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8. Summary



1. Learning Outcomes

After studying this module, you shall be able to

- Understand the need to go beyond classical Statistical Mechanics or semi-classical statistical mechanics which we have done till this point.
 - Express statistical mechanics compatible with the postulates of quantum mechanics
 - comprehend the requirement of replacing density distribution function ρ used in classical statistical averaging by density matrix $[\rho_{mn}]$ in quantum statistical averaging, a double averaging procedure one necessitated by quantum mechanics and other necessitated by the requirement of statistical procedure because of inherent lack of complete information typical characteristic of a macroscopic system.
 - arrive at generic idea of density matrix for a system under study and discuss its various properties.
 - Derive quantum mechanical analogue of Liouville's theorem.
 - Calculate the mean value of an observable physical quantity represented by a quantum mechanical operator, unfolding a prescription to calculate mean value of any observable property of the quantum macroscopic system.
 - Derive Density matrix in various ensembles
 - Apply the formalism developed to three prototype problems, namely,
 - an electron in a magnetic field,
 - a free particle in a box and
 - a linear harmonic oscillator.
- to calculate density matrix corresponding to these.
- Comprehend the consequences of indistinguishability of particles in quantum systems and symmetry properties of their wave functions in the statistical considerations of quantum macroscopic systems
 - Understand the link between spin and statistics.

2. Introduction

Up to this point in our study of statistical physics, we treated macroscopic systems either purely classically or in semi-classical sense without invoking proper quantum mechanics i.e. the solutions of the Schrodinger equation involved for the study of the system. Classically, state of the system is said to be specified once the position and momenta of all particles constituting the system gets specified. However, because of Heisenberg's Uncertainty principle, position and momenta cannot be specified simultaneously. In quantum mechanics, we deal with Hermitian operators which represent physically observable quantities with real eigen values. Some often encountered operators are \hat{H} , \hat{L} and \hat{S} representing respectively energy, angular momentum and spin angular momentum. Many physical quantities, like spin angular momentum, have no classical analogue. Each of the operators, operates on a vector space the so called Hilbert space. The state of the system at a certain time t is specified by a state vector $|\psi(t)\rangle$. Time evolution of the state $|\psi(t)\rangle$ is governed via the Schrodinger equation

$$i\hbar \frac{\partial |\psi(t)\rangle}{\partial t} = \hat{H}|\psi(t)\rangle \quad (1)$$

Knowing $|\psi(t)\rangle$ allows one to calculate all characteristics of the system equivalent to knowing the microstate of the system. The co-ordinate representation of the system is described by the wave function $\psi(\mathbf{q}, t) = \langle \mathbf{q} | \psi(t) \rangle$ an inner product of spatial and temporal function. Quantum mechanics is inherently probabilistic in nature such that $|\psi(\mathbf{q}, t)|^2$ is the probability density. The probability that a system or a particle is located in a volume element $d\mathbf{q}$ around \mathbf{q} is given by $|\psi(\mathbf{q}, t)|^2 d\mathbf{q}$. Given a physical quantity, represented by an operator \hat{O} say, As we operate \hat{O} on a quantum state, one gets its eigen value $\langle \hat{O} \rangle$, which is the expectation value of \hat{O} , which is the average value of the operator obtained during the process of measurement given by

$$\langle \hat{O} \rangle = \frac{\int \psi^*(\mathbf{q}, t) \hat{O} \psi(\mathbf{q}, t) d\tau}{\int \psi^*(\mathbf{q}, t) \psi(\mathbf{q}, t) d\tau} \quad (2)$$

Where $d\tau$ is the volume element of the co-ordinate space. If $\psi(\mathbf{q}, t)$ is normalized than

$$\int \psi^*(\mathbf{q}, t) \psi(\mathbf{q}, t) d\tau = \int |\psi(\mathbf{q}, t)|^2 d\tau = 1 \quad (3)$$

For an operator \hat{O} , there can be a set of eigen values $\{o_n\}$ with a corresponding set of orthonormal eigen functions $\{\phi_n(\mathbf{q})\}$ forming a basis set, such that $\hat{O} \phi_n(\mathbf{q}) = o_n \phi_n(\mathbf{q})$. The eigen function $\psi(\mathbf{q}, t)$ can then be expanded in terms of this basis set as a result of superposition of basis eigen functions as

$$\psi(\mathbf{q}, t) = \sum_n a_n(t) \phi_n(\mathbf{q}) \quad (4)$$

The physical significance of the coefficients lies in the fact that $|a_n(t)|^2$ gives the probability of getting in a measurement o_n corresponding to the eigenstate $\phi_n(\mathbf{q})$ out of the set of eigen function $\{\phi_n(\mathbf{q})\}$, where $a_n(t)$ is

$$a_n(t) = \int \phi_n^*(\mathbf{q}) \psi(\mathbf{q}, t) d\tau \quad (5)$$

Going to quantum statistical ensemble involves incorporation of quantum mechanical averaging besides statistical averaging leading to the so called double averaging. In this process we come across the concept of density matrix in terms of which statistics of various ensembles can be expressed and applied and is the subject matter of this module.

3. Quantum mechanical Formulation of Statistical Mechanics: Density Matrix

With the brief recapitulation of basic concepts of quantum mechanics given in the introduction we are now ready to apply these to a macroscopic system consisting of a large number of particles by using the notion of an ensemble. So we take an ensemble of \mathcal{N} identical systems, where $\mathcal{N} \gg 1$. Since these systems are identical they have a common Hamiltonian \hat{H} . The states of the various systems making the ensemble is represented by the wave functions $\psi(\mathbf{q}, t)$, where $\mathbf{q} = \{q_i\}$ denote the position coordinates relevant to the system being considered. Therefore, $\psi(\mathbf{q}, t)$ describes an equivalent of a phase point in phase space of a classical system.

Let us focus on the k th system of the ensemble. Let at a given time t the k th system of the ensemble happens to be in a normalized state $\psi^k(\mathbf{q}, t)$, where $k=1, 2, 3, \dots, \dots, \dots, \mathcal{N}$. The time evolution of this state function $\psi^k(\mathbf{q}, t)$ is given by the time dependent Schrodinger equation

$$i\hbar \frac{\partial \psi^k(t)}{\partial t} = \hat{H} \psi^k(t) \quad (6)$$

Where $\psi^k(t)$ can be expanded in terms of a set of orthonormal functions $\{\phi_n(\mathbf{q})\}$ as described in equation (4) in each system.

$$\psi^k(t) = \sum_n a_n^k(t) \phi_n(\mathbf{q}) \quad (7)$$

Where

$$a_n^k(t) = \int \phi_n^*(\mathbf{q}) \psi^k(\mathbf{q}, t) d\tau \quad (8)$$

Here $a_n^k(t)$ are the probability amplitudes of the system k to be in the state $\phi_n(\mathbf{q})$ and $|a_n^k(t)|^2$ is the probability amplitudes for the various systems of the ensemble in state $\phi_n(\mathbf{q})$. Sum of these probability amplitudes must be equal to 1.

$$\sum_n |a_n^k(t)|^2 = 1 \quad (9)$$

Equation (6) can be written in terms of the co-efficients $a_n^k(t)$ so that time variation of these coefficients is given by

$$\begin{aligned}
 i\hbar \frac{\partial a_n^k(t)}{\partial t} &= i\hbar \int \phi_n^*(q) \frac{\partial \psi^k(q, t)}{\partial t} d\tau & (10) \\
 &= \int \phi_n^*(q) \hat{H} \psi^k(t) d\tau \\
 &= \int \phi_n^*(q) \hat{H} \sum_n a_m^k(t) \phi_m(q) d\tau = \sum_m a_m^k(t) H_{mn}
 \end{aligned}$$

Where

$$H_{mn} = \int \phi_n^*(q) \hat{H} \phi_m(q) d\tau \quad (11)$$

Now let us define the density matrix by means of matrix elements

$$\rho_{mn}(t) = \frac{1}{\mathcal{N}} \sum_{k=1}^{\mathcal{N}} a_m^k(t) a_n^{k*}(t) \quad (12)$$

Since sum here is over all the systems in the ensemble divided by number of systems in the ensemble, it gives an ensemble average of the quantity $a_m^k(t) a_n^{k*}(t)$. $m = n$ in equation (12) corresponds to the diagonal element $\rho_{nn}(t)$ which is the ensemble average of the probability density $|a_n(t)|^2$ which itself is a quantum average. So density matrix involves two averages, first one being a quantum mechanical average followed by an ensemble average.

