CHAPTER III

REDUCED DENSITY MATRICES AND OFF-DIAGONAL LONG-RANGE ORDER

In studying quantum systems of identical particles, We generally require only the expectaion value of one and two-body operators. This leads to the definition of one and two-body reduced density matrices, and generally extends to higher order reduced density matrices. We will study its properties and consider the events that they will exhibit off-diagonal long-range order in the coordinate space representation. For these will lead to a new thermodynamic phase of the system that characterize superfluid He II and superconductors. But first let us consider the concept of density matrix.

3.1 DENSITY MATRICES

For quantum systems the phase space coordinates of particles do not commute. Therefore, rather than introduce a probability density on the phase space of the system, it is convenient to work with a more general object called the probability density operator $\rho(t)$. Given a density operator for a system, the expectation value of any observable O at time t in any desired representation is defined by

$$\langle \hat{O} \rangle = \mathrm{Tr}\, \rho(t) \hat{O} \qquad (3.1)$$

where the density operator is normalized so that

$$\mathrm{Tr}\,\rho(t) = 1 \qquad (3.2)$$

Since the density operator is a positive definite Hermitian operator, it can be diagonalized and it will have positive real eigenvalues. If the set $|\pi_i\rangle$ denotes the eigenstates of the density operator and p_i its eigenvalues, then the density operator can be written in the form

$$\rho(t) = \Sigma_i P_i |\pi_i(t)\rangle\langle\pi_i(t)| \qquad (3.3)$$

where P_i is the probability of finding the system in state $|\pi_i\rangle$ and

$$\Sigma_i P_i = 1 \qquad (3.4)$$

The expectation value of any operator becomes

$$\langle\hat{O}(t)\rangle = \mathrm{Tr}\,\rho(t)\hat{O} = \Sigma_i P_i \langle\pi_i(t)|\hat{O}|\pi_i(t)\rangle \qquad (3.5)$$

In Eq. (3.5), $\langle\pi_i(t)|\hat{O}|\pi_i(t)\rangle$ is the expectation value of O in the state $|\pi_i(t)\rangle$ and P_i is the probability of finding the system in that state.

If we have an arbitrary complete orthonormal set of states $|n\rangle$ which are not eigenstate of $\rho(t)$. Then the probability $P_n(t)$ that the system is in the state $|n\rangle$ at time t is given by the expectation value of the density operator in that state

$$P_n(t) = \langle n|\rho(t)|n\rangle = \Sigma_i P_i \langle n|\pi_i(t)\rangle\langle\pi_i(t)|n\rangle \qquad (3.5)$$

The expectation value of an arbitrary operator O may be evaluated with respect to any representation. Thus, in the representation $|n\rangle$, we have

$$\langle\hat{O}(t)\rangle = \mathrm{Tr}\,\rho(t)\hat{O} = \sum_{n,n'} \langle n|O|n'\rangle\langle n'|\rho(t)|n\rangle \qquad (3.7)$$

The quantity $\langle n'|\rho(t)|n\rangle$ is called the density matrix.

Since Schrödinger equation is difficult to solve. It would be quite hopeless to attemp a solution of the problem because of the enormous number of degrees of freedom (proportional to the total number of particles). So it is opportune to introduce the statisfical operators that are capable of yielding pertinent on the fundamental dynamical quantities. For this purpose we introduce reduced density matrices.

3.2 REDUCED DENSITY MATRICES

Let us consider a many-particle system with fixed number of particles, with density operator ρ , the expectation value of one-body operator $\hat{O}_1$ is

$$\langle \hat{O}_1(t)\rangle = Tr\rho(t)\ \hat{O}_1 \tag{3.8}$$

In the coordinate representation, we can write

$$\langle O_1(t)\rangle = \iint \langle \vec{x}'|\, O_1\, |\vec{x}''\rangle \langle \vec{x}''|\, \rho_1(t)\, |\vec{x}'\rangle d\vec{x}'' d\vec{x}' \tag{3.9}$$

where $\langle \vec{x}''|\rho_1(t)|\ \vec{x}'\rangle$ is the one-particle reduced density matrix and is defined by

$$\langle \vec{x}''|\rho_1|\vec{x}'\rangle = Tr\rho(t)\ \psi^+(\vec{x}'')\psi(\vec{x}') \tag{3.10}$$

where $\psi^+(\vec{x}'')$ and $\psi(\vec{x}')$ are field operators.

