PROBLEMS ON NON-EQUILIBRIUM STATISTICAL PHYSICS

A Dissertation

by

MOOCHAN KIM

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

May 2010

Major Subject: Physics

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Approved by:

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ABSTRACT

Problems on Non-Equilibrium Statistical Physics. (May 2010)

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M.S., Postech
Chair of Advisory Committee: Dr. Marlan O. Scully

Four problems in non-equilibrium statistical physics are investigated: 1. The thermodynamics of single-photon gas; 2. Energy of the ground state in Multi-electron atoms; 3. Energy state of the H_2 molecule; and 4. The Condensation behavior in N weakly interacting Boson gas.

In the single-photon heat engine, we have derived the equation of state similar to that in classical ideal gas and applied it to construct the Carnot cycle with a single photon, and showed the Carnot efficiency in this single-photon heat engine.

The energies of the ground state of multi-electron atoms are calculated using the modified Bohr model with a shell structure of the bound electrons. The differential Schrödinger equation is simplified into the minimization problem of a simple energy functional, similar to the problem in dimensional scaling in the H-atom. For the C-atom, we got the ground state energy -37.82 eV with a relative error less than 6 %.

The simplest molecular ion, H_2^+, has been investigated by the quasi-classical method and two-center molecular orbit. Using the two-center molecular orbit derived from the exact treatment of the H_2^+ molecular ion problem, we can reduce the number of terms in wavefunction to get the binding energy of the H_2 molecule, without using the conventional wavefunction with over-thousand terms. We get the binding energy for the H_2 with Hylleraas correlation factor $1 + \kappa r_{12}$ as 4.7eV, which is comparable to the experimental value of 4.74 eV.

Condensation in the ground state of a weakly interacting Bose gas in equilibrium is investigated using a partial partition function in canonical ensemble. The recursive relation for the partition function developed for an ideal gas has been modified to be applicable in the interacting case, and the statistics of the occupation number in condensate states was examined. The well-known behavior of the Bose-Einstein Condensate for a weakly interacting Bose Gas are shown: Depletion of the condensate state, even at zero temperature, and a maximum fluctuation near transition temperature. Furthermore, the use of the partition function in canonical ensemble leads to the smooth cross-over between low temperatures and higher temperatures, which has enlarged the applicable range of the Bogoliubov transformation. During the calculation, we also developed the formula to calculate the correlations among the excited states.

To my Parents, Wife and Son

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I thank all the people who helped me with my studies at Texas A&M University and getting my doctoral degree.

It's not enough to extend my thanks to Prof. Marlan O. Scully, my generous advisor. I confess that all my progress at TAMU was due to him. During these days, when I looked at him, he always reminded me of one scripture: " As iron sharpens iron, so one man sharpens another." (NIV, Proverbs 27:17) Thanks for all his hospitality and kindness, again.

I also thank my beloved wife, Nayoung Lee. She always shows her respect to me with great love. In fact, to live as a foreign student is a great opportunity, yet a great suffering also. But for a wife of a foreign student, it seems only a suffering. Thanks to her for being with me and making a good family. It was a wonderful time to live in College Station with her as one family. Furthermore, I give thanks to my energetic son, Philemon Kim. I also send my appreciation to my parents in Korea.

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Anyway, it was a great time in my life to research in a small town at a great university.

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CHAPTER I

INTRODUCTION

Quantum mechanics developed in last century has revealed the underlying mechanism of the nature in very detail: from microscopic scale such as atoms and molecules to macroscopic scale such as the structure of black hole and the galaxies.

Here, we will investigate the application of the quantum mechanics to simple four systems: a single-photon heat engine, multi-electron atoms in dimensional scaling, binding energy in hydrogen molecule, and a weakly interacting Bose gas with N particles. Even though we will use some semi-quantum methods to describe the multi-electron atoms and hydrogen molecule, quantum mechanics still provides the basic tools to treat these problems.

In Chapter II, the equation of states of a single-photon is derived and the Carnot engine with single photon is considered. In Chapter III, the dimensional scaling has been applied to the multi-electron atoms to get the energy of the ground states. In Chapter IV, the two-center molecular orbit was considered and applied to calculate the binding energy of a hydrogen molecule. In Chapter V, the condensation behavior of the weakly interacting Bose gas was calculated using the Bogoliubov transformation. Finally, summary of this dissertation is in the last chapter.

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CHAPTER II

EQUATION OF STATE OF A SINGLE PHOTON GAS

A. Introduction

The laws of thermodynamics were formulated in the nineteenth century through the epoch making work of Carnot, Classius, Joule and others. The theoretical predictions concerning the behavior of the physical systems based on these laws were found to be in complete agreement with the experimental observations. An important step in the development of thermodynamics was the formulation of the kinetic theory of gases [1] that describes the macroscopic behavior of the gases. For example, it was shown that the pressure of a gas arises due to the molecular motion and the collision of these molecules with the walls of the container. The relationship between the temperature, pressure, volume and the number of particles were formulated. These earlier studies treated atom and molecules to be classical particles.

More recently, the foundations of thermodynamics are being reexamined within the framework of quantum mechanics with the inclusion of the internal quantum states of the working molecules. These studies have shed new light on the classical formulation of the laws of thermodynamics. A classical example of such a system is a laser where atoms or molecules are prepared in an inverted state, a state corresponding to “negative temperature” [2].

Another area where a reevaluation of the laws of thermodynamics is taking place is in the study of the operating limits of ideal heat engines in light of recent developments in quantum optics, such as cavity QED [3], the micromaser [4], and the quantum coherence effects [5, 6]. For example it is shown that it is possible to obtain laser action in the hot exhaust gases of the heat engine and the Otto cycle engine efficiency can be improved beyond that of the “ideal” Otto heat engine via such a “quantum afterburner” [7].

Motivated by the role of the quantum properties of the radiation field in such considerations, we discuss the quantum thermodynamics of a “photon” gas in this paper, taking the lead from well known classical thermodynamics results.

In Section B, we review the thermodynamics of an ideal mono-atomic gas and derive the equation of state. In Section C, we derive the corresponding equation of state for a single-mode *photon* gas. In Section D, the Stefan-Boltzmann law is derived for a multi-mode photon gas. Finally, in Section E, we construct a single-photon Carnot cycle and calculate the efficiency of this cycle.

B. Ideal Gas Inside a Cavity

An ideal gas of N atoms inside a cavity of volume V in thermal equilibrium at temperature T is described by the equation of state [1]

$$PV = Nk_BT, \tag{2.1}$$

where P is the pressure of the gas and k_B is the Boltzmann constant. Although this relation can be considered as a phenomenological relation, we derive here from first principles with a simple argument.

We consider a single atom of mass m confined inside a cube of length L. This single atom is considered as the quantum ideal gas in the classical limit. The Hamiltonian is

$$H = \frac{p^2}{2m} = \frac{\hbar^2(k_x^2 + k_y^2 + k_z^2)}{2m}. \tag{2.2}$$

Due to the periodic boundary conditions, the possible values of k_x, k_y, and k_z are quantized, i.e.,

$$k_x = n_x\frac{2\pi}{L}. \qquad k_y = n_y\frac{2\pi}{L}, \qquad \text{and} \qquad k_z = n_z\frac{2\pi}{L}, \tag{2.3}$$

where n_x, n_y, and n_z are integers. The total energy of the ideal gas with N atoms is

$$E = \sum_{k_x,k_y,k_z} \frac{\hbar^2(k_x^2+k_y^2+k_z^2)}{2m} = \frac{2\pi^2\hbar^2}{mL^2}\sum_{n_x,n_y,n_z}^{N}(n_x^2+n_y^2+n_z^2). \tag{2.4}$$

It is clear that E is related to the volume $V = L^3$ via $E = f(N)/V^{2/3}$ where $f(N)$ is a function that depends only on the number of atoms. The pressure of the ideal gas is therefore given by

$$P = -\left(\frac{\partial E}{\partial V}\right)_N = \frac{2}{3}\frac{E}{V}. \tag{2.5}$$

Next we calculate the average energy $\langle E\rangle$ using the probability of the occupancy of the state, which is given by the Boltzmann factor. By changing the summation into the integration over k,

$$\langle E\rangle = \frac{\sum_{k_x,k_y,k_z} Ee^{-\frac{\hbar^2(k_x^2+k_y^2+k_z^2)}{2mk_BT}}}{\sum_{k_x,k_y,k_z} e^{-\frac{\hbar^2(k_x^2+k_y^2+k_z^2)}{2mk_BT}}} = \frac{\int \frac{\hbar^2k^2}{2m}e^{-\frac{\hbar^2k^2}{2mk_BT}}\,4\pi k^2dk}{\int e^{-\frac{\hbar^2k^2}{2mk_BT}}\,4\pi k^2dk} = \frac{3}{2}k_BT. \tag{2.6}$$

The pressure P is simply given by

$$P = \frac{2}{3}\frac{E}{V} = k_BT\frac{N}{V} \tag{2.7}$$

where we used $E = N\langle E\rangle$. This completes the derivation of the equation of state, Eq. (2.1).

C. Single-mode *Photon* Gas

We now consider a single-mode radiation field inside of a cavity at temperature T instead of an ideal gas. Such a field distribution can be obtained in cavity QED systems by, for example, passing a beam of two-level atoms that is initially prepared in a thermal distribution of the two levels through a cavity that is resonant with the atomic transition [4].

We assume that the cavity of length L_x and cross-section A can support only a single-mode of the field at frequency

$$\Omega = \Omega_n = \frac{n\pi c}{L_x} \tag{2.8}$$

where n is an integer. In equilibrium, the density matrix of the field is given by the thermal distribution [5, 6]

$$\rho_{nn'} = e^{-n\hbar\Omega/k_BT}(1 - e^{-\hbar\Omega/k_BT})\delta_{nn'}, \tag{2.9}$$

i.e., the density matrix is diagonal with vanishing off-diagonal elements. The mean number of photons $\bar{n}$ in the mode is

$$\bar{n} = \sum_{n=0}^{\infty} n\rho_{nn} = \frac{1}{e^{\hbar\Omega/k_BT} - 1}, \tag{2.10}$$

and the internal energy U of the photon gas is given by

$$U = \bar{n}\hbar\Omega. \tag{2.11}$$

Our goal is to derive an equation of state for the photon gas of the form Eq. (2.1).