So $\rho_{nn}(t)$ represents the probability that a system chosen at random from among the members of the ensemble shall be in the state ϕ_n at time t . Using equation (9) we have,

$$\sum_n \rho_{nn}(t) = \frac{1}{\mathcal{N}} \sum_{k=1}^{\mathcal{N}} \sum_n a_n^k(t) a_n^{k*}(t) = \frac{1}{\mathcal{N}} \sum_{k=1}^{\mathcal{N}} \sum_n |a_n^k(t)|^2 = 1 \quad (13)$$

Let us now express the ensemble average of an operator \hat{G}

$$\langle G \rangle = \frac{1}{\mathcal{N}} \sum_{k=1}^{\mathcal{N}} \int \psi^{k*} \hat{G} \psi^k d\tau \quad (14)$$

This can further be written using (7) as

$$\langle G \rangle = \frac{1}{\mathcal{N}} \sum_{k=1}^{\mathcal{N}} \left[\sum_{m,n} a_n^{*k}(t) a_m^k(t) G_{mn} \right] \quad (15)$$

Where

$$G_{mn} = \int \phi_n^*(q) \hat{G} \phi_m(q) d\tau \quad (16)$$

Equation (15) can be written as

$$\langle G \rangle = \sum_{m,n} \left[\frac{1}{\mathcal{N}} \sum_{k=1}^{\mathcal{N}} a_n^{*k}(t) a_m^k(t) \right] G_{mn} \quad (17)$$

Or

$$\langle G \rangle = \sum_{m,n} \rho_{nm} G_{mn} = \sum_m (\hat{\rho} \hat{G})_{mm} = \text{Tr}(\hat{\rho} \hat{G}) \quad (18)$$

Note if $\hat{G} = \hat{1}$

Then

$$\text{Tr}(\hat{\rho}) = 1 \quad (19)$$

In general if ψ^k are not normalized,

$$\langle G \rangle = \frac{\text{Tr}(\hat{\rho} \hat{G})}{\text{Tr}(\hat{\rho})} \quad (20)$$

It is obvious from the equation (20) knowledge of density matrix allows us to calculate mean value of any physical property of the system. Density matrix is the quantum analogue of the density function of the classical system.

4. Quantum Liouville's Theorem

Liouville's Theorem in quantum statistics is the quantum mechanical analogue of the Liouville's Theorem in classical statistics. It provides us information about the time dependence of density matrix. For this we need to determine the equation of motion of the density matrix. As a matter of convenience here after we will express derivative of a variable with respect to time by putting a dot over the variable, i.e. $\dot{\rho} = \frac{\partial \rho}{\partial t}$. Therefore, from equation (12) we have

$$i\hbar \dot{\rho}_{mn}(t) = \frac{1}{\mathcal{N}} \sum_{k=1}^{\mathcal{N}} i\hbar [a_m^k(t) a_n^{*k}(t) + a_m^k(t) \dot{a}_n^{*k}(t)] \quad (21)$$

From equation (9) it follows that

$$i\hbar\dot{\rho}_{mn}(t) = \frac{1}{\mathcal{N}} \sum_{k=1}^{\mathcal{N}} \left[\left\{ \sum_l a_l^k(t) H_{ml} \right\} a_n^{k*}(t) - a_m^k(t) \left\{ \sum_l H_{nl}^* a_l^k(t) \right\} \right] \quad (22)$$

Note the negative sign on the left hand side which arises because of complex conjugation procedure. Or equation (22) can be written as

$$i\hbar\dot{\rho}_{mn}(t) = \left[\left\{ \sum_l H_{ml} \rho_{ln} \right\} - \left\{ \sum_l \rho_{ml} H_{nl}^* \right\} \right] \quad (23)$$

Since \hat{H} is a Hermitian operator $H_{ln}^* = H_{nl}$

Therefore,

$$i\hbar\dot{\rho}_{mn}(t) = \left[\sum_l [H_{ml} \rho_{ln} - \rho_{ml} H_{ln}] \right] = (\hat{H}\hat{\rho} - \hat{\rho}\hat{H})_{mn} \quad (24)$$

Or this equation can be written as

$$i\hbar\dot{\rho}(t) = [\hat{H}, \hat{\rho}]_- \quad (25)$$

If we compare this equation with classical Liouville's theorem which we derived in Module XI, we will notice that Poisson bracket has been replaced $\frac{[\hat{H}, \hat{\rho}]_-}{i\hbar}$.

Now coming back to the requirement for the system to be in equilibrium, the corresponding ensemble must be stationary, i.e. $\dot{\rho}_{mn}(t) = 0$. For this condition to be true, we must have

- (i) $\hat{\rho}$ an explicit function of \hat{H} i.e. $\rho(\hat{H})$, which implies that $\rho(\hat{H})$ commutes with \hat{H} .
- (ii) \hat{H} should not be an explicit function of time t i.e. $\dot{\hat{H}} = 0$

Furthermore, if basis function set $\{\phi_n\}$ happens to be a set of eigen functions of \hat{H} then the matrices defined by the elements H_{mn} and ρ_{mn} must be diagonal i.e.

$$H_{mn} = E_n \delta_{mn} \text{ and } \rho_{mn} = \rho_n \delta_{mn} \quad (26)$$

If the basis set happens to be other than basis set of the Hamiltonian, the matrices corresponding to \hat{H} and $\hat{\rho}$ will not be diagonal, but it shall be symmetric i.e. $H_{mn} = H_{nm}$ and $\rho_{mn} = \rho_{nm}$, this is desirable for the system to go from state $m \rightarrow n$ must be the same as going from state $n \rightarrow m$, satisfying the principle of detailed balancing.

5. Density Matrix and Various Ensembles

In the following we derive density matrix in various ensembles so that the result embodied in equation (20) may be applied to different systems in different surrounding environments, namely when system is completely isolated (micro canonical ensemble) from the surroundings, system is allowed to exchange energy with the surroundings (canonical ensemble) and when the system can exchange both energy and particles with the surroundings (Grand canonical ensemble).

5.1 The Microcanonical Ensemble

In micro canonical ensemble an isolated system in equilibrium is specified by constant values of number of particles N , constant volume V and energy lying in a narrow interval around E : $(E - \frac{1}{2}\Delta, E + \frac{1}{2}\Delta)$, with $\Delta \ll E$. Let the number of distinct microstates accessible to the system be Ω , which is to be computed quantum mechanically. Then according to postulate of equal a priori probability for each microstate is $\frac{1}{\Omega}$, then the density matrix in the energy representation, which has to be in diagonal form is

$$\rho_{mn} = \rho_n \delta_{mn} \quad (27)$$

Where

$$\rho_n = \begin{cases} \frac{1}{\Omega} & \text{for each accessible microstate} \\ 0 & \text{for all other micro states} \end{cases} \quad (28)$$

One can see that the normalization condition is clearly satisfied

$$\sum_{mn} \rho_{mn} = \sum_{mn} \rho_n \delta_{mn} = \sum_n \rho_n = \frac{1}{\Omega} \left(\sum_n 1 \right) = \frac{1}{\Omega} \Omega = 1 \quad (29)$$

This result is true in representations other than energy representation considered here.