For two-body operator, we get the similar expression, that is

$$\langle \hat{O}_2(t)\rangle = Tr\rho(t)\ \hat{O}_2$$
$$= \frac{1}{2}\iiiint \langle \vec{x}'_1, \vec{x}'_2|O_2|\vec{x}''_1, \vec{x}''_2\rangle \langle \vec{x}''_1, \vec{x}''_2|\rho_2(t)|\ \vec{x}'_1, \vec{x}'_2\rangle$$
$$d\vec{x}''_1 d\vec{x}''_2 d\vec{x}'_1 d\vec{x}'_2 \tag{3.11}$$

where $\langle \vec{x}"_1, \vec{x}"_2 | \rho_2(t) | x'_1, x'_2 \rangle$ is the two-particle reduced density matrix and is defined by

$$\langle \vec{x}"_1, \vec{x}"_2 | \rho_2(t) | \vec{x}'_1, \vec{x}'_2 \rangle = \mathrm{Tr}\rho(t)\psi^+(\vec{x}"_1)\psi^+(\vec{x}"_2)\psi(\vec{x}'_2)\psi(\vec{x}'_1) \qquad (3.12)$$

Equation (3.10) and (3.12) are the expressions for the one and two-body reduced density matrices. They can be generally extended to the n-body reduced density matrix

Next we will examine the properties of these reduced density matrices (3). We will first consider the diagonal matrix elements of ρ_1 with respect to any given state that it gives the average number of that state, that is, from Eq.(3.10)

$$\langle \vec{x} | \rho_1 | \vec{x} \rangle = \mathrm{Tr}\rho(t)\psi^+(\vec{x})\psi(\vec{x}) = n(\vec{x},t) \qquad (3.13)$$

where $n(\vec{x},t)$ is the average number of particles at position $\vec{x}$ at time t. The one-particle reduced density matrix is normalized to the total number of particles, that is

$$\int \langle \vec{x} | \rho_1 | \vec{x} \rangle d\vec{x} = \int \langle n(\vec{x},t) \rangle \, d\vec{x} = N \qquad (3.14)$$

where N is the total number of particles.

The two-particle reduced density matrix is normalized to N (N-1)

$$\iint \langle \vec{x}_1, \vec{x}_2 | \rho_2 | \vec{x}_1, \vec{x}_2 \rangle d\vec{x}_1 d\vec{x}_2 = N(N-1) \qquad (3.15)$$

If λ_n is the largest eigenvalue of ρ_n. From Eqs. (3.14) and (3.15), we see that $\lambda_1 \leq N$ and $\lambda_2 \leq N(N-1)$ etc.

For our purpose we will consider in the case of

fermions. For fermions the expectation value $\psi^{+}(\vec{x})\,\psi(\vec{x})$ for any states is less than 1 (Pauli exclusion principle). Therefore $\lambda_1 \leq 1$.

