1} \psi_{p_3} \psi_{p_4} \dots]}\right] + = 0 \end{aligned}}$$

g) (1.3) $\Rightarrow$ $\boxed{\hat{H}_{ATOM,s}|\psi_{ATOM,s}\rangle = \epsilon_{ATOM_s}|\psi_{ATOM,s}\rangle}$ $s = 1, 2, \dots N$ (1.4)

∴ B) Now assume random dyn. of nucleus, electron cloud, COM are all stat. indep. ∴

{C.O.M = ATOM's center-of-mass

(2.1a) a) $\hat{H}_{ATOM,s} = \hat{H}_{nuc,s} + \hat{H}_{e,s} + \hat{H}_{t,s}$

(2.1b) b) $|\psi_{A,s}\rangle = |\psi_{n,s}\rangle|\psi_{e,s}\rangle|\psi_{t,s}\rangle$

(2.1c) c) $\epsilon_{A,s} = \epsilon_{n,s} + \epsilon_{e,s} + \epsilon_{t,s}$

$s = 1, 2, \ldots, N$

n = nuc = nucleus
e = electron cloud
COM = translation of COM

A = ATOM

∴ d) Using same steps as on pg 1:

(2.2a) $\hat{H}_{nuc,s}|\psi_{n,s}\rangle = \epsilon_{n,s}|\psi_{n,s}\rangle$

(2.2b) $\hat{H}_{e,s}|\psi_{e,s}\rangle = \epsilon_{e,s}|\psi_{e,s}\rangle$

(2.2c) $\hat{H}_{t,s}|\psi_{t,s}\rangle = \epsilon_{t,s}|\psi_{t,s}\rangle$

$s = 1, 2, 3, \ldots N$

II) METHOD (ARGUMENT) FOR OBTAINING $Q_{sys\ classical}$, where

$$\frac{Q_{sys\ classical}}{N!} = \frac{\sum_j e^{-\beta \epsilon_{sys,j}}}{N!} = $$

proper classical limit of system quantum distbn. fn., that accts for particles indistinguishability

A) METHOD / ARG:

a) N-particle system is in canonical ensemble of $\tilde{N}$ replica systems

b) $\tilde{N} = n_1 + n_2 + n_3 + \ldots$

$\tilde{E} = n_1 E_1 + n_2 E_2 + n_3 E_3 + \ldots$

$$W(\{n\}) = \frac{N!}{n_1! n_2! n_3! \ldots}$$

$$F \equiv \ln W(\{n\}) - \alpha\left[\tilde{N} - \sum_r n_r\right] - \beta\left[\tilde{E} - \sum_r n_r E_r\right]$$

$$\frac{\partial F}{\partial n_r} = 0 \Rightarrow \boxed{\frac{n_r^*}{\tilde{N}} = \frac{\exp[-\beta E_r]}{\sum_{r'} e^{-\beta E_{r'}}}} \quad (3.1)$$

n_j = no. of N-ptcl systems in quant system eigenstate E_j

$\tilde{N}$ = total no. of replica N-ptcl systems in canonical ens. ($\tilde{N}$ fixed).

$\tilde{E}$ = total (fixed) energy of $\tilde{N}$ systems in ensemble

c) In (3.1), $\boxed{Q \equiv \sum_{r'} e^{-\beta E_{r'}}}$ (3.2)

Q IN (3.2) II) CONT'D

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- Λ corresponds to $Q^{sys}_{classical}$ AT TOP OF PG. (3)

(1) Q in (3.2) implicitly assumes that the $\tilde{N}$ systems are identifiable, distinguishable. $\boxed{\text{GIBB'S}}$ ARGUED, IN $\boxed{\text{AD HOC}}$ FASHION, THAT TO OBTAIN CORRECT MACROSCOPIC THERMODYNAMIC EXPRESSIONS,

$Q = Q^{sys}_{classical}$ MUST BE DIVIDED BY $N!$ ($\Leftarrow$ GIBB'S FACTOR)

III) (7) $\boxed{\text{LECTURE 18h}}$ shows that a RIGOROUS QUANTUM MECHANICS-BASED ARGUMENT LEADS, ORGANICALLY, TO

$$\boxed{Q^{sys}_{\substack{proper\\ \text{QUANTUM,}\\ \text{HIGH T,}\\ \text{LOW N/V}\\ \text{LIMIT}}} = \frac{Q^{sys}_{classical}}{N!}} \quad (4.1)$$

III) HILL'S DEMONSTRATION THAT

$$Q_{\substack{\text{sys}\\\text{classical}\\N\text{-ptcl}}} = \left(q_{1\,\text{ptcl}}\right)^N$$

HIGH TEMP, LOW N/V LIMIT; NON-INTERACTING N-ptcl system

Ref: Hill pg. 61

A) EXPRESS SYSTEM QUANTUM ENERGY, E, AS sum of individual ptcl Q. Energies

(5.1) $\boxed{E = \epsilon_a + \epsilon_b + \epsilon_c + \ldots}$

where ϵ_a is the energy of energy of (distinguishable) ptcl a, and ptcls is labeled as a, b, c, d . . .