There are two possible cases for the value of Ω , $\Omega = 1$ and $\Omega > 1$.

When $\Omega = 1$, then the member systems of the ensemble are in the same state and hence there is one diagonal element $\rho_{nn} = \rho = 1$ and $\rho^2 = \rho$. Then according to Boltzmann formula entropy $S = \ln \Omega$, gives $S = 0$. The system is said to be in pure state.

When $\Omega > 1$, the system is said to be in mixed state. Ω for a macroscopic system is going to be very large number. In energy representation the density matrix is still given by equations (27) and (28). However, in any other representation, the density matrix has the following two properties:

- (i) All the diagonal elements are equal (equal a priori probability postulate).
- (ii) All off diagonal elements are equal to zero. (A consequence of postulate of random phases)

Postulate of random phases is a requirement of the quantum mechanics. According to this ψ_k (equation 7) which is a super position of the basis set $\{\phi_n\}$ is such that it is not a coherent superposition of the basis set functions but is such that $a_n^k = a e^{i\theta_n^k}$ where $e^{i\theta_n^k}$ is the random phase factor. Such that

$$\begin{aligned} \rho_{mn}(t) &= \frac{1}{\mathcal{N}} \sum_{k=1}^{\mathcal{N}} a_m^k(t) a_n^{k*}(t) = \rho_{mn}(t) = \frac{1}{\mathcal{N}} \sum_{k=1}^{\mathcal{N}} |a|^2 e^{i(\theta_m^k - \theta_n^k)} \\ &= |a|^2 \langle e^{i(\theta_m^k - \theta_n^k)} \rangle \end{aligned} \quad (30)$$

Where, $\langle e^{i(\theta_m^k - \theta_n^k)} \rangle$ is the time average equal to δ_{mn} . Thus the result is similar to equation (27) as expected for micro canonical ensemble.

5.2 The Canonical Ensemble

In canonical ensemble, system is in thermal equilibrium with the surroundings and is described by the three parameters N , V and T . System and surroundings can exchange energy and hence becomes a variable.. As was found in module XIII. The probability that the system possesses energy E_r is proportional to the Boltzmann factor $e^{-\beta E_r}$ given by:

$$P_r = \frac{e^{-\beta E_r}}{\sum_r e^{-\beta E_r}} = \frac{e^{-\beta E_r}}{Z} \quad (31)$$

Where Z is the partition function.

In energy representation, the density matrix elements are represented as $\rho_{mn} = \rho_n \delta_{mn}$, so that in canonical ensemble, we have

$$\rho_{mn} = \rho_n \delta_{mn} = \frac{e^{-\beta E_n}}{Z} \quad (32)$$

In bra ket notation the density matrix element can be written as

$$\rho_{mn} = \langle \phi_m | \hat{\rho} | \phi_n \rangle \quad (33)$$

Then since

$$\rho_{mn} = \sum_l \langle \phi_m | \phi_l \rangle \rho_l \langle \phi_l | \phi_n \rangle \quad (34)$$

Comparing (33) and (34)

We have

$$\hat{\rho} = \sum_n |\phi_n\rangle \rho_n \langle \phi_n| \quad (35)$$

Or

$$\begin{aligned} \hat{\rho} &= \sum_n |\phi_n\rangle \frac{e^{-\beta E_n}}{Z} \langle \phi_n| = \frac{e^{-\beta H}}{Z} \sum_n |\phi_n\rangle \langle \phi_n| = \frac{e^{-\beta \hat{H}}}{Z} \\ &= \frac{e^{-\beta \hat{H}}}{\text{Tr}(e^{-\beta \hat{H}})} \end{aligned} \quad (36)$$

Where, we have used the fact that $\sum_n |\phi_n\rangle \langle \phi_n|$ is the unit operator.

The expectation value of a physical quantity corresponding to the system G represented by the operator \hat{G} is then given by

$$\langle G \rangle_N = \text{Tr}(\hat{\rho} \hat{G}) = \frac{\text{Tr}(\hat{G} e^{-\beta \hat{H}})}{Z} = \frac{\text{Tr}(\hat{G} e^{-\beta \hat{H}})}{\text{Tr}(e^{-\beta \hat{H}})} \quad (37)$$

Where following the convention, since number of particles stay constant in this ensemble subscript explicitly describes this.

For a pure state there is only one state with $\rho_n = 1$ and using (35) density matrix is given by

$$\hat{\rho} = |\phi\rangle \langle \phi|$$

This expression can be used for finding $\hat{\rho}$ of the pure states and density matrix of the mixed states made from a number of pure states with suitable proportion of the mixture.

5.3 The Grand Canonical Ensemble

In a fashion similar to the one which we followed in section 5.2 the density operator ρ can be defined. However we must note that the system can exchange both energy and particles, Keeping parameters μ , V and T constant. The Probability of the system of grand canonical ensemble to be in a state r with energy E_r with number of particles N_r is given by

$$P_r = \frac{e^{-\beta(E_r - \mu N_r)}}{\sum_r e^{-\beta(E_r - \mu N_r)}} = \frac{e^{-\beta(E_r - \mu N_r)}}{\mathcal{Z}} \quad (38)$$

Where, $\mathcal{Z} = \sum_r e^{-\beta(E_r - \mu N_r)} = \text{Tr}(e^{-\beta(\hat{H} - \mu \hat{n})})$ stands for grand partition function, and \hat{n} is the number operator.

Here we must note that density operator shall not only commute with Hamiltonian \hat{H} but also with number operator \hat{n} with eigen values $N_i = 0, 1, 2, \dots, \infty$.

Thus density operator can be written as

$$\hat{\rho} = \frac{e^{-\beta(\hat{H} - \mu \hat{n})}}{\text{Tr}(e^{-\beta(\hat{H} - \mu \hat{n})})} \quad (39)$$

The ensemble average of a physical quantity G of the system can now be written as

$$\langle G \rangle = \text{Tr}(\hat{\rho} \hat{G}) = \frac{\text{Tr}(\hat{G} e^{-\beta(\hat{H} - \mu \hat{n})})}{\text{Tr}(e^{-\beta(\hat{H} - \mu \hat{n})})} \quad (40)$$

6. Calculation of Density Matrix: Some Prototype applications

In the following we look at some problems where we apply the procedure developed above to calculate density matrix and mean value of a physical quantity of interest to us.