3.3 OFF-DIAGONAL LONG-RANGE ORDER (ODLRO)

Consider a system of N fermions or bosons in a periodic box of volume V in thermal equilibrium. ρ commutes with the total momentum, thus in the momentum representation ρ_1 is diagonal

$$\langle \vec{p}" | \rho_1 | \vec{p}' \rangle = n_{\vec{p}'} \delta_{\vec{p}',\vec{p}"} \qquad (3.16)$$

where $n_{\vec{p}'}$ is the average occupation number of the single particle at state $\vec{p}'$. In coordinate representation

$$\begin{aligned} \langle \vec{x}" | \rho_1 | \vec{x}' \rangle &= \sum_{\vec{p}"\vec{p}'} \langle \vec{x}" | \vec{p}" \rangle \langle \vec{p}" | \rho_1 | \vec{p}' \rangle \langle \vec{p}' | \vec{x}' \rangle \\ &= \frac{1}{V} \sum_{\vec{p}"\vec{p}'} \exp\left(i\frac{\vec{p}"\cdot\vec{x}"}{\hbar}\right) \exp\left(-i\frac{\vec{p}'\cdot\vec{x}'}{\hbar}\right) n_{\vec{p}'} \delta_{\vec{p}',\vec{p}"} \\ &= \frac{1}{V} \sum_{\vec{p}'} n_{\vec{p}'} \exp\left(i\frac{\vec{p}'\cdot(\vec{x}"-\vec{x}')}{\hbar}\right) \\ &= g(\vec{x}"-\vec{x}') \end{aligned} \qquad (3.17)$$

For fermions or bosons at high temperature, n are finite then

$$\lim_{\vec{x}"_1 \succ \vec{x}'_1} \langle \vec{x}"_1 | \rho_1 | \vec{x}'_1 \rangle = 0 \qquad (3.18)$$

But for bosons below the Bose-Einstein transition temperature, $n_o = \alpha N$ where α is finite fraction, then Eq (3.18) becomes

$$\lim_{\vec{x}_1 \prec \vec{x}"_1} \langle \vec{x}" | \rho_1 | \vec{x}' \rangle = \alpha \frac{N}{V} \qquad (3.19)$$

Thus the Bose-Einstein condensation is characterized by the nonvanishing behavior of $\langle \vec{x}" | \rho_1 | \vec{x}' \rangle$. A system that yields according to Eq. (3.19) is said to exhibit off-diagonal long-range order in the one-reduced

density matrix. For fermions system because of Pauli exclusion principle, i.e. $\lambda_1 \leq 1$, they cannot exhibit ODLRO in one-body reduced density matrix. But for bosons system they can exhibit ODLRO in $\langle \vec{x}"|\rho_1|\vec{x}'\rangle$ That is what happens when gauge symmetry is broken in bosons system that they become superfluid.

Next we consider the case of N particles with any boundary condition and any given density matrix ρ. By taking the trial function $|\vec{x}\rangle = \frac{1}{V^{1/2}}$, Eq (3.19) implies that it has a large eigenvalue of order $\propto N$ for ρ_1. Conversely if ρ_1 has a large eigenvalue $\propto N$ with an eigenfunction $\phi(\vec{x})$, we can take

$$\langle \vec{x}"|\rho_1|\vec{x}'\rangle = \propto N \phi^*(\vec{x}")\phi(\vec{x}') + \rho'_1 \qquad (3.20)$$

where ρ'_1 is a positive operator. An eigenfunction $\phi(x)$ has a normalization factor $\frac{1}{V^{1/2}}$. Equation (3.20) implies that

$$\lim_{\vec{x}" \to \vec{x}'} \langle \vec{x}"|\rho_1|\vec{x}'\rangle = 0 \qquad (3.21)$$

Equation (3.21) can take as the definition of the existence of ODLRO in ρ_1. Its existence is equivalent to that of the existence of a large eigenvalue for ρ_1 of the order of N.

If ODLRO exists in ρ_1, then $\langle \vec{x}"_1|\rho_1|\vec{x}'_1\rangle$ remains nonvanishing for all values of $\vec{x}_1$ and $\vec{x}_2$. For $\langle \vec{x}"_1, \vec{x}"_2|\rho_2|\vec{x}'_1, \vec{x}'_2\rangle$, a large contribution of ρ_2 comes from $\langle \vec{x}"_1|\rho_1|\vec{x}'_1\rangle\langle \vec{x}"_2|\rho_1|\vec{x}'_2\rangle$, then ρ_2 remains nonvanishing for all values of $\vec{x}'_1, \vec{x}'_2, \vec{x}"_1$ and $\vec{x}"_2$.