For this purpose, we first note that the entropy of the photon gas S_{ph} is given by [8]

$$S_{\text{ph}} = -k_B \text{Tr}\, \rho \ln \rho = -k_B \sum_n \rho_{nn} \ln \rho_{nn}. \tag{2.12}$$

On substituting from Eq. (9) for ρ_{nn}, we obtain

$$S_{\text{ph}} = \bar{n}\frac{\hbar\Omega}{T} - k_B \ln\left(1 - e^{-\hbar\Omega/k_B T}\right), \tag{2.13}$$

where we note the diagonalization condition $\sum_n \rho_{nn} = 1$. Next we consider the Helmholtz free energy, which by definition is given by

$$F \equiv U - TS = k_B T \ln\left(1 - e^{-\hbar\Omega/k_B T}\right) \tag{2.14}$$

and where we have used Eq. (2.11). Now we show that the pressure of the photon gas P is given by

$$P = -\left(\frac{\partial F}{\partial V}\right)_T. \tag{2.15}$$

It follows from the definition of the Helmholtz free energy F that

$$dF = dU - TdS - SdT. \tag{2.16}$$

We recall that, according to the first law of thermodynamics,

$$dU = TdS - PdV, \tag{2.17}$$

yielding

$$dF = -PdV - SdT. \tag{2.18}$$

Eq. (2.14) now follows in a straightforward manner.

We consider the change of volume only along x-direction so that $P = -(\partial F/A\partial L_x)_T$.

Recalling Eq. (2.8), the pressure P is given by

$$P = -\frac{1}{A_x}\left(\frac{\partial F}{\partial L_x}\right)_T = \frac{\bar{n}\hbar\Omega}{V}, \tag{2.19}$$

and the equation of state for a single-mode photon gas is

$$PV = \bar{n}\hbar\Omega. \tag{2.20}$$

This equation has a similar form as Eq. (2.1) for an ideal gas. In an ideal gas the number of atoms N is well defined and k_BT is the average energy of each atom. Here the energy of each photon $\hbar\Omega$ is well defined and $\bar{n}$ is the average number of photons.

These basic ideas for a *photon* gas developed in this section provide a foundation for treating more complicated problems relating to quantum heat engines. For example, we shall discuss a Carnot cycle (Fig. 1) engine in which the operating gas is composed of light quanta instead of a collection of atoms or molecules.

D. Multi-mode *Photon* Gas

So far we considered only a single mode of the cavity. We now consider the general case of multi-mode photon field in thermal equilibrium at temperature T inside the cavity.

Each mode of the radiation field is statistically independent. Therefore the equation of state for each mode (say in the x-direction) is

$$P_{n_x}V = \bar{n}_{n_x}\hbar\Omega_{n_x}. \tag{2.21}$$

The total pressure P is the sum of the partial pressures of each mode. For simplicity, we consider the cavity to be a simple cubic with side L. The relations among modes

$(\Omega_{n_x},\,\Omega_{n_y},\,\Omega_{n_z})$ and wave vector $\mathbf{k}$ is

$$\Omega_{n_x} = k_x c, \qquad \Omega_{n_y} = k_y c \quad \text{and} \quad \Omega_{n_z} = k_z c. \tag{2.22}$$

The total pressure is

$$\begin{aligned} P &= \frac{1}{V}\sum_{n_x} \hbar\Omega_{n_x}\bar{n}_{n_x} && (2.23) \\ &= \frac{1}{3V}\sum_{k_i(i=x,y,z)} \hbar\Omega_{k_i}\bar{n}_{k_i}. \end{aligned}$$

We now change the summation into an integral in phase space, so that

$$\begin{aligned} P &= 2\frac{1}{3}\int \frac{1}{(2\pi)^3}(4\pi k^2 dk)\,\hbar\Omega(k)\bar{n}(k) \\ &= \frac{\hbar}{3\pi^2 c^3}\int d\Omega\,\frac{\Omega^3}{e^{\hbar\Omega/k_BT}-1} \\ &= \frac{\hbar}{3\pi^2 c^3}\left(\frac{k_BT}{\hbar}\right)^4\int_0^\infty \frac{x^3 dx}{e^x-1} \\ &= \frac{1}{3}\frac{\pi^2}{15}\frac{(k_BT)^4}{(\hbar c)^3} \\ &= \frac{4}{3}\frac{\sigma}{c}T^4, && (2.24) \end{aligned}$$

where $\sigma = \pi^2 k_B^4/60\hbar^3 c^2$ is the Stefan-Boltzmann constant. We introduced a factor of 2 in the first line to account for the two possible states of polarization. Eq. (2.24) is the Stefan-Boltzmann law of blackbody radiation.

E. Application to the Carnot Cycle with One Photon

The Szilard had suggested that the quantum engine can be operated by a sinlge atom [9]. Similarly, we may construct the quantum engine operated by a single photon.

To construct the Carnot cycle engine, let's compare both equations of states: one for the ideal gas and the other for the single photon. In the equation of state of the single photon

$$PV = \bar{n}\hbar\Omega, \tag{2.25}$$

the dependence on temperature is not shown explicitly. However, the average number of photons $\bar{n}$ has dependence on the temperature T, and on the volume V. The volume dependency is imposed by the boundary condition to the available frequency Ω implicitly.

Furthermore, the total internal energy U for the single photon is

$$U = \bar{n}\hbar\Omega. \tag{2.26}$$

It means that internal energy is dependent on volume V and this is also the difference from the usual ideal gas.

F. Quantum Carnot Cycle

Carnot cycle consists of two processes : the isothermal process (constant temperature) and the adiabatic process (constant entropy). The corresponding diagram in T-S plane is just a rectangular, shown in Fig. (1) : The horizontal lines correspond to the isothermal process, and the vertical lines to the adiabatic process.

Let's explicitly see the processes for the system which is confined in a cylinder with one movable side as like in a usual piston.

1. During 1 → 2 (or 3 → 4) : (Isothermal Process)

Since the entropy of the single photon is

$$S_{\text{ph}} = \bar{n}\frac{\hbar\Omega}{T} - k_B \ln\left(1 - e^{-\hbar\Omega/k_B T}\right), \tag{2.27}$$

the heat transfer in this process is

$$Q_{\text{in}} = T\Delta S = U_2 - U_1 + k_B T \ln\left(\frac{1+\bar{n}_2}{1+\bar{n}_1}\right). \tag{2.28}$$

The change of internal energy is NOT vanished since it depends on the volume through the frequency Ω. We can get the transferred heat into the system.

Since

$$\Omega = \frac{n\pi c}{L_x} \quad \rightarrow \quad \Omega \propto \frac{1}{L_x}, \tag{2.29}$$

we can calculate the average number of photons for the given volume V_2 at stage 2

$$\bar{n}_2 = \frac{1}{\left(1+\frac{1}{\bar{n}_1}\right)^{\frac{1}{\chi}} - 1} \tag{2.30}$$

and the pressure

$$P_2 = \frac{\bar{n}_2 \hbar\Omega_2}{V_2} = \frac{\hbar\Omega_1}{\chi^2 V_1} \frac{1}{\left(1+\frac{1}{\bar{n}_1}\right)^{\frac{1}{\chi}} - 1} \tag{2.31}$$

with the volume expansion factor $\chi = \frac{V_2}{V_1} = \frac{L_{x2}}{L_{x1}} = \frac{\Omega_1}{\Omega_2}$ (cavity length expansion factor).

2. During 2 → 3 (or 4 → 1) (Adiabatic Process)

Since

$$\bar{n} = \frac{1}{e^{\hbar\Omega/k_B T} - 1}, \tag{2.32}$$

we may rewrite the entropy in terms of $\bar{n}$.

$$S_2 = \bar{n}_2 \frac{\hbar\Omega_2}{T_2} + k_B \ln\left(1+\bar{n}_2\right). \tag{2.33}$$

By equating the entropy at 2 and 3,

$$\bar{n}_2 \frac{\hbar\Omega_2}{T_2} + k_B \ln\left(1+\bar{n}_2\right) = \bar{n}_3 \frac{\hbar\Omega_3}{T_3} + k_B \ln\left(1+\bar{n}_3\right). \tag{2.34}$$

It's nontrivial equation for the adiabatic process. However, there's a trivial solution.

$$\frac{\Omega_2}{T_2} = \frac{\Omega_3}{T_3} \quad \longrightarrow \quad \bar{n}_2 = \bar{n}_3. \tag{2.35}$$

$$\bar{n} = \frac{P_2 V_2}{\hbar\Omega_2} = \frac{P_3 V_3}{\hbar\Omega_3} \tag{2.36}$$

or

$$PV^2 = \text{const.} \tag{2.37}$$

Refer the exponent is $\frac{5}{3}$ for the classical monatomic ideal gas.

The work done during these process will be

$$\Delta W = \Delta U = U_2 - U_3. \tag{2.38}$$

3. Model System for Carnot Cycle

Let's assume a system of a single photon, and set the processes in Carnot cycle as following :

1. (Stage 1 → 2) isothermal process with double expansion of the cavity
2. (Stage 2 → 3) adiabatic process with decrease of the temperature by two-third
3. (Stage 3 → 4) isothermal compression of the cavity
4. (Stage 4 → 1) adiabatic process with increase of the temperature

The above processes are shown in the Table I. The processes are controlled by the change of the volume by moving the movable wall of the cylinder. In isothermal process the contact with temperature reservoir is sustained, and in adiabatic process the system was disconnected from the reservoir.

All the above processes are summarized in the P-V diagram which is shown in Fig. 2.

4. The Efficiency

One of the controversies in quantum system is that the possibilities for the overcome of the efficiency of the usual Carnot cycle [1]. The efficiency of this Quantum Carnot engine with single-photon gas is

$$\eta = \frac{\Delta W}{Q_{\text{in}}} = \frac{T_h(S_2 - S_1) - T_l(S_2 - S_1)}{T_h(S_2 - S_1)} = 1 - \frac{T_h}{T_l}, \tag{2.39}$$

and has the same efficiency as the usual Carnot cycle.

CHAPTER III

H-ATOM IN D-SCALING AND MULTI-ELECTRON ATOMS IN BOHR MODEL

One of the important question in quantum mechanics is that to calculate the energy spectrum in any given quantum system. Since we can easily identify the kinetic energy and interactions among the entities in the system, we might construct the corresponding Schrödinger equation, even a relativistic one. Anyway, to solve the problem in analytic or numerical way is not simple problem, even if only 3 particles are in the system, like He-atom. Historically, for He-atom we can calculate the energy spectrum using the several methods using a large number of variational parameters [10]. Here, we introduce another approach to this problem in more practical sense : to search an *easy* method to calculate the energy in a complicate system. One of the way is that Dimensional scaling (D-Scaling) which will be shown in this chapter, and the application to multi-electron atoms.

A. H-atom in D-scaling

To describe the D-Scaling method, let's try to solve the Schrödinger equation for the H-atom in atomic unit to get the physics about the system.