6.1 Electron in a Magnetic Field

As a simple problem, let us consider an electron in a magnetic field \vec{B} applied along z-axis. An electron has an intrinsic spin $\vec{s} = \frac{1}{2} \hbar \vec{\sigma}$, with magnetic moment $\vec{\mu} = \frac{e\hbar}{2mc} \vec{\sigma} = \mu_B \vec{\sigma}$, where $\mu_B = \frac{e\hbar}{2mc}$ is Bohr magneton and $\vec{\sigma}$ is the Pauli spin operator with components

$$\hat{\sigma}_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \hat{\sigma}_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \hat{\sigma}_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad (41)$$

In the magnetic field \vec{B} the electron has only two spin orientations, one parallel to the magnetic field and the other perpendicular to the magnetic field. The configurational Hamiltonian of the spin in the magnetic field is

$$\hat{H} = -\mu_B \vec{\sigma} \cdot \vec{B} = -\mu_B \hat{\sigma}_z B \quad (42)$$

This is equivalent to a two state problem done earlier in module XII, with energy of the two states as

$$E_1 = -\mu_B B, E_2 = \mu_B B \quad (43)$$

The density matrix for the canonical ensemble would be

$$\hat{\rho} = \frac{e^{-\beta \hat{H}}}{\text{Tr}(e^{-\beta \hat{H}})} = \frac{e^{\beta \mu_B \hat{\sigma}_z B}}{\text{Tr}(e^{\beta \mu_B \hat{\sigma}_z B})} \quad (44)$$

Where

$$e^{\beta \mu_B \hat{\sigma}_z B} = \begin{pmatrix} e^{\beta \mu_B B} & 0 \\ 0 & e^{-\beta \mu_B B} \end{pmatrix} \quad (45)$$

Therefore,

$$\hat{\rho} = \frac{1}{e^{\beta \mu_B B} + e^{-\beta \mu_B B}} \begin{pmatrix} e^{\beta \mu_B B} & 0 \\ 0 & e^{-\beta \mu_B B} \end{pmatrix} \quad (46)$$

We can use this result to find the expectation value of μ_z

$$\begin{aligned} \langle \hat{\mu}_z \hat{\sigma}_z \rangle &= \text{Tr}(\mu_B \hat{\sigma}_z \hat{\rho}) = \mu_B \text{Tr}(\hat{\sigma}_z \hat{\rho}) = \mu_B \frac{e^{\beta \mu_B B} - e^{-\beta \mu_B B}}{e^{\beta \mu_B B} + e^{-\beta \mu_B B}} \\ &= \mu_B \tanh(\beta \mu_B B) \end{aligned} \quad (47)$$

6.2 Free Particle in a Box

It is an interesting problem which is taught in every elementary course of quantum mechanics, a free particle in cubical box of side L . The Hamiltonian operator of the system is

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 = -\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \quad (48)$$

With eigen-functions of the Hamiltonian operator satisfying periodic boundary conditions

$$\phi(x + L, y, z) = \phi(x, y, z) = \phi(x + L, y, z) = \phi(x, y, z) \quad (49)$$

Which gives

$$\phi_E(\mathbf{r}) = \frac{1}{L^3} e^{i\vec{k}\cdot\vec{r}} \quad (50)$$

With eigen values

$$E = \frac{\hbar^2 \mathbf{k}^2}{2m}, \quad (51)$$

Where \mathbf{k} takes on values $\mathbf{k} = (k_x, k_y, k_z) = (n_x, n_y, n_z)$, with quantum numbers n_x, n_y, n_z taking values $0, \pm 1, \pm 2, \pm 3, \dots$. With the knowledge of the energy wave functions, we write the density matrix $\hat{\rho}$ in canonical ensemble in co-ordinate representation as

$$\langle \vec{r} | \hat{\rho} | \vec{r}' \rangle = \langle \vec{r} | \frac{e^{-\beta\hat{H}}}{\text{Tr}(e^{-\beta\hat{H}})} | \vec{r}' \rangle = \frac{\langle \vec{r} | e^{-\beta\hat{H}} | \vec{r}' \rangle}{\text{Tr}(e^{-\beta\hat{H}})} = \frac{\langle \vec{r} | e^{-\beta\hat{H}} | \vec{r}' \rangle}{\int \langle \vec{r} | e^{-\beta\hat{H}} | \vec{r}' \rangle d^3\mathbf{r}} \quad (52)$$

In the light of equation (52), we first calculate the numerator

$$\langle \vec{r} | e^{-\beta\hat{H}} | \vec{r}' \rangle = \sum_E \langle \vec{r} | E \rangle e^{-\beta E} \langle E | \vec{r}' \rangle = \sum_E e^{-\beta E} \phi_E(\vec{r}) \phi_E(\vec{r}') \quad (53)$$

Using equation (50) and (51), (53) can be written as

$$\langle \vec{r} | e^{-\beta\hat{H}} | \vec{r}' \rangle = \frac{1}{L^3} \sum_{\mathbf{k}} e^{-\frac{\beta\hbar^2}{2m}k^2 + i\mathbf{k}\cdot(\vec{r}-\vec{r}')} \quad (54)$$

Since $\sum_{\mathbf{k}} \frac{1}{L^3} \rightarrow \frac{1}{(2\pi)^3} \int d^3\mathbf{k}$, equation (54) becomes

$$\langle \vec{r} | e^{-\beta\hat{H}} | \vec{r}' \rangle \approx \frac{1}{(2\pi)^3} \int_{-\infty}^{+\infty} e^{-\frac{\beta\hbar^2}{2m}k^2 + i\mathbf{k}\cdot(\vec{r}-\vec{r}')} d^3\mathbf{k} \quad (55)$$

The integral in the above integral can be evaluated by noting that

$$\begin{aligned} & \frac{1}{(2\pi)^3} \int e^{-\frac{\beta\hbar^2}{2m}k^2 + ik \cdot (\vec{r} - \vec{r}')} d^3k \quad (56) \\ &= \frac{1}{(2\pi)^3} \left[\int_{-\infty}^{+\infty} e^{-\frac{\beta\hbar^2}{2m}k^2} \cos k \cdot (\vec{r} - \vec{r}') d^3k \right. \\ & \quad \left. + i \int_{-\infty}^{+\infty} e^{-\frac{\beta\hbar^2}{2m}k^2} \sin k \cdot (\vec{r} - \vec{r}') d^3k \right] \end{aligned}$$

Here one can note that first term is an even function of \mathbf{k} and the second term is an odd function of \mathbf{k} , therefore, since second integral vanishes and first integral can be written as

$$2 \int_0^{+\infty} e^{-\frac{\beta\hbar^2}{2m}k^2} \cos k \cdot (\vec{r} - \vec{r}') d^3k = \left(\frac{2m\pi}{\beta\hbar^2} \right)^{\frac{3}{2}} e^{-\frac{(|\vec{r} - \vec{r}'|)^2 m}{2\beta\hbar^2}} \quad \text{and hence equation (56)}$$

can be written as

$$\begin{aligned} \langle \vec{r} | e^{-\beta\hat{H}} | \vec{r}' \rangle &= \left(\frac{1}{2\pi} \right)^3 \int e^{-\frac{\beta\hbar^2}{2m}k^2 + ik \cdot (\vec{r} - \vec{r}')} d^3k \quad (57) \\ &= \left(\frac{m}{2\pi\beta\hbar^2} \right)^{\frac{3}{2}} e^{-\frac{(|\vec{r} - \vec{r}'|)^2 m}{2\beta\hbar^2}} \end{aligned}$$

Furthermore, denominator in equation (52) can be written, since $\mathbf{r} = \mathbf{r}'$, as

$$\int \langle \vec{r} | e^{-\beta\hat{H}} | \vec{r}' \rangle d^3r = \left(\frac{m}{2\pi\beta\hbar^2} \right)^{\frac{3}{2}} \int d^3r = V \left(\frac{m}{2\pi\beta\hbar^2} \right)^{\frac{3}{2}} \quad (58)$$

Thus the matrix element of the density operator $\langle \vec{r} | \hat{\rho} | \vec{r}' \rangle$ using equations (57) and (58) can be written as

$$\langle \vec{r} | \hat{\rho} | \vec{r}' \rangle = \frac{1}{V} e^{-\frac{(|\vec{r} - \vec{r}'|)^2 m}{2\beta\hbar^2}} \quad (59)$$

The density operator matrix has some interesting properties

- (i) $\langle \vec{r} | \hat{\rho} | \vec{r}' \rangle = \langle \vec{r}' | \hat{\rho} | \vec{r} \rangle$, i.e. density matrix is symmetric between the states \vec{r} and \vec{r}' .
- (ii) The diagonal element $\langle \vec{r} | \hat{\rho} | \vec{r} \rangle = \frac{1}{V}$ is independent of \vec{r} , implying that single particle is equally likely to be anywhere in the box.
- (iii) The coefficient of $(|\vec{r} - \vec{r}'|)^2$ in the exponential part of matrix element, $\frac{\hbar^2}{mk_B T}$, has dimensions of reciprocal of the length square and represent mean thermal

wave length square and represent the spread of the the wave packet and measure an uncertainty in the location of the particle in the box.