As in Eq (3.17), two-body reduced density matrix in coordinate representation

$$\langle \vec{x}''_1, \vec{x}''_2 | \rho_2 | \vec{x}'_1, \vec{x}'_2 \rangle = g(\vec{x}''_1 - \vec{x}'_1) g(\vec{x}''_2 - \vec{x}'_2) + g(\vec{x}''_1 - \vec{x}'_2) g(\vec{x}''_2 - \vec{x}'_1) \quad (3.22)$$

If it exhibits ODLRO in ρ_1, then $\rho_2 \neq 0$ for all $\vec{x}''_1, \vec{x}''_2, \vec{x}'_1, \vec{x}'_2$, but if it does not exhibit ODLRO in ρ_1 then $\rho_2 = 0$ except in the neighbourhood of $\vec{x}'_1 = \vec{x}''_1$, $\vec{x}'_2 = \vec{x}''_2$, $\vec{x}'_2 = \vec{x}''_1$ and $\vec{x}'_1 = \vec{x}''_2$.

From Eq. (3.19), we see that the largest eigenvalue of ρ_2 is of the order of N^2. But we want to find it in the order of N, it can be thus said that it exhibits ODLRO in ρ_2. this is not the case of free bosons in equilibrium but may obtain in other systems.

Similary to Eq. (3.20), we may separate ρ_2 as

$$\langle \vec{x}''_1, \vec{x}''_2 | \rho_2 | \vec{x}'_1, \vec{x}'_2 \rangle = \alpha N \phi^*(\vec{x}''_1, \vec{x}''_2) \phi(\vec{x}'_1, \vec{x}'_2) + \rho'_2 \quad (3.23)$$

where ρ'_2 is positive operator. The eigenfunction $\phi(\vec{x}'_1, \vec{x}'_2)$ is zero for large separation of $\vec{x}'_1$ and $\vec{x}'_2$ but has a normalization factor $\frac{1}{V^{1/2}}$ for the neighbourhood of $\vec{x}'_1$ and $\vec{x}'_2$. This is different from equation (3.22) for it exhibits ODLRO in ρ_2 but not in ρ_1 and $\rho_2 = 0$ except in the neightbourhood of $\vec{x}'_1 = \vec{x}''_1$, $\vec{x}'_2 = \vec{x}''_2$, $\vec{x}'_1 = \vec{x}''_2$ $\vec{x}'_2 = \vec{x}''_1$ and the last $\vec{x}'_1 = \vec{x}'_2$, $\vec{x}''_1 = \vec{x}''_2$. This indicates that ρ_2 has an eigenvalue of the order N.

For a system of fermions, since $\lambda_1 \leq 1$, then ODLRO does not occur in ρ_1. But equation (3.23) indicates that ρ_2 may have eigenvalues in the order of N, thus for fermions they can exhibit ODLRO in ρ_2.

For a free fermions system in equilibrium, all eigenvalues of ρ_2 are finite but do not in the order of N , then ODLRO does not occur in ρ_1 and ρ_2. But for a system of a pair occupation, that is a hypothesis of Bardeen, Cooper and Schrieffer, ρ_2 has an eigenvalue of the order N. Thus the superconducting state is characterized by the existence of ODLRO in $\langle e"_1, e"_2 | \rho_2 | e'_1, e'_2 \rangle$ where $e"_1$, $e"_2$, e'_1 and e'_2 represent electron states for a system in thermal equilibrium.

We conclude that in a fermions system there is a superconducting state if ODLRO occurs in two-body reduced density matrix, or equivalently, by the condition that $\langle e"_1, e"_2 | \rho_2 | e'_1, e'_2 \rangle$ has an eigenvalue of the order N , where N is the number of electrons in the system.