The Schrödinger equation is

$$H = \frac{\mathbf{p}^2}{2} + \frac{Z}{r} = -\frac{1}{2}\nabla^2 + \frac{Z}{r}. \tag{3.1}$$

The energy eigenvalues [8] are

$$E_n = -\frac{Z^2}{2n^2}. \tag{3.2}$$

1. Transformation of the Hamiltonian in D-scaling

Since the potentials for any multi-electron systems are well-described by the Coulomb potential, or the electrostatic interaction, the operators in Hamiltonian are only in the kinetic energy. To generalize the system into large dimension, and finally to infinite dimension, let's generalize the problem into arbitrary large D-dimension. For simplicity, with vector notation the distance is transformed as

$$r^2 = \sum_{i=1}^{3} x_i^2 \quad \rightarrow \quad r^2 = \sum_{i=1}^{D} x_i^2. \tag{3.3}$$

Similarly the Laplacian in kinetic energy,

$$\sum_{i=1}^{3} \frac{\partial^2}{\partial x_i^2} \quad \rightarrow \quad \sum_{i=1}^{D} \frac{\partial^2}{\partial x_i^2}. \tag{3.4}$$

Since the potential terms has only r-dependence, we simply assume the same form as in 3-D. Because we only concern the lower states of the system with more symmetries, let's use the hyper-spherical coordinate for simplicity. The transformation rule for

D-dimensional space is [11]

$$\begin{aligned}
x_1 &= r\cos\theta_1 \sin\theta_2 \sin\theta_3 \cdots \sin\theta_{D-1}, \\
x_2 &= r\sin\theta_1 \sin\theta_2 \sin\theta_3 \cdots \sin\theta_{D-1}, \\
x_3 &= r\cos\theta_2 \sin\theta_3 \sin\theta_4 \cdots \sin\theta_{D-1}, \\
x_4 &= r\cos\theta_3 \sin\theta_4 \sin\theta_5 \cdots \sin\theta_{D-1}, \\
&\vdots \\
x_j &= r\cos\theta_{j-1} \sin\theta_j \sin\theta_{j+1} \cdots \sin\theta_{D-1}, \\
&\vdots \\
x_{D-1} &= r\cos\theta_{D-2} \sin\theta_{D-1}, \\
x_D &= r\cos\theta_{D-1},
\end{aligned} \tag{3.5}$$

where

$$0 \leq \theta_1 \leq 2\pi, \quad 0 \leq \theta_j \leq \pi \quad \text{for } j = 2, 3, \cdots, D-1, \tag{3.6}$$

and D is a positive integer and $D \geq 3$.

Then, the Laplacian becomes

$$\nabla_D^2 = \sum_{i=1}^{D} \frac{\partial^2}{\partial x_i^2} = K_{D-1}(r) - \frac{L_{D-1}^2}{r^2} \tag{3.7}$$

where

$$K_{D-1}(r) = \frac{1}{r^{D-1}} \frac{\partial}{\partial r} \left(r^{D-1} \frac{\partial}{\partial r} \right), \tag{3.8}$$

$$L_k(r) = -\frac{1}{\sin^{k-1}\theta_k} \frac{\partial}{\partial \theta_k} \sin^{k-1}\theta_k \frac{\partial}{\partial \theta_k} + \frac{L_{k-1}^2}{\sin^2\theta_k}, \tag{3.9}$$

and

$$L_1^2 = -\frac{\partial^2}{\partial\theta_1^2}. \tag{3.10}$$

The proof for (3.7) is in Appendix A. If we only consider the state with spherical symmetry, then the hyper-angular part satisfy that

$$L_{D-1}^2 Y(\Omega_{D-1}) = l(l+D-2)Y(\Omega_{D-1}), \tag{3.11}$$

and the Hamiltonian is simplified into

$$H = -\frac{1}{2}K_{D-1}(r) + \frac{l(l+D-2)}{2r^2} + V(r). \tag{3.12}$$

After generalizing the dimension of the system, let's rescaling the wavefunction. By the following transformation

$$\Psi = e^{-\frac{D-1}{2}}\Phi, \tag{3.13}$$

the rescaled Schrödinger equation is

$$H\Psi = E\Psi \quad \rightarrow \quad \left[-\frac{1}{2}\frac{\partial^2}{\partial r^2} + \frac{\Lambda(\Lambda+1)}{2r^2} + V(r)\right]\Phi = E\Phi \tag{3.14}$$

with $\Lambda = l + \frac{1}{2}(D-3)$, resembling the usual angular momentum quantum number l in 3-D.

Then, with the rescaled distance and energy,

$$r_s = \frac{4}{(D-1)^2}r, \tag{3.15}$$

$$E_s = \frac{(D-1)^2}{4}E, \tag{3.16}$$

the Schrödinger equation is

$$\left[-\frac{1}{2}\frac{4}{(D-1)^2}\frac{\partial^2}{\partial r_s^2}+\frac{(D-3)}{2(D-1)r_s^2}-\frac{Z}{r_s}\right]\Phi = E_s\Phi. \tag{3.17}$$

In the limit $D \to \infty$, the final form is

$$\left[\frac{1}{2r_s^2}-\frac{Z}{r_s}\right]\Phi = E_s\Phi. \tag{3.18}$$

The differential equation reduces into a simple algebraic equation. Since our interest is on the lowest energy, that is the energy of the ground state, the minimum position for r_s and the corresponding energy is given by a differentiation with r_s.

$$r_s = \frac{1}{Z}, \tag{3.19}$$

$$E_s = -\frac{Z^2}{4}. \tag{3.20}$$

B. Quantization Rule and Shell Structure

The dimensional scaling which is introduced in earlier section can easily handle the ground-state for H-atom. And the result is same for the original Bohr model. To extend these concept to multi-electron atoms, we need one result from quantum mechanics : shell structure of the electrons in the atoms. Fermionic property of the electrons and their angular momenta construct the shell structure of the atoms. Here, we simply introduce this shell structure by the quantization rule. The acceptable momentum is

$$r_i p_i = n_i \quad \text{with positive integer } n_i. \tag{3.21}$$

By the analogy with Eq. (3.18), the kinetic energy in the Bohr model is transformed into a simple polynomial function of radius r_i.

$$\sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2} = -\sum_{i=1}^{N} \frac{\nabla_i^2}{2} \quad \rightarrow \quad -\frac{1}{2} \sum_{i=1}^{N} \frac{n_i^2}{r_i^2}. \tag{3.22}$$

C. Multi-electron Atoms in D-scaling

By replacing the Laplacian $\frac{n^2}{r^2}$, the Hamiltonian is reduced into a simple polynomial function.

$$H = \sum_i \left(-\frac{1}{2} \frac{n_i^2}{r^2} \right) - \sum_{i \neq j} \frac{Z_i Z_j}{r_{ij}}. \tag{3.23}$$

The problem is simplified from to solve the eigenvalue problem of a differential equation into to get the minimum of a polynomial function.

Due to the Pauli exclusion principle, each electron should occupy different state because it is fermion. And the quantization of the eigen-energies in H-atom shows the shell structure which is well-known since the early Quantum mechanics. From the shell structure of the multi-electron atoms, let's assume that the quantum number n_i is shown in Table. (II). For example, the 3p-state has maximally 6 electrons in the state and the corresponding quantum number is $n_i = 3$ with two-fold spin degeneracy.

For the ground state of the multi-electron atoms, the Hamiltonian can be constructed by assigning proper quantum number n_i for each electron in the atoms. Since the number of variables in multi-electron atoms with N-electrons are $3N$, we will use the Downhill Simplex Method (DSM) as minimization for the Hamiltonian function [12].

The results are shown for several atoms. Especially, for the carbon atom with 6-electrons, its configuration of the ground state is in Fig. 7, which shows the (sp^2)-hybridization similar to the result of quantum mechanics.

The results for the energy of the multi-electron atoms are summarized in Table (III). The C-atom has the minimum relative error, and the atoms has the relative errors less than 6 %.

CHAPTER IV

BINDING ENERGY IN HYDROGEN MOLECULE

After solving the hydrogen atom problem in quantum mechanics, the next stage might be the system with a few constituents : for example, He-atom or H_2 molecule [13]. In this chapter, we might go to the molecular problem : H_2 molecule. Even though we can write the corresponding Schrödinger equation for molecules, it's almost impossible to solve the problem analytically to get the energy eigenstate, and difficult even in numerical methods.

Here, we will introduce two different method to solve this simplest molecular problem: One is the quasiclassical method and the other is quantum mechanical method.

Usually, the classical method fails to describe the quantum system. In the first part of this chapter, we will describe how to treat the electron's trajectory in H_2^+ molecular ion, and calculate the lowest energy of this molecular ion. In the second part, we will to construct the Molecular orbit for the system with two centers in quantum mechanics. After getting the two-center molecular orbit, we will apply it to get the energy of ground state in H_2 molecule. Just using only one ground state molecular orbital, modified by a simple electronic correlation factor and without any free (variational) fitting and find a binding energy of 4.5 eV. With the same form (the exact solution for H_2^+), but with a couple of the constants interpreted as variational parameters, the binding energy is found to be 4.7 eV [13]. The present results are obtained (and strengthened) by independent numerical and analytical calculations, with different choices for the representation of the exact H_2^+ solution.

A. System with Two Centers

Let's consider a simple system with two nuclei and one-electron. Then, the Hamiltonian is

$$H = \frac{\mathbf{P}_a^2}{2M_a} + \frac{\mathbf{P}_b^2}{2M_b} + \frac{\mathbf{p}^2}{2m} - \frac{Z_a e^2}{r_{a1}} - \frac{Z_b e^2}{r_{b1}} + \frac{Z_a Z_b e^2}{R}. \tag{4.1}$$

Since the mass ratio between the nuclei (that is, proton in H_2^+ ion) and electron is $M_a/m = M_b/m \sim 1836$, we might neglect the motion of nuclei and consider as a fixed particle with infinite mass, that is the Born-Oppenheimer approximation [14]. Then, the Hamiltonian is reduced into

$$H = \frac{\mathbf{p}^2}{2m} - \frac{Z_A e^2}{r_{A1}} - \frac{Z_B e^2}{r_{B1}} + \frac{Z_A Z_B e^2}{R}. \tag{4.2}$$

In coordinate representation,

$$H = -\frac{\hbar^2}{2m}\nabla^2 - \frac{Z_A e^2}{r_{A1}} - \frac{Z_B e^2}{r_{B1}} + \frac{Z_A Z_B e^2}{R}. \tag{4.3}$$

For simplicity, let's use the atomic unit for the system. That the distance is measured by the Bohr radius $a_0 = \frac{4\pi\epsilon_0\hbar^2}{me^2} = 0.529\text{Å}$ and the energy is measured by the twice of Rydberg energy $E_{Ryd} = 2\frac{me^4}{8\epsilon_0^2\hbar^3 c} = 27.21\,\text{eV} = 2\,\text{Ry}$. In fact, $1\,\text{Ry}$ is the energy of the ground state of the Hydrogen atom. Then, the rescaled Hamiltonian with redefined variables is

$$H = -\frac{1}{2}\nabla^2 - \frac{Z_a}{r_{a1}} - \frac{Z_b}{r_{b1}} + \frac{Z_a Z_b}{R}. \tag{4.4}$$

Here, r_{a1} (r_{b1}) is the distance from Nucleus A (B) shown in Fig. 9. In the above form, there's only dimensionless parameters to simplify the arithmetics of the energy calculation. The final form is also gotten by replacing $\hbar = m = e = 1$. The detail explanation for the atomic unit is found in Englert's book [15].