- (iv) As $\beta \rightarrow 0$ the matrix element approaches the behavior of the Dirac-delta function leading to classical behavior of the system as a point particle.

Now to get the expectation value of \hat{H} we need to calculate

$$\langle \hat{H} \rangle = \frac{\text{Tr}(\hat{H}e^{-\beta\hat{H}})}{\text{Tr}(e^{-\beta\hat{H}})} = -\frac{\partial(\ln \text{Tr}(e^{-\beta\hat{H}}))}{\partial\beta} \quad (60)$$

Using (58), we have

$$\langle \hat{H} \rangle = -\frac{\partial \left(\ln V \left(\frac{m}{2\pi\beta\hbar^2} \right)^{\frac{3}{2}} \right)}{\partial\beta} = \frac{3}{2} \frac{\partial(\ln \beta)}{\partial\beta} = \frac{3}{2} k_B T \quad (61)$$

6.3 Linear Harmonic Oscillator

As the next example let us calculate the density matrix element of the one dimensional Linear Harmonic Oscillator in the q representation. The Hamiltonian of the linear harmonic oscillator is given by

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial q^2} + \frac{1}{2} m\omega^2 q^2 \quad (62)$$

With eigenvalues and eigenfunctions given by

$$E_n = \left(n + \frac{1}{2} \right) \hbar\omega, \quad n = 0, 1, 2, \dots \dots \dots \quad (63)$$

$$\phi_n(q) = \left(\frac{m\omega}{\pi\hbar} \right)^{\frac{1}{4}} \frac{H_n(\xi)}{(2^n n!)^{\frac{1}{2}}} e^{-\frac{1}{2}\xi^2} \quad (64)$$

Where $\xi = \left(\frac{m\omega}{\hbar} \right)^{\frac{1}{2}} q$ and $H_n(\xi) = (-1)^n e^{\xi^2} \frac{d^n(e^{-\xi^2})}{d\xi^n}$ is the Hermite polynomial. The n th derivative of $e^{-\xi^2}$ can be easily evaluated by using the Fourier transform relation of $e^{-\xi^2}$

$$e^{-\xi^2} = \frac{1}{\pi^{\frac{1}{2}}} \int_{-\infty}^{\infty} e^{-u^2 + 2i\xi u} du \quad (65)$$

So Hermite polynomial in integral form can be written as

$$H_n(\xi) = (-1)^n e^{\xi^2} \frac{(2i)^n}{\pi^{\frac{1}{2}}} \int_{-\infty}^{\infty} u^n e^{-u^2 + 2i\xi u} du \quad (66)$$

So the density matrix in q representation can be written as

$$\begin{aligned} \langle q | \hat{\rho} | q' \rangle &= \sum_{n=0}^{\infty} e^{-\beta E_n} \phi_n(q) \phi_n(q') \\ &= \left(\frac{m\omega}{\pi\hbar} \right)^{\frac{1}{2}} e^{-\frac{1}{2}(\xi^2 + \xi'^2)} \sum_{n=0}^{\infty} e^{-\beta E_n} \frac{H_n(\xi) H_n(\xi')}{2^n n!} \\ &= \left(\frac{m\omega}{\pi\hbar} \right)^{\frac{1}{2}} e^{-\frac{\beta\hbar\omega}{2}} e^{-\frac{1}{2}(\xi^2 + \xi'^2)} \sum_{n=0}^{\infty} e^{-\beta(n\hbar\omega)} \frac{H_n(\xi) H_n(\xi')}{2^n n!} \end{aligned} \quad (67)$$

Using equation (66), equation (67) can be expressed as

$$\begin{aligned} \langle q | \hat{\rho} | q' \rangle &= \left(\frac{m\omega}{\pi^3 \hbar} \right)^{\frac{1}{2}} e^{-\frac{\beta\hbar\omega}{2}} e^{\frac{1}{2}(\xi^2 + \xi'^2)} \\ &\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \sum_{n=0}^{\infty} \frac{(-2)^n}{n!} (e^{-\beta\hbar\omega} uv)^n e^{(-u^2 - v^2 + 2i(\xi u + \xi' v))} dudv \end{aligned} \quad (68)$$

In (68) integral involving summation can be solved, let us look at the summation first

$$\sum_{n=0}^{\infty} \frac{(2)^n}{n!} (e^{-\beta\hbar\omega} uv)^n = \sum_{n=0}^{\infty} \frac{(-2e^{-\beta\hbar\omega} uv)^n}{n!} = e^{(-e^{-\beta\hbar\omega} 2uv)} \quad (69)$$

Using (69), equation (68) can be written as

$$\begin{aligned} \langle q | \hat{\rho} | q' \rangle &= \left(\frac{m\omega}{\pi^3 \hbar} \right)^{\frac{1}{2}} e^{-\frac{\beta\hbar\omega}{2}} e^{\frac{1}{2}(\xi^2 + \xi'^2)} \\ &\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{(-u^2 - v^2 + 2i(\xi u + \xi' v) - 2uve^{-\beta\hbar\omega})} dudv \end{aligned} \quad (70)$$

We state general integral formula

$$\int \dots \int_{-\infty}^{\infty} e^{[-\frac{1}{2} \sum_j^n \sum_k^n a_{jk} x_j x_k + i \sum_k^n b_k x_k]} dx_1 \dots \dots \dots dx_n \quad (71)$$

$$= \frac{(2\pi)^{\frac{n}{2}}}{[\det(A)]^{\frac{1}{2}}} e^{(-\frac{1}{2} \sum A_{jk}^{-1} b_j b_k)}$$

Comparing integrand in equation (70) with integrand in (71), we have $k = 1, 2, j = 1, 2, x_1 = u, x_2 = v, n = 2; a_{11} = 1, a_{12} = e^{-\beta\hbar\omega}, a_{21} = e^{-\beta\hbar\omega}, a_{22} = 1; b_1 = 2\xi, b_2 = 2\xi', \det A = 4(1 - e^{-2\beta\hbar\omega})$ and $A^{-1} = \frac{1}{2(1 - e^{-2\beta\hbar\omega})} \begin{bmatrix} 1 & -e^{-\beta\hbar\omega} \\ -e^{-\beta\hbar\omega} & 1 \end{bmatrix}$