B) CONSIDER A SYSTEM OF 2 ptcls (N=2), each [a] and [b] having access to 2 SINGLE ptcl quantum energy states. In this case;

(5,1)
$$\boxed{Q_{\substack{\text{sys}\\\text{classical}}} = \left(\sum_{j=1}^{2} e^{-B\epsilon_{a_j}}\right)\left(\sum_{j=1}^{2} e^{-B\epsilon_{b_j}}\right)}$$

$$= \left(e^{-Ba_1} + e^{-Ba_2}\right)\left(e^{-Bb_1} + e^{-Bb_2}\right)$$

$$= \left(\left(e^{-B(a_1+b_1)} + e^{B(a_1+b_2)} + \right.\right.$$

$$+ e^{-\beta(\epsilon_{a_2} + \epsilon_{b_1})} + e^{-\beta(\epsilon_{a_2} + \epsilon_{b_2})} \} \}$$

IN OTHER WORDS, SINCE

$$(6.1) \quad \boxed{\begin{aligned} Q_{\substack{sys \\ classical}} = \; & e^{-\beta(\epsilon_{a_1} + \epsilon_{b_1})} + \\ & + e^{-\beta(\epsilon_{a_1} + \epsilon_{b_2})} + \\ & + e^{-\beta(\epsilon_{a_2} + \epsilon_{b_1})} + \\ & + e^{-\beta(\epsilon_{a_2} + \epsilon_{b_2})} \end{aligned}}$$

THE product decomposition in EQ (5.1) provides all possible combinations of ϵ_{a_j} and ϵ_{b_j}.

c) Defining $\boxed{\sum_j e^{-\beta\epsilon_{a_j}}}$ as $\boxed{q_a}$, the partition fn for ptcl. $\boxed{a}$, etc, in (5.1):

$$(6.1) \quad \boxed{Q_{\substack{sys \\ class}} = q_a \cdot q_b \cdot q_c \cdots q_N}$$

D) IN THE CASE where all N ptcls are the same,

$$\boxed{q_a = q_b = q_c = \ldots = q_N \equiv q} \quad (7.1)$$

so that:

$$\boxed{Q_{\substack{sys\\class}} = (q)^N} \quad (7.2)$$

E) FINALLY, THE PROPER = PHYSICALLY RIGOROUS PARTITION FN, (WHICH ACCOUNTS FOR PARTICLE INDISTINGUISHABILITY) – SEE LECTURE 18h.

IS GIVEN BY

$$\boxed{Q_{\substack{proper\\sys}} = \frac{Q_{sys}}{N!} = \frac{q^N}{N!}} \quad (7.3)$$

EASY / TRIVIAL

V) EXTENSION OF HILL'S ARG LEADING TO $Q_{SYS\ classical} = (q)^N$, TO SHOW THAT

$$(8.1)\quad q_{ATOM} = q_{NUC} \cdot q_{\substack{elec\\cloud}} \cdot q_{translation}$$

a) $$\boxed{q_{ATOM} = \sum_{ijk} e^{-\beta \varepsilon_{ATOM}(i,j,k)}} \quad (8.2)$$

b) TO SHOW THAT (8.2) CAN BE expressed as

$$q_{ATOM} = \left(\sum_{n_j=1}^{\overset{w_{n_j}}{\vee}} e^{-\beta\epsilon_{n_j}}\right)\left(\sum_{j=1}^{\overset{w_{e_j}}{\vee}} e^{-\beta\epsilon_{el_j}}\right)\left(\sum_{j=1}^{\overset{w_{t_j}}{\vee}} e^{-\beta\epsilon_{t_j}}\right)$$

CONSIDER THE CASE WHERE the nucleus, electron cloud, and C. O. Mass ~~are~~ can each be found in 2 quantum states

$$\sum_{n_j=1}^{2} \overset{w_{n_j}}{\vee} e^{-\beta\epsilon_{n_j}} = w_{n_1} e^{-\beta\epsilon_{n_1}} + w_{n_2} e^{-\beta\epsilon_{n_2}}$$

$$\sum_{j=1}^{2} \overset{w_{el_j}}{\vee} e^{-\beta\epsilon_{el_j}} = w_{e_1} e^{-\beta\epsilon_{el_1}} + w_{e_2} e^{-\beta\epsilon_{el_2}}$$

$$\sum_{j=1}^{2} w_{t_j} e^{-\beta\epsilon_{t_j}} = w_{t_1} e^{-\beta\epsilon_{t_1}} + w_{t_2} e^{-\beta\epsilon_{t_2}}$$

V c) using same argument as on pp. 5-6,

$$\boxed{q_{atom} = q_n \cdot q_e \cdot q_t} \qquad (9.1)$$

where

$$\boxed{\begin{aligned} q_n &= \sum_{j=1} \omega_{n_j} e^{-\beta \epsilon_{n_j}} \\ q_e &= \sum_{j=1} \omega_{e_j} e^{-\beta \epsilon_{e_j}} \\ q_t &= \sum_{j=1} \omega_{t_j} e^{-\beta \epsilon_{t_j}} \end{aligned}} \qquad (9.1a)$$

VI) Finally, collecting results, for a high temp, low N/V non-interacting system of N atoms (of single kind):

$$\boxed{Q_{proper} = \frac{Q_{sys\ classical}}{N!} = \frac{(q_{atom})^N}{N!}} \qquad (9.2)$$

or

$$\boxed{Q_{proper} = \frac{q_n^N q_e^N q_t^N}{N!}} \qquad (9.3)$$