B. Hamiltonian in Two-center Coordinate

Since there's two centers given by two nuclei, the proper coordinate is also that with two centers.

Here, we might use the spheroidal coordinate that is defined through following definition.

$$\lambda = \frac{r_a + r_b}{R}, \tag{4.5}$$

$$\mu = \frac{r_a - r_b}{R}. \tag{4.6}$$

with azimuthal angle ϕ which is in usual 3-D cylindrical coordinate. Fig. 10 clearly shows the meaning of (λ, μ, ϕ).

Then, the above Hamiltonian can be written in terms of (λ, μ, ϕ) gives the corresponding Schrödinger equation for H_2^+ molecular ion as

$$\begin{aligned} \frac{\partial}{\partial\lambda}\left[(\lambda^2-1)\frac{\partial\psi}{\partial\lambda}\right] + \frac{\partial}{\partial\mu}\left[(1-\mu^2)\frac{\partial\psi}{\partial\mu}\right] + \left[\frac{1}{\lambda^2-1} + \frac{1}{1-\mu^2}\right]\frac{\partial^2\psi}{\partial\phi^2} \\ + 2R^2\left[\frac{1}{4}\left(E - \frac{1}{R}\right)(\lambda^2-\mu^2) + \frac{1}{R}\lambda\right]\psi = 0. \end{aligned} \tag{4.7}$$

C. Quasiclassical Description of Chemical Bonding of H_2^+ Molecular Ion

If electron motion is in the plane passing through the molecular axis then the action is given by

$$S = -Et + \int^{\lambda} \sqrt{\frac{1}{2}mR^2E + \frac{\beta + 2mR\lambda}{\lambda^2-1}}\,d\lambda + \int^{\mu} \sqrt{\frac{1}{2}mR^2E - \frac{\beta}{1-\mu^2}}\,d\mu, \tag{4.8}$$

where m is the electron mass, E is the electron energy and β is a constant of motion. For finite motion $E < 0$, $\beta < 0$. In dimensionless units

$$R \to a_0 R, \quad E \to E_0 E, \quad t \to t/E_0, \tag{4.9}$$

where $a_0 = \hbar^2/me^2$ is the Bohr radius, $E_0 = e^2/a_0$ is one Hartree, the action reads

$$S = -Et + \hbar \int^{\lambda} \sqrt{\frac{1}{2}R^2 E + \frac{\beta + 2R\lambda}{\lambda^2 - 1}}\, d\lambda + \hbar \int^{\mu} \sqrt{\frac{1}{2}R^2 E - \frac{\beta}{1-\mu^2}}\, d\mu. \tag{4.10}$$

Canonical momenta associated with λ and μ are

$$p_\lambda = \frac{\partial S}{\partial \lambda} = \hbar \sqrt{\frac{1}{2}R^2 E + \frac{\beta + 2R\lambda}{\lambda^2 - 1}}, \tag{4.11}$$

$$p_\mu = \frac{\partial S}{\partial \mu} = \hbar \sqrt{\frac{1}{2}R^2 E - \frac{\beta}{1-\mu^2}}. \tag{4.12}$$

If electron moves in a plane then its motion is determined by four initial conditions: initial values of λ, μ, p_λ and p_μ. We are interested in trajectories which correspond to periodic motion. For the planar electron motion the periodic trajectories exist if, e.g., the electron at some point moves with zero velocity. This point is determined by the condition $p_\lambda = 0$ and $p_\mu = 0$, which yields

$$\lambda_{\max} = -\frac{2}{RE}\left[1 + \sqrt{1 - \frac{E}{2}\left(\beta - \frac{R^2 E}{2}\right)}\right], \tag{4.13}$$

$$\lambda_{\min} = -\frac{2}{RE}\left[1 - \sqrt{1 - \frac{E}{2}\left(\beta - \frac{R^2 E}{2}\right)}\right], \tag{4.14}$$

$$\mu_{\max} = -\sqrt{1 - \frac{2\beta}{R^2 E}}. \tag{4.15}$$

At initial moment of time the electron starts to move with zero velocity from a point with coordinates $\lambda_{\max}$, $\mu_{\max}$. During the motion μ changes from $\mu_{\max}$ to -1 and then back to $\mu_{\max}$. The electron trajectory can be obtained from the equations $\partial S/\partial E = C_1$, $\partial S/\partial \beta = C_2$, where constants C_1 and C_2 are given by the initial conditions. The second equation yields

$$\int\limits_{\lambda}^{\lambda_{\max}} \frac{d\lambda}{\sqrt{\lambda^2-1}\sqrt{(\lambda_{\max}-\lambda)(\lambda-\lambda_{\min})}} = \int\limits_{\mu}^{\mu_{\max}} \frac{d\mu}{\sqrt{1-\mu^2}\sqrt{\mu^2-\mu_{\max}^2}}, \tag{4.16}$$

while the first one leads to

$$-\frac{\sqrt{|E|}t}{\sqrt{2}\hbar R} = \int\limits_{\lambda}^{\lambda_{\max}} \frac{\sqrt{\lambda^2-1}d\lambda}{\sqrt{(\lambda_{\max}-\lambda)(\lambda-\lambda_{\min})}} + \int\limits_{\mu}^{\mu_{\max}} \frac{\sqrt{1-\mu^2}d\mu}{\sqrt{\mu^2-\mu_{\max}^2}}. \tag{4.17}$$

Eq. (4.16) can be solved in theorems of Jacobi elliptic functions. After some algebra we obtain the following formula for the trajectory

$$\lambda + 1 =$$

$$\frac{1+\lambda_{\max}}{1+\frac{1}{2}(\lambda_{\max}-1)\mathrm{sn}^2\left[\frac{\sqrt{2}\sqrt{\lambda_{\max}-\lambda_{\min}}}{1-\mu_{\max}}F\left(\arcsin\sqrt{\frac{(1-\mu_{\max})(\mu_{\max}-\mu)}{(1+\mu_{\max})(-\mu_{\max}-\mu)}}, \frac{1+\mu_{\max}}{1-\mu_{\max}}\right), \sqrt{\frac{(\lambda_{\max}-1)(\lambda_{\min}+1)}{2(\lambda_{\max}-\lambda_{\min})}}\right]}, \tag{4.18}$$

where $F(\varphi, k) = \int_0^{\varphi} \frac{d\varphi}{\sqrt{1-k^2\sin^2\varphi}}$ is the elliptic integral of the first kind, $\mathrm{sn}(\varphi, k)$ is the elliptic sinus.

The electron motion is completely specified by two constants: the initial coordinates $\lambda_{\max}$, $\mu_{\max}$ or equivalently by the energy E and the constant β. However, the motion is periodic only if periods of $\lambda(t)$ and $\mu(t)$ are commensurate. For the ground state this suggests that when $\mu = -1$ it should be $\lambda = \lambda_{\max}$. Then from Eq. (4.18) we obtain a constraint for possible values of $\lambda_{\max}$ and $\mu_{\max}$:

$$\lambda_{\max} = -1 + \frac{1+\lambda_{\max}}{1+\frac{1}{2}(\lambda_{\max}-1)\mathrm{sn}^2\left[\frac{\sqrt{2}\sqrt{\lambda_{\max}-\lambda_{\min}}}{1-\mu_{\max}}F\left(\frac{\pi}{2},\frac{1+\mu_{\max}}{1-\mu_{\max}}\right),\sqrt{\frac{(\lambda_{\max}-1)(\lambda_{\min}+1)}{2(\lambda_{\max}-\lambda_{\min})}}\right]}. \tag{4.19}$$

As a result, only one free parameter, e.g. the electron energy E, remains unknown.

Figure 11 shows a periodic electron trajectory. The spacing between nuclei is $R = 2$ a.u.. Electron starts to move from a point $\lambda = 1.82$, $\mu = -0.12$. The trajectory crosses the molecular axis twice at $\lambda = 1$, $\mu = -0.33$ and $\lambda = 1.82$, $\mu = -1$. At the second crossing point the trajectory is perpendicular to the molecular axis. The total energy is $E_{\text{total}} = E + 1/R = -0.60$ a.u.

To find the potential energy curve $E(R)$ we need an additional equation that constrains E (or β). A possible way is to use the force equation:

$$F_e(E,R) = -\frac{\partial E(R)}{\partial R}, \tag{4.20}$$

where $F_e(E,R)$ is the average force of interaction between a nucleus and the electron, $E(R)$ is the electron energy. The average force on the nucleus 1 due to the interaction with electron points along the molecular axis and is given by

$$F_e(E,R) = \frac{1}{T}\int_0^T \frac{\cos\theta(t)}{r_1^2(t)}dt, \tag{4.21}$$

where T is the period of electron motion, θ is the angle between $\mathbf{r}_1$ and molecular axis. The force can be written as

$$F_e(E,R) = \frac{\int_{-1}^{\mu_{\max}} \frac{\cos\theta}{r_1^2}\frac{d\mu}{\dot{\mu}}}{\int_{-1}^{\mu_{\max}} \frac{d\mu}{\dot{\mu}}}. \tag{4.22}$$

From Eqs. (4.16) and (4.17) we obtain

$$\dot{\mu} \propto \frac{\sqrt{1-\mu^2}\sqrt{\mu^2-\mu_{\max}^2}}{\lambda^2-\mu^2}. \tag{4.23}$$

Then using $\cos\theta = (1+\lambda\mu)/(\lambda+\mu)$ and $r_1 = (\lambda+\mu)R/2$ Eq. (4.22) yields

$$F_e(E,R) = \frac{4}{R^2}\frac{\int_{-1}^{\mu_{\max}} \frac{(1+\lambda\mu)(\lambda-\mu)}{(\lambda+\mu)^2\sqrt{1-\mu^2}\sqrt{\mu^2-\mu_{\max}^2}}d\mu}{\int_{-1}^{\mu_{\max}} \frac{(\lambda^2-\mu^2)}{\sqrt{1-\mu^2}\sqrt{\mu^2-\mu_{\max}^2}}d\mu}. \tag{4.24}$$

In this equation λ is given by Eq. (4.18). Eqs. (4.20) and (4.24) provide the additional constraint equation. However since Eq. (4.20) is differential we have to specify one point in the potential curve (initial condition). As soon as this point is specified the whole potential curve is obtained by solving the differential equation. However the initial point remains arbitrary and has to be determined by additional arguments.