Therefore,

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{(-u^2 - v^2 + 2i(\xi u + \xi' v) - 2uv e^{-\beta\hbar\omega})} dudv \quad (72)$$

$$= \frac{\pi}{(1 - e^{-2\beta\hbar\omega})^{\frac{1}{2}}} \left[e^{-\left(\frac{1}{1 - e^{-2\beta\hbar\omega}}\right)(\xi^2 - 2e^{-\beta\hbar\omega}\xi\xi' + \xi'^2)} \right]$$

$$\langle q | \hat{p} | q' \rangle = \left(\frac{m\omega}{\pi\hbar} \right)^{\frac{1}{2}} \quad (73)$$

$$\frac{e^{-\frac{\beta\hbar\omega}{2}}}{(1 - e^{-2\beta\hbar\omega})^{\frac{1}{2}}} \left[e^{\left[\frac{1}{2}(\xi^2 + \xi'^2) - \left(\frac{1}{1 - e^{-2\beta\hbar\omega}}\right)(\xi^2 - 2e^{-\beta\hbar\omega}\xi\xi' + \xi'^2) \right]} \right]$$

Or

$$\langle q | \hat{p} | q' \rangle = \left(\frac{m\omega}{2\pi\hbar \sinh(\beta\hbar\omega)} \right)^{\frac{1}{2}} \left[e^{\left[-\frac{1}{2}(\xi^2 + \xi'^2) \coth(\beta\hbar\omega) - \left(\frac{\xi\xi'}{\sinh(\beta\hbar\omega)}\right) \right]} \right] \quad (74)$$

Putting the value of ξ and ξ' , (74) becomes

$$\langle q | \hat{p} | q' \rangle = \left(\frac{m\omega}{2\pi\hbar \sinh(\beta\hbar\omega)} \right)^{\frac{1}{2}} \left[e^{\left(\frac{-m\omega}{4\hbar} \left[2(q^2 + q'^2) \coth(\beta\hbar\omega) + \left(\frac{4qq'}{\sinh(\beta\hbar\omega)} \right) \right] \right)} \right] \quad (75)$$

Recall $2(q^2 + q'^2) = (q+q')^2 + (q-q')^2$ and $4qq' = (q+q')^2 - (q-q')^2$

$$\begin{aligned} 2(q^2 + q'^2) \coth(\beta\hbar\omega) + \left(\frac{4qq'}{\sinh(\beta\hbar\omega)}\right) \\ = (q+q')^2 \left(\coth \beta\hbar\omega + \frac{1}{\sinh \beta\hbar\omega}\right) + (q-q')^2 \left(\coth \beta\hbar\omega - \frac{1}{\sinh \beta\hbar\omega}\right) \\ = (q+q')^2 \left(\tanh \frac{\beta\hbar\omega}{2}\right) + (q-q')^2 \left(\coth \frac{\beta\hbar\omega}{2}\right) \end{aligned}$$

Density matrix element in equation (75) can be written as

$$\begin{aligned} \langle q|\hat{\rho}|q'\rangle \\ = \left(\frac{m\omega}{2\pi\hbar \sinh(\beta\hbar\omega)}\right)^{\frac{1}{2}} \left[e^{(-\frac{m\omega}{4\hbar})(q+q')^2 \left(\tanh \frac{\beta\hbar\omega}{2}\right) + (q-q')^2 \left(\coth \frac{\beta\hbar\omega}{2}\right)} \right] \end{aligned} \quad (76)$$

Now we can calculate the partition function $Tr(e^{-\beta\hat{H}})$:

$$\begin{aligned} Tr(e^{-\beta\hat{H}}) &= \int \langle q|\hat{\rho}|q\rangle dq \\ &= \left(\frac{m\omega}{2\pi\hbar \sinh(\beta\hbar\omega)}\right)^{\frac{1}{2}} \int \left[e^{(-\frac{4m\omega}{4\hbar})(q)^2 \left(\tanh \frac{\beta\hbar\omega}{2}\right)} \right] dq \\ &= \frac{1}{2 \sinh\left(\frac{\beta\hbar\omega}{2}\right)} = \frac{e^{-\frac{\beta\hbar\omega}{2}}}{1 - e^{-\beta\hbar\omega}} \end{aligned} \quad (77)$$

Interesting once again we have arrived at the partition function of a linear harmonic oscillator (See module X.....).

WE can calculate the mean energy of the harmonic oscillator $\langle \hat{H} \rangle$

$$\langle \hat{H} \rangle = -\frac{\partial}{\partial \beta} \ln Tr(e^{-\beta\hat{H}}) = \frac{\hbar\omega}{2} \coth \frac{\beta\hbar\omega}{2} \quad (78)$$

Equation (76) provide us the probability density for the linear harmonic oscillator coordinate near q is

$$\langle q|\hat{\rho}|q\rangle = \left(\frac{m\omega}{2\pi\hbar \sinh(\beta\hbar\omega)}\right)^{\frac{1}{2}} \left[e^{(-\frac{m\omega q^2}{\hbar}) \left(\tanh \frac{\beta\hbar\omega}{2}\right)} \right] \quad (79)$$

It is a Gaussian distribution in q, with mean value zero and root mean square deviation

$$q_{r.m.s} = \left[\frac{\hbar}{2m\omega \tanh \frac{\beta\hbar\omega}{2}} \right]^{\frac{1}{2}} \quad (80)$$

For the classical limiting case $\beta\hbar\omega \ll 1$, $\sinh(\beta\hbar\omega) \rightarrow \beta\hbar\omega$ and $\tanh \frac{\beta\hbar\omega}{2} \rightarrow \beta\hbar\omega$, probability density becomes

$$\langle q | \hat{\rho} | q \rangle = \left(\frac{m\omega^2 k_B T}{2\pi\hbar^2\omega^2} \right)^{\frac{1}{2}} \left[e^{-\frac{m\omega^2 q^2}{k_B T}} \right] \quad (81)$$

The density matrix calculated above also allows us to calculate $\langle q^2 \rangle$ and $\langle p^2 \rangle$

Recalling that

$$\frac{\int_{-\infty}^{\infty} x^2 e^{-\frac{1}{2}\alpha x^2} dx}{\int_{-\infty}^{\infty} e^{-\frac{1}{2}\alpha x^2} dx} = \frac{d}{d\alpha} \ln \int_{-\infty}^{\infty} e^{-\frac{1}{2}\alpha x^2} dx = \frac{1}{\alpha} \quad (82)$$

$$\begin{aligned} \langle q^2 \rangle &= \frac{\int_{-\infty}^{\infty} q^2 \langle q | \hat{\rho} | q \rangle dq}{\int_{-\infty}^{\infty} \langle q | \hat{\rho} | q \rangle dq} = \frac{d}{d\alpha} \ln [C \int_{-\infty}^{\infty} e^{-\frac{1}{2}\alpha q^2} dq] \\ &= \frac{1}{m\omega^2} \frac{\hbar\omega}{2} \coth \left(\frac{1}{2} \beta \hbar\omega \right) = \frac{1}{m\omega^2} \langle \hat{H} \rangle \end{aligned} \quad (83)$$

Where $\alpha = \left(\frac{2m\omega}{\hbar} \right) \left(\tanh \frac{\beta\hbar\omega}{2} \right)$ and $C = \left(\frac{m\omega}{2\pi\hbar \sinh(\beta\hbar\omega)} \right)^{\frac{1}{2}}$

Or

$$\frac{1}{2} m\omega^2 \langle q^2 \rangle = \frac{1}{2} \langle \hat{H} \rangle \quad (84)$$

Thus potential energy of the oscillator is $\frac{1}{2} \langle \hat{H} \rangle$

Similarly one can show that

$$\langle p^2 \rangle = \left\langle -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial q^2} \right\rangle = m \langle \hat{H} \rangle \quad (85)$$

Or $\frac{\langle p^2 \rangle}{2m} = \frac{1}{2} \langle \hat{H} \rangle$ i.e. Mean value of kinetic energy and potential energy of the harmonic oscillator are the same and equal to half the total mean energy.

