Formulation of Quantum Statistical Mechanics

Hamiltonian for N indistinguishable particles

$$\hat{H}(1, \dots, N).$$

P_{ij} : permutation operator.

$$\hat{P}_{ij}\, \Psi(\dots, \underset{\uparrow\,\text{spin + position}}{x_i}, \dots, x_j, \dots) = \Psi(\dots, x_j, \dots, x_i, \dots)$$

For indistinguishable particles:

$$\underbrace{[\hat{P}_{ij}, \hat{H}]}_{\text{commutator.}} = 0$$

$\rightarrow$ $\hat{P}_{ij}$ and $\hat{H}$ have simultaneous eigenstates:

$$\hat{H}|\Psi\rangle = E|\Psi\rangle$$

$$\hat{P}_{ij}|\Psi\rangle = \lambda|\Psi\rangle.$$

We have $\hat{P}_{ij}^2 = \mathbb{1} \rightarrow \lambda^2 = 1$ and λ is real

$$\rightarrow \lambda = \pm 1.$$

Spin-Statistics theorem

Half-integer spin : $\lambda = -1$ always Fermions

Integer spin : $\lambda = +1$ always Bosons.

Examples: 2 particle wave functions:

$$\langle x_1 x_2|\Psi\rangle = \frac{1}{\sqrt{2}}\left(\langle x_1|\chi_1\rangle\langle x_2|\chi_2\rangle \pm \langle x_1|\chi_2\rangle\langle x_2|\chi_1\rangle\right)$$

Many-body fermion wavefunction:

$$\langle\{x_i\}|\Psi_F\rangle = \frac{1}{\sqrt{N!}}\begin{vmatrix} \langle x_1|\chi_1\rangle & \cdots & \langle x_1|\chi_N\rangle \\ \langle x_2|\chi_1\rangle & \cdots & \langle x_2|\chi_N\rangle \\ \vdots & & \\ \langle x_N|\chi_1\rangle & \cdots & \langle x_N|\chi_N\rangle \end{vmatrix}$$

antisymmetric, normalized.

Slater determinant

$$= \frac{1}{\sqrt{N!}} \sum_P \underbrace{\epsilon_p}_{\text{sign, } \pm 1} \langle x_1|\chi_{P_1}\rangle \cdots\cdots \langle x_N|\chi_{P_N}\rangle$$

Note: at most 1 particle / orbital (Pauli principle).

For Bosons:

$$\langle\{x_i\}|\Psi_B\rangle = \frac{1}{\sqrt{N!}}\sum_P \langle x_1|\chi_{P_1}\rangle \cdots \langle x_N|\chi_{P_N}\rangle.$$

$\rightarrow$ More than one particle per orbital possible.

Norm: $\langle\Psi_B|\Psi_B\rangle = n_1!\, n_2! \cdots$

nr of particles in state 1 etc.

Example: $\langle x_1|\chi\rangle\langle x_2|\chi\rangle$ is a symmetric, normalized state

$$\frac{1}{\sqrt{2!}}\left(\langle x_1|\chi\rangle\langle x_2|\chi\rangle + \langle x_2|\chi\rangle\langle x_1|\chi\rangle\right) = \sqrt{2!}\,\langle x_1|\chi\rangle\langle x_2|\chi\rangle.$$

For $\hat{H} = \hat{h}_1 + \hat{h}_2 + \cdots + \hat{h}_N$, (Free particles)

these (anti)symmetrized wavefunctions are eigenfunctions of $\hat{H}$, provided that

$$\underline{\hat{h}|\chi_j\rangle = \epsilon_j|\chi_j\rangle}$$

If $\hat{H}$ contains interactions, these wavefunctions are no longer eigenstates of $\hat{H}$.

However, they can still be used as a basis of the Hilbert space.

$\neq$

Example Free particles in a box

$$\hat{H} = \sum_{j=1}^{N} \frac{p_j^2}{2m}. \qquad \langle \underline{r} | \chi_{\underline{k}} \rangle = \frac{1}{L^{3/2}} e^{i\underline{k}\cdot\underline{r}} \;;\; \epsilon_{\underline{k}} = \frac{\hbar^2 k^2}{2m}$$

Partition function:

$$\mathrm{Tr}\, e^{-\beta\hat{H}} = \sum_{\underline{k}_1 \dots \underline{k}_N} {}_{F,B}\langle \underline{k}_1 \dots \underline{k}_N | e^{-\beta\hat{H}} | \underline{k}_1 \dots \underline{k}_N \rangle_{F,B} = Z_N$$

sums over all permutations.

If in a permutation in the left state the k for particle j is different from that in the right state, we obtain a 0.

Therefore the k's in the left and right state should occur in the same order.

$$\rightarrow \langle \underline{k}_1 \dots \underline{k}_N | e^{-\beta\hat{H}} | \underline{k}'_1 \dots \underline{k}'_N \rangle = e^{-\beta\sum_{j=1}^{N}\frac{\hbar^2 k_j^2}{2m}} \prod_{j=1}^{N} \delta^3(\underline{k}_j - \underline{k}'_j)$$

Note that $\sum_{\underline{k}} \rightarrow \frac{L^3}{(2\pi)^3}\int d^3k$

$$\text{so} \quad Z_N = \frac{L^{3N}}{(2\pi)^{3N}} \frac{1}{N!} \int d^3k_1 \dots d^3k_N \, e^{-\beta\sum_{j=1}^{N}\frac{\hbar^2 k^2}{2m}}$$

$$= \frac{V^N}{N!} \lambda^{3N}$$ $\to$ The same as the classical part. function!

Two particles.

'reduced' density matrix.

$$\mathbb{1} = \sum_{\underline{k}} |\underline{k}\rangle\langle\underline{k}|$$

$$\langle \underline{r}_1, \underline{r}_2 | e^{-\beta\hat{H}} | \underline{r}_1, \underline{r}_2 \rangle =$$

$$\frac{V^2}{4} \int \frac{d^3k_1}{(2\pi)^3} \frac{d^3k_2}{(2\pi)^3} \left(\langle \underline{r}_1 \underline{r}_2 | \underline{k}_1 \underline{k}_2 \rangle \pm \langle \underline{r}_1 \underline{r}_2 | \underline{k}_2 \underline{k}_1 \rangle \right) e^{-\beta \frac{\hbar^2}{2m}(k_1^2 + k_2^2)} \left(\langle \underline{k}_1 \underline{k}_2 | \underline{r}_1 \underline{r}_2 \rangle \pm \langle \underline{k}_2 \underline{k}_1 | \underline{r}_1 \underline{r}_2 \rangle \right)$$

$$\frac{1}{L^3} e^{i(\underline{k}_1 \cdot \underline{r}_1 + \underline{k}_2 \cdot \underline{r}_2)} \qquad \frac{1}{L^3} e^{i(\underline{k}_1 \cdot \underline{r}_2 + \underline{k}_2 \cdot \underline{r}_1)}$$

$$= \frac{1}{4} \left(\frac{1}{\lambda^6} + \frac{1}{\lambda^6} + \int \frac{d^3k_1 \, d^3k_2}{(2\pi)^6} e^{-\beta\frac{\hbar^2}{2m}(k_1^2 + k_2^2)} e^{i k_1 (\underline{r}_1 - \underline{r}_2)} e^{i k_2 (\underline{r}_2 - \underline{r}_1)} + c.c. \right)$$

$$= \frac{1}{2\lambda^6} \left[1 \overset{B}{\underset{F}{\pm}} \underbrace{e^{-2\pi (r_{12}/\lambda)^2}} \right]$$