Another way to obtain a constraint equation is to use an adiabatic invariant

$$\oint p ds = 2\pi\hbar n, \tag{4.25}$$

where

$$p = \sqrt{2}\hbar\sqrt{E + \frac{2}{R}\left(\frac{1}{\lambda+\mu} + \frac{1}{\lambda-\mu}\right)} \tag{4.26}$$

is the electron momentum and the integral is taken along the electron trajectory. Taking into account

$$ds = \frac{R}{2}\sqrt{\lambda^2-\mu^2}\sqrt{\frac{d\lambda^2}{\lambda^2-1} + \frac{d\mu^2}{1-\mu^2}} \tag{4.27}$$

and

$$\left(\frac{d\lambda}{d\mu}\right)^2 = \frac{(\lambda^2-1)(\lambda_{\max}-\lambda)(\lambda-\lambda_{\min})}{(1-\mu^2)(\mu^2-\mu_{\max}^2)}, \tag{4.28}$$

we obtain the constraint equation

$$\int_{-1}^{\mu_{\max}} \sqrt{ER^2 + 2R\left(\frac{1}{\lambda+\mu} + \frac{1}{\lambda-\mu}\right)}\sqrt{\lambda^2-\mu^2}\sqrt{\frac{(\lambda_{\max}-\lambda)(\lambda-\lambda_{\min})}{(1-\mu^2)(\mu^2-\mu_{\max}^2)} + \frac{1}{1-\mu^2}}d\mu$$
$$= \frac{\pi}{\sqrt{2}}n. \tag{4.29}$$

The "quantum number" n (not necessarily integer or half integer) in the right side of the equation remains a free parameter.

The adiabatic invariant constraint and the force equation constraint are equivalent to each other. Both these equations contain a free parameter that has to be specified. The parameter can be determined if we know, e.g., one point in the potential energy curve.

Fig. 12 compares potential energy curves of H_2^+ molecule obtained using the present technique (solid lines) with "exact" quantum mechanical dots. We plot two curves calculated using the force equation for two choices of the initial point. For the lower curve we chose the initial point by matching $E(R)$ with the quantum mechanical answer at $R = 2$ a.u., while for the upper curve we make a match at $R = 1$ a.u. We also plot the Bohr model result obtained using quantization relative to both nuclei (dashed line) and molecular axis (dot line).

1. ∞-like Trajectory

Another class of periodic trajectories corresponds to motion of the electron from one nucleus to another. For ∞-like motion the electron passes through the molecular center $\lambda = 1$, $\mu = 0$. Equation of the trajectory is

$$\int_1^{\lambda} \frac{d\lambda}{\sqrt{\lambda^2-1}\sqrt{(\lambda_{\max}-\lambda)(\lambda-\lambda_{\min})}} = \int_0^{\mu} \frac{d\mu}{\sqrt{1-\mu^2}\sqrt{\mu^2-\mu_{\max}^2}}. \tag{4.30}$$

It can be expressed in terms of elliptic functions as

$$\lambda-\lambda_{\min}$$
$$=\frac{1-\lambda_{\min}}{1-\frac{(\lambda_{\max}-1)}{(\lambda_{\max}-\lambda_{\min})}\mathrm{sn}^2\left[\frac{\sqrt{\lambda_{\max}-\lambda_{\min}}}{\sqrt{2}\sqrt{1-\mu_{\max}^2}}F\left(\arcsin\mu\sqrt{\frac{1-\mu_{\max}^2}{\mu^2-\mu_{\max}^2}},\frac{1}{\sqrt{1-\mu_{\max}^2}}\right),\sqrt{\frac{(\lambda_{\max}-1)(\lambda_{\min}+1)}{2(\lambda_{\max}-\lambda_{\min})}}\right]}. \tag{4.31}$$

For the ∞-like orbit $\mu_{\max}^2<0$. The motion is periodic if at the point $\mu=-1$, where the electron crosses molecular axis, $\lambda=\lambda_{\max}$. This yields the following constraint

$$\lambda_{\max}=\lambda_{\min}+\frac{1-\lambda_{\min}}{1-\frac{(\lambda_{\max}-1)}{(\lambda_{\max}-\lambda_{\min})}\mathrm{sn}^2\left[\frac{\sqrt{\lambda_{\max}-\lambda_{\min}}}{\sqrt{2}\sqrt{1-\mu_{\max}^2}}F\left(\frac{\pi}{2},\frac{1}{\sqrt{1-\mu_{\max}^2}}\right),\sqrt{\frac{(\lambda_{\max}-1)(\lambda_{\min}+1)}{2(\lambda_{\max}-\lambda_{\min})}}\right]}. \tag{4.32}$$

Figure 13 shows ∞-like trajectory. The spacing between nuclei is $R=2$ a.u. The trajectory crosses the molecular axis three times at $\lambda=1$, $\mu=0$ and $\lambda=1.646$, $\mu=\pm1$. At the outer crossing points the trajectory is perpendicular to the molecular axis. The total energy is $E_{\text{total}}=E+1/R=-0.6025$ a.u.

To find the ground state potential energy curve of H_2^+ molecule we use the quantization conditions

$$\oint p_\lambda d\lambda=2\pi\hbar\left(n_\lambda+\frac{1}{2}\right), \tag{4.33}$$

$$\oint p_\mu d\mu=2\pi\hbar\left(n_\mu+\frac{1}{2}\right), \tag{4.34}$$

where 1/2 appears because the coordinates are bound between two turning points.

We assume that electron motion remains periodic (∞-like) under change in the internuclear spacing R. This imposes constraint (4.32) on E and β. To find E we need only one additional equation which comes from the quantization conditions. Since only one equation is necessary the conditions (4.33) and (4.34) can not be satisfied simultaneously. Instead we assume that a linear combination of Eqs. (4.33) and (4.34) remains invariant. We found that for the ground state of H_2^+ the proper invariant combination is

$$3\oint p_\lambda d\lambda + 2\oint p_\mu d\mu = 2\pi\hbar\left(3n_\lambda + 2n_\mu + \frac{5}{2}\right) \tag{4.35}$$

with $n_\lambda = 0$ and $n_\mu = 1$. In terms of elliptic integrals one can write Eq. (4.35) as

$$\frac{3}{\pi}\sqrt{2R^2|E|}\int\limits_1^{\lambda_{\max}}\frac{\sqrt{(\lambda_{\max}-\lambda)(\lambda-\lambda_{\min})}}{\sqrt{\lambda^2-1}}d\lambda + \frac{2}{\pi}\sqrt{2R^2|E|}\sqrt{1-\mu_{\max}^2}E\left(\frac{\pi}{2}, \frac{1}{\sqrt{1-\mu_{\max}^2}}\right)$$
$$= 3n_\lambda + 2n_\mu + \frac{5}{2}, \tag{4.36}$$

where $E(\varphi, k) = \int\limits_0^{\varphi}\sqrt{1-k^2\sin^2\varphi}d\varphi$ is the elliptic integral of the second kind. Eqs. (4.32) and (4.36) determine the potential energy curve.

Fig. 14 compares potential energy curve of H_2^+ molecule obtained by solving Eqs. (4.32) and (4.36) with $n_\lambda = 0$ and $n_\mu = 1$ (solid line) and "exact" quantum mechanical dots. At $R > 4.72$ a.u. the periodic ∞-like trajectory ceases to exist. Near the bond length and large R our result yields accuracy comparable with those obtained in [17] using a uniform quantization method. However at small R the present approach works better. For example, at $R = 0.5$ a.u. the uniform quantization result deviates from the "exact" dot by 0.07 Hartree, while our answer has the accuracy of 0.03 Hartree.

Fig. 15 compares our result (solid line) with those of Ref. [17] obtained using primitive (dash-dot) and uniform quantization (dashed line).

D. Two-center Molecular Orbit

Now, let's change the two-center molecular orbit to solve the Schrödinger problem for H_2 molecule problem.

With the separation of variables,

$$\psi(\lambda,\mu,\phi)=L(\lambda)M(\mu)e^{im\phi}, \qquad m=0,\pm1,\pm2,\cdots . \tag{4.37}$$

The detailed procedure is shown in Appendix B. The separated equations for the λ and μ are

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}\lambda}\left\{(\lambda^2-1)\frac{\mathrm{d}\Lambda}{\mathrm{d}\lambda}\right\}+\left\{A+2R_1\lambda-p^2\lambda^2-\frac{m^2}{\lambda^2-1}\right\}\Lambda=0,\\ R_1\equiv\frac{R}{2}\frac{Z_a+Z_b}{2},\end{aligned} \tag{4.38}$$

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}\mu}\left\{(1-\mu^2)\frac{\mathrm{d}M}{\mathrm{d}\mu}\right\}+\left\{-A-2R_2\mu+p^2\mu^2-\frac{m^2}{1-\mu^2}\right\}M=0,\\ R_2\equiv\frac{R}{2}\frac{Z_a-Z_b}{2}.\end{aligned} \tag{4.39}$$

Note that A and p^2 are unknown and must be solved from (4.38) and (4.39) as eigenvalues of the coupled system. Once A and p are solved, then the energy E can be obtained from (B.12).

1. Two Useful Types of Eigenfunction of $\Lambda(\lambda)$ for H_2^+ Molecular Ion

To solve the differential equations, it is important to understand the asymptotics of the solution. Rewrite (4.38) as

$$(\lambda^2-1)\Lambda''(x)2\lambda\Lambda'(x)+\left(A+2R_1\lambda-p^2\lambda^2-\frac{m^2}{\lambda^2-1}\right)\Lambda(x)=0. \tag{4.40}$$

First, consider the case $\lambda \gg 1$; we have

$$0 = \Lambda''(x) + \frac{2\lambda}{\lambda^2 - 1}\Lambda'(x) + \left[\frac{A + 2R_1\lambda}{\lambda^2 - 1} - p^2\frac{\lambda^2}{\lambda^2 - 1} - \frac{m^2}{(\lambda^2 - 1)^2}\right)\Lambda(x) \tag{4.41}$$

$$\approx \Lambda''(x) - p^2\Lambda(\lambda), \qquad \text{for } \lambda \gg 1. \tag{4.42}$$

This gives

$$\Lambda(x) \approx a_1 e^{-p\lambda} + a_2 e^{p\lambda}, \qquad \text{for } \lambda \gg 1, \text{ where } p > 0. \tag{4.43}$$

The term $a_2 e^{p\lambda}$ has exponential growth for large λ, which is physically inappropriate and must be discarded. Thus

$$\Lambda(x) \approx a_1 e^{-p\lambda}, \qquad \text{for } \lambda \gg 1. \tag{4.44}$$

Next, we consider the case $\lambda > 1$ but $\lambda \approx 1$. In such a limit we have

$$\Lambda(\lambda) \approx (\lambda - 1)^{|m|/2} \sum_{k=0}^{\infty} c_k (\lambda - 1)^k. \tag{4.45}$$

The proof is in Appendix C.

Our results in (4.44) and (4.45) suggest that the form

$$\Lambda(\lambda) = e^{-p\lambda}(\lambda - 1)^{|m|/2}\lambda^{\beta} f(\lambda), \qquad \text{for some function } f(\lambda), \tag{4.46}$$

would contain the right asymptotics for both $\lambda \gg 1$ and $\lambda \approx 1$.

Here, there's two kinds of useful solutions which have different function forms. One is called as Jaffé's type and the other is the simple series solution with Laguerre function.