7. Indistinguishability of Particles and Quantum Statistical Mechanics

Till this point to take care of indistinguishability of particles, we made use of adhoc explanations to correct the counting of microstates as was done in the case of resolving of Gibbs Paradox earlier. However, quantum mechanical description requires us to deal with great care in describing systems composed of indistinguishable particles. The key idea lies in symmetrization of wave functions which is closely related with indistinguishability of particles leading to special correlations which are attractive in the case of particles obeying Bose-Einstein Statistics and repulsive in the case of particles obeying Fermi-Dirac-Statistics. We shall study these aspects by considering a gas of N non-interacting identical particles. The Hamiltonian, \hat{H} for such a system is a sum of the individual single particle Hamiltonians \hat{H}_i .

$$\hat{H}(\vec{q}, \vec{p}) = \sum_{i=0}^N \hat{H}_i(\mathbf{q}_i, \mathbf{p}_i) \quad (86)$$

Identical nature of particles here means that except for the values of the arguments \mathbf{q}_i and \mathbf{p}_i , \hat{H}_i are formally identical.

The time independent Schrodinger equation of the system is

$$\hat{H} \psi_E(\vec{q}) = E \psi_E(\vec{q}) \quad (87)$$

Where $\psi_E(\mathbf{q})$ is a product of single particle eigenfunctions $\mathbf{u}_{\epsilon_i}(\mathbf{q}_i)$ of the single particle Hamiltonian $\hat{H}_i(\mathbf{q}_i, \mathbf{p}_i)$ with energy ϵ_i .

$$\psi_E(\vec{q}) = \prod_{i=1}^N \mathbf{u}_{\epsilon_i}(\mathbf{q}_i) \quad (88)$$

With

$$E = \sum_{i=1}^N \epsilon_i \quad (89)$$

This situation can be alternately described in terms of a distribution set $\{n_i\}$, such that n_i number of particles are in an eigenstate with energy ϵ_i such that

$$\sum_i n_i = N \quad (90)$$

And

$$E = \sum_i n_i \epsilon_i \quad (91)$$

The eigen state described by equation (90) and (91) can be written as

$$\psi_E(\vec{q}) = \prod_{m=1}^{n_1} u_1(m) \prod_{m=n_1+1}^{n_1+n_2} u_2(m) \dots \dots \dots \quad (92)$$

Where $u_i(m) = u_{\epsilon_i}(q_m)$.

7.1 Symmetrization of State Functions and Gibbs Paradox

So far this simple looking multi particle wave function describes the state of the system. However, we need to ask the question what happens when we permute the co-ordinates $(1, 2, 3, 4 \dots, N)$ in (92) such that new co-ordinates become $(P1, P2, P3, P4 \dots, PN)$ say the resulting wave function $P\psi_E(q)$ becomes

$$P\psi_E(\vec{q}) = \prod_{m=1}^{n_1} u_1(Pm) \prod_{m=n_1+1}^{n_1+n_2} u_2(Pm) \dots \dots \dots \quad (93)$$

Now if the particles are distinguishable, this results in a new microstate of the system. So in the case of N distinguishable particles with n_1 particles in a state with energy ϵ_1 and n_2 particles in a state with energy ϵ_2 and so on, the for a distribution set $\{n_i\}$, the number of distinct microstates is

$$\frac{N!}{n_1! n_2! n_3! \dots \dots} \quad (94)$$

This weight factor on applying Gibbs correction becomes

$$W_C\{n_i\} = \frac{1}{n_1! n_2! n_3! \dots \dots} \quad (95)$$

This adhoc removal of $N!$ was realization of the intrinsic indistinguishability of particles. Though applying of this correction led to extensive nature of entropy, quantum

mechanically permutations among identical particles should not get us a new microstate of the system. The effect of permutation therefore should not lead to any new microstate implying that the weight factor described by equation (95) should be identically equal to unity for a given distribution set $\{n_i\}$, provided there is no physical reason disallowing the set itself.

Therefore,

$$W_q\{n_i\} = 1 \quad (96)$$

What are the implications of this for the wave function described by equation (93), since permutation of the arguments shall lead to a mathematically and physically distinct state. But this is not desirable since mere interchange of the co-ordinates should not lead to a new microstate.

7.2 Construction of Symmetric and Antisymmetric Wavefunctions

To achieve this, it is required that $N!$ possible wavefunctions obtained after permutations should not lead to a new microstate thereby making $\psi_E(\mathbf{q})$ unaffected by these permutations. In quantum mechanics, we can do this by expressing $\psi_E(\mathbf{q})$ as a linear combination of all the $N!$ wave functions such that the original wavefunction ψ and the permuted wavefunction $P\psi$ should be such that their probability amplitude must be the same as stated below

$$|P\psi|^2 = |\psi|^2 \quad (97)$$

This means either

$$P\psi = \psi \text{ for all } P \quad (98)$$

Or

$$P\psi = \begin{cases} +\psi & \text{if } P \text{ is an even permutation} \\ -\psi & \text{if } P \text{ is an odd permutation} \end{cases} \quad (99)$$

Equation (98) implies that wave function is *symmetric* and equation (99) implies that wave function is *antisymmetric* in its arguments. Mathematically, the two types of wave functions can be written as:

$$\psi_S(\vec{q}) = \text{const.} \sum_P P \psi(\vec{q}) \quad (100)$$

And

$$\psi_A(\vec{q}) = \text{const.} \sum_P \delta_P P \psi(\vec{q}) \quad (101)$$

Where δ_P is +1 for P to be even and is -1 for P to be odd. For example for a three particle system, symmetric wave function can be written as

$$\psi_S(\vec{q}) = \text{const.} [\psi(1, 2, 3) + \psi(2, 3, 1) + \psi(3, 2, 1) + \psi(1, 3, 2) + \psi(3, 2, 1) + \psi(2, 1, 3)] \quad (102)$$

Here first three terms involve even permutations and last three odd permutations.

Similarly for a three particle system antisymmetric wave function can be written as

$$\psi_A(\vec{q}) = \text{const.} [\psi(1, 2, 3) + \psi(2, 3, 1) + \psi(3, 2, 1) - \psi(1, 3, 2) - \psi(3, 2, 1) - \psi(2, 1, 3)] \quad (103)$$

In terms of single particle states $\psi(1, 2, 3) = u_1(1)u_2(2)u_3(3)$, $\psi(2, 3, 1) = u_1(2)u_2(3)u_3(1)$,, $\psi_A(\vec{q})$ can be expressed as a slater determinant

$$\psi_A(\vec{q}) = \text{Const.} \begin{vmatrix} u_1(1) & u_1(2) & u_1(3) \\ u_2(1) & u_2(2) & u_2(3) \\ u_3(1) & u_3(2) & u_3(3) \end{vmatrix} \quad (104)$$

As one expands the determinant, the positive and negative signs appear automatically, on interchanging the arguments the antisymmetric wave function changes the sign as required. Also if two or more particle happens to be in the same state corresponding rows become identical and determinant vanishes implying that such state is not physically possible, equivalent to Pauli's exclusion principle.

In other words, we can say that a system of particles which follows exclusion principle must have an antisymmetric wave function. Such particles are said to obey Fermi Dirac statistics and are described as fermions. In this case quantum statistical weight factor described by equation (96), now called $W_{F.D.}\{n_i\}$ is such that the as long as distribution set elements n_i have value either 0 or 1 it is unity else zero i.e.

$$W_{F.D.}\{n_i\} = \begin{cases} 1 & \text{if } \sum_i n_i = N \\ 0 & \text{if } \sum_i n_i > N \end{cases} \quad (105)$$

For systems characterized by symmetric wavefunctions, n_i can be 0 or positive integers. Such systems are said to follow Bose-Einstein Statistics and are described as bosons. The weight factor $W_{B.E.}\{n_i\}$ for such a system is identically equal to 1, whatever the value of number $\{n_i\}$:

$$W_{B.E.}\{n_i\} = 1, n_i = 0, 1, 2, \dots \dots \quad (106)$$

7.3 Spin and Statistics

The spin of a particle and statistics it obeys are intimately connected. According to relativistic quantum field theory, particles with half integer spin have got antisymmetric wave functions and particles with integer spin has wave functions which are symmetric. Accordingly particles with half integer spin follow Fermi-Dirac Statistics and particles which have integer spin follow Bose-Einstein Statistics. Examples of fermions are electrons, positrons, neutrons, protons, μ mesons. Examples of bosons are photons, π mesons. A composite particle with constituents as fermions and bosons can either be a boson or a fermion, depending on the spin of the composite particle which is resultant of the spin of the constituents. Accordingly He^3 (two electrons, two protons and one neutron) is a fermion wher as He^4 (two electrons, two protons and two neutrons) is a boson.

6. Summary

In this module we have learnt

- That quantum statistical ensembles involves double averaging on corresponding to quantum mechanical averaging and the other corresponding to statistical averaging.
- That density matrix element is defined as

$$\rho_{mn}(t) = \frac{1}{\mathcal{N}} \sum_{k=1}^{\mathcal{N}} a_m^k(t) a_n^{k*}(t)$$

Where sum is over all the systems in the statistical ensemble.

- That for $n = m$ the diagonal matrix element of ρ involves probability density $|a_n^k(t)|^2$ which is a result of quantum average. Summation over all systems of the ensemble divided by the total number of ensembles in the system results in statistical averaging.
- That physically $\rho_{nn}(t)$ represents the probability that a system chosen at random from among the members of the ensemble shall be in the state ϕ_n at time t such that

$$\sum_n \rho_{nn}(t) = \frac{1}{\mathcal{N}} \sum_{k=1}^{\mathcal{N}} \sum_n |a_n^k(t)|^2 = 1$$

- That density matrix is the quantum analogue of the density function of the classical statistical system
- That ensemble average of a physical quantity represented by quantum mechanical operator \hat{G} can be obtained as

$$\langle G \rangle = \sum_{m,n} \rho_{nm} G_{mn} = \sum_m (\hat{\rho} \hat{G})_{mm} = \text{Tr}(\hat{\rho} \hat{G}), \text{ if states are normalized}$$

Else $\langle G \rangle = \frac{\text{Tr}(\hat{\rho} \hat{G})}{\text{Tr}(\hat{\rho})}$. Implying thereby that knowledge of density matrix allows us to calculate mean value of any physical property of the system.

- How to derive quantum Liouville's theorem $\dot{\rho}_{mn}(t) = 0$, which implied that
 - a. $\hat{\rho}$ an explicit function of \hat{H} i.e. $\rho(\hat{H})$, which implies that $\rho(\hat{H})$ commutes with \hat{H} .
 - b. \hat{H} should not be an explicit function of time t i.e. $\dot{\hat{H}} = 0$
- To calculate the density matrix element in three ensembles as given in the table below:

Type of ensemble	Density Matrix
Micro-canonical ensemble	$\rho_{mn} = \rho_n \delta_{mn}$ where $\rho_n = \begin{cases} \frac{1}{\Omega} & \text{for each accessible microstate} \\ 0 & \text{for all other micro states} \end{cases}$ And Ω is the total number of accessible microstates
Canonical ensemble	$\hat{\rho} = \frac{e^{-\beta \hat{H}}}{Z} = \frac{e^{-\beta \hat{H}}}{\text{Tr}(e^{-\beta \hat{H}})}$
Grand canonical ensemble	$\hat{\rho} = \frac{e^{-\beta(\hat{H} - \mu \hat{n})}}{\text{Tr}(e^{-\beta(\hat{H} - \mu \hat{n})})}$

- The mean value of a physical quantity. \hat{G} , in canonical ensemble is given by

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

- The mean value of a physical quantity, \hat{G} , in canonical ensemble is given by

$$\langle G \rangle = \text{Tr}(\hat{\rho}\hat{G}) = \frac{\text{Tr}(\hat{G} e^{-\beta(\hat{H}-\mu\hat{n})})}{\text{Tr}(e^{-\beta(\hat{H}-\mu\hat{n})})}$$

- How to calculate density matrix for three prototype systems and the expectation value of some physical quantity corresponding to these systems.

System	Density Matrix	Expectation values of some physical quantities
Electron in a magnetic field	$\hat{\rho} = \frac{1}{e^{\beta\mu_B B} + e^{-\beta\mu_B B}} \begin{pmatrix} e^{\beta\mu_B B} & 0 \\ 0 & e^{-\beta\mu_B B} \end{pmatrix}$	$\langle \hat{\mu}_z \hat{\sigma}_z \rangle = \mu_B \tanh(\beta\mu_B B)$
Free particle in a box	$\langle \vec{r} \hat{\rho} \vec{r}' \rangle = \frac{1}{V} e^{-\frac{(\vec{r}-\vec{r}')^2 m}{2\beta\hbar^2}}$	$\langle \hat{H} \rangle = \frac{3}{2} k_B T$
Linear harmonic oscillator	$\langle q \hat{\rho} q' \rangle = \left(\frac{m\omega}{2\pi\hbar \sinh(\beta\hbar\omega)} \right)^{\frac{1}{2}} \left[e^{(-\frac{m\omega}{4\hbar})(q+q')^2 (\tanh\frac{\beta\hbar\omega}{2}) + (q-q')^2 (\coth\frac{\beta\hbar\omega}{2})} \right]$	$\langle \hat{H} \rangle = \frac{\hbar\omega}{2} \coth \frac{\beta\hbar\omega}{2}$ $\langle K.E. \rangle = \langle P.E. \rangle = \frac{1}{2} \langle \hat{H} \rangle$

- That quantum mechanical description requires us to deal with great care in describing systems composed of indistinguishable particles. The key idea lies in symmetrization of wave functions which is closely related with indistinguishability of particles
- how to construct the symmetrized wave functions for a system of N particles such that $N!$ permutations of particles should not lead to a new microstate and probability density corresponding to the permuted particles should be the same as the probability density of a particle without permutation.
- That there are two types of symmetrized wave functions: Symmetric wave functions and antisymmetric wave functions and, such that

$$\psi_S(\vec{q}) = \text{const.} \sum_P P \psi(\vec{q})$$

$$\psi_A(\vec{q}) = \text{const.} \sum_P \delta_P P \psi(\vec{q})$$

Where P is the permutation operator and $\delta_P = +1$ for even number of permutations and $\delta_P = -1$ for odd number of permutations.

- The number of particles n_i in each state can be either 0 or 1 in the case of particles obeying Fermi-Dirac Statistics.

- The number of particles n_i in each state can be 0,1,2,3..... in the case of particles obeying Bose-Einstein Statistics.
- That systems with antisymmetric wave function follow Fermi-Dirac Statistics and systems with symmetric wave function follow Bose-Einstein Statistics.
- That there is a close relation between spin and statistics with particles having half integer spin obeying Fermi-Dirac Statistics and particles having integer spin obeying Bose-Einstein Statistics

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