The form known as Jaffé's type is

$$\Lambda_J(\lambda) = e^{-p\lambda}(\lambda^2 - 1)^{|m|/2}(\lambda + 1)^{\sigma} \sum_n g_n \left(\frac{\lambda - 1}{\lambda + 1}\right)^n, \tag{4.47}$$

and

$$\sigma \equiv \frac{R_1}{p} - |m| - 1. \tag{4.48}$$

This leads to a 3-term recurrence relation

$$\alpha_n g_{n-1} - \beta_n g_n + \gamma_n g_{n+1} = 0, \qquad n = 0, 1, 2, \ldots; \qquad g_{-1} = 0, \tag{4.49}$$

where

$$\alpha_n = (n - 1 - \sigma)(n - 1 - \sigma - m), \tag{4.50}$$

$$\beta_n = 2n^2 + (4p - 2\sigma)n - A + p^2 - 2p\sigma - (m + 1)(m + \sigma), \tag{4.51}$$

$$\gamma_n = (n + 1)(n + m + 1), \tag{4.52}$$

and, consequently, the continued fraction

$$\frac{\beta_0}{\gamma_0} = \cfrac{\alpha_1}{\beta_1 - \cfrac{\gamma_1 \alpha_2}{\beta_2 - \cfrac{\gamma_2 \alpha_3}{\beta_3 - \cdots}}} \tag{4.53}$$

for A and p.

The other form is known as Hylleraas' solution and the form is

$$\Lambda_H(\lambda) = e^{-p(\lambda-1)}(\lambda^2 - 1)^{|m|/2} \sum_n \frac{c_n}{(m + n)!} L^m_{m+n}(x), \qquad x \equiv 2p(\lambda - 1), \tag{4.54}$$

where L^m_{m+n} is the associated Laguerre polynomial and c_n satisfy the 3-term recurrence relation

$$\alpha_n c_{n-1} - \beta_n c_n + \gamma_n c_{n+1} = 0, \qquad n = 0, 1, 2, \ldots; \qquad c_{-1} \equiv 0, \tag{4.55}$$

where

$$\alpha_n =(n-m)(n-m-1-\sigma), \tag{4.56a}$$

$$\beta_n =2(n-m)^2+2(n-m)(2p-\sigma)-[A-p^2+2p\sigma+(m+1)(m+\sigma)], \tag{4.56b}$$

$$\gamma_n =(n+1)(n-2m-\sigma), \tag{4.56c}$$

and the same form of continued fractions (4.53).

2. Solution of the M-function

Eq. (4.39) has close resemblance in form with (4.38) and, thus, it can almost be expected that the way to solve (4.39) will be similar to that of (4.38). First, we make the following substitution

$$M(\mu) = e^{\pm p\mu}\tilde{M}(\mu), \qquad -1 \geq \mu \geq 1, \tag{4.57}$$

in order to eliminate the $p^2\mu^2$ term in (4.38). We obtain

$$[(1-\mu^2)\tilde{M}']' \pm 2p(1-\mu^2)\tilde{M}' + \left[(-2R_2 \mp 2p)\mu + (p^2-A) - \frac{m^2}{1-\mu^2}\right]\tilde{M} = 0. \tag{4.58}$$

To simplify notation, let us just consider the case $M(\mu) = e^{-p\mu}\tilde{M}(\mu)$, but note that for $M = e^{p\mu}\tilde{M}(\mu)$, we need only make the changes of $p \to -p$ in (4.61) below. Write

$$M(\lambda) = e^{-p\mu}\sum_{k=0}^{\infty} f_k P_{m+n}^m(\mu), \tag{4.59}$$

where $P_{m+n}^m(\mu)$ is the associated Legendre polynomials, and the 3-term recurrence relation for f_k is

$$\alpha_n f_{n-1} - \beta_n f_n + \gamma_n f_{n+1} = 0, \qquad n = 0,1,2,\ldots; \qquad f_{-1} \equiv 0, \tag{4.60}$$

where

$$\alpha_n = \frac{1}{2(m+n)-1}[-2nR_2 + 2pn(m+n)], \tag{4.61a}$$

$$\beta_n = A - p^2 + (m+n)(m+n+1), \tag{4.61b}$$

$$\gamma_n = \frac{2m+n+1}{2(m+n)+3}\left\{-2R_2 - 2p(m+n+1)\right\}, \tag{4.61c}$$

and, consequently, again the continued fractions of the same form as (4.53). The continued fractions obtained here should be *coupled* with the continued fraction (4.53) for the variable μ to solve A and p.

In the *homonuclear* case, $R_2 = R(Z_a - Z_b)/2 = 0$, (4.39) reduces to

$$[(1-\mu^2)M']' + \left(-A + p^2\mu^2 - \frac{m^2}{1-\mu^2}\right) M = 0. \tag{4.62}$$

Even several different optional representations of M might be used, we will choose

$$M(\mu) = (1-\mu^2)^{|m|/2} \sum_{k=0}^{\infty} c_k P^m_{m+2k}(\mu), \tag{4.63}$$

$$M(\mu) = (1-\mu^2)^{|m|/2} \sum_{k=0}^{\infty} c_k P^m_{m+2k+1}(\mu), \tag{4.64}$$

or

$$M(\mu) = \sum_{s=0}^{\infty} B_s P^m_{m+2s}(\mu). \tag{4.65}$$

where $L_n(x)$ is the Laguerre function and $x = 2\alpha(\lambda - 1)$.

The wavefunction for the ground state in H_2^+ has two different, equivalent function forms. The symmetry of the ground state sets that $m = 0$, and we will get two types of function forms.

$$\phi^J_{H_2^+}(\lambda,\mu) = \mathcal{N}_J e^{-\alpha\lambda}(\lambda+1)^{\alpha_1}\left[1 + a_1\left(\frac{\lambda-1}{\lambda+1}\right) + a_2\left(\frac{\lambda-1}{\lambda+1}\right)^2 + \cdots\right]$$
$$\times\left[1 + b_2P_2(\mu) + b_4P_4(\mu) + \cdots\right], \tag{4.66}$$
$$\phi^H_{H_2^+}(\lambda,\mu) = \mathcal{N}_H e^{-\alpha\lambda}\left[1 + A_1L_1(x) + \frac{A_2}{2}L_2(x) + \cdots\right]$$
$$\times\left[1 + B_2P_2(\mu) + \cdots\right], \tag{4.67}$$

where $P_l(\mu)$ is the Legendre Polynomial and coefficients a_i and b_i are determined by a recursion relation.

E. Wavefunction for the Ground State of H_2 Molecule

From the exact wavefunction for the H_2^+ molecular ion, we can simply construct the trial wavefunction of the H_2 molecule since two electrons occupy same spatial state with different spin state. Without the electronic repulsion between the electrons, the simplest wavefunction for H_2 molecule is

$$\Psi^J(1,2) = \phi^J(\lambda_1,\mu_1)\phi^J(\lambda_2,\mu_2), \tag{4.68}$$
$$\Psi^H(1,2) = \phi^H(\lambda_1,\mu_1)\phi^H(\lambda_2,\mu_2). \tag{4.69}$$

The Hamiltonian for H_2 molecule is

$$H = \left(-\frac{1}{2}\nabla_1^2 - \frac{Z_a}{r_{a1}} - \frac{Z_b}{r_{b1}}\right) + \left(-\frac{1}{2}\nabla_2^2 - \frac{Z_a}{r_{a2}} - \frac{Z_b}{r_{b2}}\right) + \left(\frac{1}{r_{12}} + \frac{Z_aZ_b}{R}\right). \tag{4.70}$$

1. Correlation Factor

When we construct the wave-function of the H_2 molecule, we have neglected the repulsion between two electrons due to both same electric charges of them. This repulsion tends to prefer the farther presence between two electrons, so that it reduce the probability for the occupation in near distance. Though it is difficult to consider this effect analytically, we might use a simple function to produce similar behavior. The well-known factor is the Hylleraas Correlation factor [16] such as

$$f(1,2) = 1 + \kappa r_{12} \tag{4.71}$$

where κ is the parameter to shows the qualitative degree of repulsive correlation. Usually, the cusp condition sets that

$$\kappa = \frac{1}{2}, \tag{4.72}$$

which is explained in Appendix D.

In our calculation, the variational methods determines the value for κ.

F. Binding Energy of H_2 Molecule

Binding energy is defined as the energy difference between the energy of the molecule and the total energy of each atom at infinity. For the H_2 molecule, the binding energy is defined as

$$E_{\text{BE}} = (E_{H_2\text{molecule}} - 2E_{H\ \text{atom}}) \tag{4.73}$$

$$\approx (\langle H \rangle_{H_2\text{molecule}} - 2E_{H\ \text{atom}}) \tag{4.74}$$

where $\langle H \rangle_{H_2\text{molecule}}$ is the expectation value of the Hamiltonian gotten from the trial function Eq. (4.68) and Eq. (4.69) with or without Eq. (4.71).

With full variational parameters, we obtain a binding energy of 4.7 eV, which is comparable to the experimental value of 4.74 eV.

CHAPTER V

CONDENSATION IN A WEAKLY INTERACTING BOSON GAS WITH THE PARTIAL CANONICAL ENSEMBLE

A. Introduction

After liquefying the Helium-4 by Kamerlingh Onnes in 1908, new area in physics has been opened: very low temperature physics, or cryogenics. After observing the superconductivity of the mercury at 1911, new physical phenomena have been investigated: superconductivity, superfluidity, etc. [18, 19] One of the great achievement in low temperature physics is the manifestation of the macroscopic quantum states, eps. the condensation phenomenon in Boson system, which was predicted by Bose in 1924 and Einstein in 1925. [20, 21] After seventy years later, the Bose-Einstein Condensation (BEC) has clearly realized in dilute atomic system by Eric Cornell and Carl Wieman in Rubidium gas at 1995. [22]

Even though the theoretical research had begun about the properties of BEC, the progress was very slow. After Uhlenbeck pointed out that the cusp in transition temperature is unusual thing [23], many different aspects on BEC was studied.

The usual method to calculate the thermodynamic properties in equilibrium for many-body system is using the Grand Canonical Ensemble (GCE). In BEC problem, the calculation for the condensation behavior done by the GCE seems good : seemingly clear behavior of the condensation.

However, for the fluctuation in GCE the results are worse : Since the variance in GCE is $\langle(\delta n_0)^2\rangle = \langle n_0\rangle\,(1+\langle n_0\rangle)$, the fluctuation seems to show a divergent behavior as temperature goes below the transition temperature, since almost particles are in ground state in lower temperature and $\langle(\delta n_0)^2\rangle \to n_0^2$ with macroscopic number of particles n_0 in condensate state. However, intuitively in very low temperature there're few excited particles to participate in fluctuation, that is, small fluctuation is expected. Furthermore, the number fluctuation is related to the compressibility as following :

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = \frac{V}{TN}\frac{\langle(\Delta N)^2\rangle}{N}, \tag{5.1}$$

which can be measured in experiment.[24] So, the divergence of the number fluctuation in GCE should be solved when we deal the BEC problem.

And this suggests that we abandon the GCE and choose another ones : Canonical Ensemble (CE) or Microcanonical Ensemble (MCE). Here, we choose CE to investigate the BEC phenomena for finite N boson system. [24, 25, 26, 27, 28]

The correlation function in a physical system is the general measure of correlation between two quantities, and is used in broad areas of physics. Here, we will treat a different type of correlation, which is existed in a system with a finite total number N of particles. Since the available number of particles in one state is restricted by that in another state by the finite total number of particles, the mutual correlations of the occupation numbers between them may be nonzero. Even though two states is statistically independent in thermodynamic limit where $N \to \infty$, they might have a nonzero mutual correlation in finite N. For example, in two-level system with two boson particles in equilibrium, the mutual correlation of the occupation numbers $\langle \delta\hat{n}_1 \delta\hat{n}_2 \rangle = \langle \hat{n}_1 \hat{n}_2 \rangle - \langle \hat{n}_1 \rangle \langle \hat{n}_2 \rangle$ can be easily calculated to show negative.

B. Ideal Bose Gas in Canonical Ensemble

Before treating the condensation in the boson system with interaction, let's consider the system with N ideal boson particles for simplicity. The model system is contained in 3-D cubic box with length L. The Schrödinger equation gives the energy spectrum for this ideal gas.

$$H\Psi = \frac{\mathbf{p}^2}{2m}\Psi = E\Psi. \tag{5.2}$$

The periodic boundary condition gives

$$E = \frac{\hbar^2\mathbf{k}^2}{2m} \tag{5.3}$$

where the spatial quantization gives

$$\mathbf{k} = (k_x, k_y, k_z) = \frac{2\pi}{L}(n_x, n_y, n_z) \tag{5.4}$$

where n_x, n_y and n_z are integers. [1, 8]

1. Density Operator for an Ideal Bose Gas

At thermal equilibrium, we can construct the density operator for an ideal bose gas in diagonal form with the occupation number in each state. The density operator can be represented as

$$\rho_{IdBG} = \sum_{\{n_\mu\}} P(\{n_\mu\}\,|N)\,|\{n_\mu\}\rangle\,\langle\{n_\mu\}|\,, \tag{5.5}$$

where $\{n_\mu\}$ denotes the accessible configuration and the corresponding probability $P(\{n_\mu\}\,|N)$. Since the total number of particles is fixed, we specify total number N in the probability.

In the canonical ensemble (CE) which conserves the total number of particles, we can calculate the explicit form of the probability for $P(\{n_\mu\}\,|N)$ for n-state, as shown in Appendix F.

2. Construction of the Partition Function in Canonical Ensemble

In CE, the restriction of the total number of particles is not easy to handle in analytic form since the construction of the partition function is non-trivial when we compare to the same problem in GCE. The partition function in CE is

$$Z_N = \sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} \cdots \; e^{-\beta \sum_{\{\mu\}} \epsilon_\mu n_\mu} \delta(N - \sum_{\{\mu\}} n_\mu) \tag{5.6}$$

where index μ runs over each state and n_μ, the number of particles in μ-th state, runs from 0 to infinity and $\beta = (k_B T)^{-1}$. The δ-function is the Kronecker-δ which is one when the argument is zero or zero otherwise. This makes sure that there're only N particles in the system.

From the definition of the partition function, we can derive the probability of occupation in each state and the recursion relation which can evaluate the N-particle partition function.

$$\begin{aligned} P(n_\mu = n|N) &= \langle \delta(n_\mu - n) \rangle \\ &= \langle \Theta(n_\mu - n) \rangle - \langle \Theta(n_\mu - (n+1)) \rangle \\ &= P(n_\mu \geq n|N) - P(n_\mu \geq n+1|N) \\ &= e^{-n\beta\epsilon_\mu} \frac{Z_{N-n}}{Z_N} - e^{-(n+1)\beta\epsilon_\mu} \frac{Z_{N-n-1}}{Z_N} \end{aligned} \tag{5.7}$$

and

$$Z_N(\beta) = \frac{1}{N} \sum_{n=1}^{N} Z_1(n\beta) Z_{N-n}(\beta). \tag{5.8}$$

The proofs for Eq. (5.7) and Eq. (5.8) are in Appendix F.

3. Probability Distribution for the Condensate State for Ideal Bose Gas

The occupation probability for the ground state is given by Eq. (5.7).

$$p(n_0) = P(n_0|N) = \frac{Z_{N-n_0}}{Z_N} - \frac{Z_{N-n_0-1}}{Z_N}. \tag{5.9}$$

We can derive $p(n_0)$ from the density operator ρ_{IdBG}. Since the ideal Bose particles are non-interacting and the discrete quantum state is statistically independent, the occupation probability for the ground state can be given by the projection of the density operator into the ground state eliminating all higher excited state.

$$p(n_0) = \sum_{\{n_\mu\}}{}' P(n_0, \{n_\mu\} \,|N) = \sum_{\{n_\mu\}}{}' \left\langle n_0, \{n_\mu\} \left|\rho_{IdBG}\right| n_0, \{n_\mu\} \right\rangle . \tag{5.10}$$

where $'$ means that the sum goes over all states except the ground state.

From the above probability distribution, we can construct the reduced density operator for the condensate state.

$$\rho_{\text{reduced}} = \mathrm{Tr}_{\{\mu\}}\big(\rho_{IdBG}\big) = \sum_{\{n_\mu\}}{}' P(n_0, \{n_\mu\} \,|N) \left|n_0\right\rangle \left\langle n_0\right| = \sum_{n_0=0}^{N} p(n_0) \left|n_0\right\rangle \left\langle n_0\right| , \tag{5.11}$$

where n_0 denotes the number of particles in condensate state, and the distribution from the reduced density operator is

$$p(n_0) = \left\langle n_0 \left|\rho_{\text{reduced}}\right| n_0 \right\rangle = P(n_0|N). \tag{5.12}$$

4. Average, Variance and 3rd Moment

From the probability distribution for the occupation number of the ground state, all moments can be calculated. The explicit forms for the lowest 4 moments are

$$\langle n_0 \rangle = \sum_{n_0=0}^{N} n_0 p(n_0), \tag{5.13}$$

$$\left\langle (\delta n_0)^2 \right\rangle = \left\langle (n_0 - \langle n_0 \rangle)^2 \right\rangle = \left\langle n_0^2 \right\rangle - \langle n_0 \rangle^2 , \tag{5.14}$$

$$\left\langle (\delta n_0)^3 \right\rangle = \left\langle n_0^3 \right\rangle - 3 \left\langle n_0^2 \right\rangle \langle n_0 \rangle + 2 \langle n_0 \rangle^3 \tag{5.15}$$

with

$$\left\langle n_0^k \right\rangle = \sum_{n_0=0}^{N} n_0^k \, p(n_0). \tag{5.16}$$

Fig. (16) shows the condensation of the ground state with a system with different number particles. At $T = 0$, all the particles stay at the condensate state and become agitated to the excited states as temperature increases. Over the transition temperature $T_c = \frac{2\pi\hbar^2}{m} \left(\frac{N}{V\zeta(3/2)} \right)^{2/3}$, which is defined in thermodynamic limit as $N \to \infty$, the occupation number of particles in the ground state doesn't vanish and shows a long tail in the condensation. The qualitative behavior of the condensation is clearly shown for moderate number of particles, in $N = 200$ and $N = 1000$, which we will select this value for N in the interacting Boson gas, also.

For the fluctuation of the occupation number, at $T = 0$ zero-fluctuation is predicted by physical intuition due to the perfect condensation in ideal Bose gas. As temperature increases, the particles in condensate states are excited by thermal agitation, and it will be shown as fluctuation, or the nonzero variance. However, as temperature goes over $T_c = \frac{2\pi\hbar^2}{m} \left(\frac{N}{V\zeta(3/2)} \right)^{2/3}$, the bosonic property of the system can be ignored and goes to the usual classical ideal gas and should be exponentially vanished since we only consider the fluctuation of the single quantum state. To connect these behavior smoothly, there should be a maximum near $T = T_c$. For $N > 50$, the maximum lies near T_c, and for $N < 50$ the maximum lies at $T > T_c$. For $N = 200$, the maximum variance is near $T \approx T_c$. Furthermore, as N increases, the normalized maximum of variance is also increased, and seems to diverge at thermodynamic limit where $N \to \infty$, and this may be related to the cusp behavior of condensation at that limit.

Finally, the third-moment of the occupation number is nonvanishing, which shows that the fluctuation is non-Gaussian. And there's sign change from negative to positive near $T \simeq T_c$.

When the results are compared to them in CNB3 [27] and CNB5 [28], this partition function method is better to describe the condensation behavior of the ideal boson gas. In fact, the results from CNB5 are exactly same to the method described by the partition function in the ideal boson gas.

C. Model System for Interacting Bose Gas

Now, let's try to investigate the interacting Bose gas. Let's consider a dilute homogeneous Bose gas with a weak interaction of an interatomic scattering. The system is described by the well-known Hamiltonian [27]

$$H = \sum_{\mathbf{k}} \frac{\hbar^2 \mathbf{k}^2}{2M} a_{\mathbf{k}}^\dagger a_{\mathbf{k}} + \frac{1}{2V} \sum_{\{\mathbf{k}_i\}} \langle \mathbf{k}_3 \mathbf{k}_4 \left| U \right| \mathbf{k}_1 \mathbf{k}_2 \rangle \, a_{\mathbf{k}_4}^\dagger a_{\mathbf{k}_3}^\dagger a_{\mathbf{k}_2} a_{\mathbf{k}_1} \tag{5.17}$$

where $V = L^3$ is a volume of cubic box containing the gas with periodic boundary conditions, which is given by Eq. (5.4).

The number operator $n_{\mathbf{k}}$ from the creation and annihilation operators constructs the many-body Fock space, i.e.

$$n_{\mathbf{k}} = a_{\mathbf{k}}^{\dagger} a_{\mathbf{k}}, \tag{5.18}$$

$$n_{\mathbf{k}} \left| \psi_{\mathbf{k}}^{(n)} \right\rangle = n \left| \psi_{\mathbf{k}}^{(n)} \right\rangle, \tag{5.19}$$

$$a_{\mathbf{k}}^{\dagger} \left| \psi_{\mathbf{k}}^{(n)} \right\rangle = \sqrt{n+1} \left| \psi_{\mathbf{k}}^{(n+1)} \right\rangle. \tag{5.20}$$

The finiteness of the total number N of Boson, or $n_0 + \sum_{\mathbf{k}} n_{\mathbf{k}} = N$, enables us to choose a subspace in the Fock space.

At extremely low temperatures where the condensation occurs, the occupation number of the ground state is enormously large, and the expected occupation n_0 is comparable to N, so that we might describe the kinetics of the system by the interactions between the condensate state and excited states. To describe this type of interactions, we can use the quasi-particle description.

$$\beta_{\mathbf{k}} = \beta_0^{\dagger} a_{\mathbf{k}}, \qquad \beta_{\mathbf{k}}^{\dagger} = a_{\mathbf{k}}^{\dagger} \beta_0 \tag{5.21}$$

with $\beta_0 = (1 + n_0)^{-1/2} a_0$. Then, the commutation relations are satisfied for $\mathbf{k} \neq 0$ states.

$$\left[\beta_{\mathbf{k}}^{\dagger}, \beta_{\mathbf{k}'} \right] = \delta_{\mathbf{k}\mathbf{k}'}. \tag{5.22}$$

The proof is in Appendix G. Furthermore, this quasi-particle operator $\beta_{\mathbf{k}}$ gives the same statistics for the occupation number as that of particle operator $a_{\mathbf{k}}$ for nonzero $\mathbf{k}$ state.

$$n_{\mathbf{k}} = a_{\mathbf{k}}^{\dagger} a_{\mathbf{k}} = \beta_{\mathbf{k}}^{\dagger} \beta_{\mathbf{k}}. \tag{5.23}$$

D. Energy Spectrum of the Quasi-particle System

With the quasi-particle operator $\beta_{\mathbf{k}}$, we can rewrite the atom-number-conserving Bogoliubov Hamiltonian. (Eq. (62) in CNB3[27])

$$\begin{aligned} H_B = \frac{N(N-1)U_0}{2V} &+ \sum_{\mathbf{k}\neq 0}\left(\frac{\hbar^2\mathbf{k}^2}{2M} + \frac{(\hat{n}_0+1/2)U_{\mathbf{k}}}{V}\right)\hat{\beta}^\dagger_{\mathbf{k}}\hat{\beta}_{\mathbf{k}} \\ &+ \frac{1}{2V}\sum_{\mathbf{k}\neq 0}\left(U_{\mathbf{k}}\sqrt{(1+\hat{n}_0)(2+\hat{n}_0)}\hat{\beta}^\dagger_{\mathbf{k}}\hat{\beta}^\dagger_{-\mathbf{k}} + H.C.\right). \end{aligned} \tag{5.24}$$

To get the diagonalized Hamiltonian, let's make approximation that the operator $\hat{n}_0$ into the c-number n_0 in Eq. (5.24). Here, we choose this c-number n_0 as the average number $\overline{n}_0$ of occupation in condensate state.

$$\begin{aligned} H_{Bn} = \frac{N(N-1)U_0}{2V} &+ \sum_{\mathbf{k}\neq 0}\left(\frac{\hbar^2\mathbf{k}^2}{2M} + \frac{(\overline{n}_0+1/2)U_{\mathbf{k}}}{V}\right)\hat{\beta}^\dagger_{\mathbf{k}}\hat{\beta}_{\mathbf{k}} \\ &+ \frac{1}{2V}\sum_{\mathbf{k}\neq 0}\left(U_{\mathbf{k}}\sqrt{(1+\overline{n}_0)(2+\overline{n}_0)}\hat{\beta}^\dagger_{\mathbf{k}}\hat{\beta}^\dagger_{-\mathbf{k}} + H.C.\right). \end{aligned} \tag{5.25}$$

Then, with the following Bogoliubov transformation,

$$\hat{\beta}_{\mathbf{k}} = u_{\mathbf{k}}\hat{b}_{\mathbf{k}} + v_{\mathbf{k}}\hat{b}^\dagger_{-\mathbf{k}}, \tag{5.26a}$$

$$\hat{\beta}^\dagger_{\mathbf{k}} = u_{\mathbf{k}}\hat{b}^\dagger_{\mathbf{k}} + v_{\mathbf{k}}\hat{b}_{-\mathbf{k}} \tag{5.26b}$$

with

$$
\begin{aligned}
\frac{v_{\mathbf{k}}}{u_{\mathbf{k}}} &= A_{\mathbf{k}} \\
&= \frac{-\left(\frac{\hbar^2\mathbf{k}^2}{2M} + \frac{(\overline{n}_0+1/2)U_{\mathbf{k}}}{V}\right) \pm \sqrt{\left(\frac{\hbar^2\mathbf{k}^2}{2M} + \frac{(\overline{n}_0+1/2)U_{\mathbf{k}}}{V}\right)^2 - 4\left(\frac{U_{\mathbf{k}}}{2V}\sqrt{(1+\overline{n}_0)(2+\overline{n}_0)}\right)^2}}{2\frac{U_{\mathbf{k}}}{2V}\sqrt{(1+\overline{n}_0)(2+\overline{n}_0)}},
\end{aligned}
\tag{5.27a}
$$

$$
u_{\mathbf{k}} = \frac{1}{\sqrt{1-A_{\mathbf{k}}^2}}, \tag{5.27b}
$$

$$
v_{\mathbf{k}} = \frac{A_{\mathbf{k}}}{\sqrt{1-A_{\mathbf{k}}^2}}, \tag{5.27c}
$$

we will get the diagonalized form of the atom-number-conserving Hamiltonian is

$$
H_{Bn} = E_0 + \sum_{\mathbf{k}\neq 0} E_{\mathbf{k}} + \sum_{\mathbf{k}\neq 0} \epsilon_{\mathbf{k}} b_{\mathbf{k}}^{\dagger} b_{\mathbf{k}}, \tag{5.28}
$$

where

$$
E_0 = \frac{N(N-1)U_0}{2V}, \tag{5.29}
$$

$$
E_{\mathbf{k}} = \left(\frac{\hbar^2\mathbf{k}^2}{2M} + \frac{(\overline{n}_0+1/2)U_{\mathbf{k}}}{V}\right) v_{\mathbf{k}}^2 + \frac{1}{V}U_{\mathbf{k}}\sqrt{(1+\overline{n}_0)(2+\overline{n}_0)}u_{\mathbf{k}}v_{\mathbf{k}}, \tag{5.30}
$$

$$
\epsilon_{\mathbf{k}} = \left(\frac{\hbar^2\mathbf{k}^2}{2M} + \frac{(\overline{n}_0+1/2)U_{\mathbf{k}}}{V}\right)(u_{\mathbf{k}}^2 + v_{\mathbf{k}}^2) + \frac{2}{V}U_{\mathbf{k}}\sqrt{(1+\overline{n}_0)(2+\overline{n}_0)}u_{\mathbf{k}}v_{\mathbf{k}}. \tag{5.31}
$$

$E_{\mathbf{k}}$ means the shift of the ground states and depends on the number of condensate particles $\overline{n}_0$, and $\epsilon_{\mathbf{k}}$ gives the relative energy of the each excited states. Here, it should be noticed that all parameters and the energy spectrum of the excited states depend on the average number of condensate particles $\overline{n}_0$.

Before going to the next section, let's simply review CNB3 paper, which has calculated moments through the characteristic function. From the characteristic function $\Theta_{\pm\mathbf{k}}(u)$ (Eq. (68) in CNB3), the statistics of the occupation number can be calculated, and many properties of the system has shown. The derivation of this characteristic function can be simplified using the Wigner function. [29, 30, 31] We will show the derivation in Appendix E.

E. Quasi-Particle Canonical Ensemble

Since we know the energy spectrum for all the excited states of the quasi-particles, we can calculate the thermodynamic quantities using the partition function method in the canonical ensemble, for example the occupation probability for each state.

However, the absence of the ground state in quasi-particle basis gives another difficulty in canonical ensemble, that is, physical quantities related to the condensate state should be calculated indirectly through the excited states.

1. Construction of the Thermal Density-operator for Quasi-particles in Canonical Ensemble

Since we include the interaction which can be diagonalized by Bogoliubov transformation, we can construct the corresponding density operator in equilibrium at the quasi-particle system easily. The main difference between ideal and interacting case is the exclusion of the ground state in interacting case.

The most general form of the density operator in particle basis is

$$\rho_{\text{Int}} = \sum_{\{n_\mu\},\{m_\mu\}} P(\{n_\mu\},\{m_\mu\}|N)|\{n_\mu\}\rangle\,\langle\{m_\mu\}|, \tag{5.32}$$

with $\hat{n}_\mu = \hat{a}^\dagger_\mu \hat{a}_\mu$. Since the Hamiltonian is diagonal in Bogoliubov transformed operator $\hat{b}_\mu$ basis, the density operator for the quasi-particle at equilibrium can be written as

$$\rho_{\text{Int}} = \sum_{M=0}^{N} P(n_0 = N - M|N) \sum_{\{n_\mu\}_b} P(\{n_\mu\}_b|M)|\{n_\mu\}_b\rangle\langle\{n_\mu\}_b| \tag{5.33}$$

with $\{n_\mu\}_M$ for the configuration of Bogoliubov-transformed quasi-particles in excited states, and $\sum_{\mu\neq 0} n_\mu = M$. The sum for all states covers only for the excited states, not the ground state. The explicit form of the probabilities are given in Appendix,and

$$P(n_0 = N - M|N) = e^{-(N-M)\beta\epsilon_0}\frac{Z_M}{Z_N} - e^{-(N-M+1)\beta\epsilon_0} Z_{M-1} Z_N \tag{5.34}$$

$$= \frac{Z_M - Z_{M-1}}{Z_N} = \frac{Z_M^*}{Z_N}. \tag{5.35}$$

2. Canonical Ensemble as Sum of Partial Canonical Ensemble

The omission of the ground state in quasi-particle basis prohibits the direct access to the ground state of the particle, but through the statics of the excited states. So, the partition function of the quasi-particles should be constructed without the ground state.

For the partition function of the single particle, we can define the partition function without the ground state as

$$Z_1^* = Z_1 - e^{-\beta\epsilon_0} \tag{5.36}$$

where the usual single particle partition function

$$Z_1(\beta) = \sum_{\mu=0}^{\infty} e^{-\beta\epsilon_\mu} \tag{5.37}$$

and $\beta = (k_B T)^{-1}$.

Similarly, we can construct the partial partition function Z_M^* without the ground state.

$$Z_M^* = \sum_{n_2=0}^{\infty}\sum_{n_3=0}^{\infty}\cdots e^{-\beta\sum_{\mu=2}^{\infty}\epsilon_\mu n_\mu}\delta(M - \sum_{\mu=2}^{\infty} n_\mu), \tag{5.38}$$

where M is the total number of quasi-particles in the excited states.

Furthermore, this partial partition function also satisfies the recursion relation in CE because the omission of one specific state doesn't affect to the structure of the partition function in CE. The relation between Z_M^* and Z_N is

$$Z_N(\beta) = \sum_{M=0}^{N} e^{-(N-M)\beta\epsilon_0} Z_M^*(\beta), \tag{5.39}$$

or that the summation of the partial partition function Z_M^* gives the usual partition function Z_N. The derivation of the above identity is in Appendix I.

For example, let's consider the 3 bosonic particles distributed in 3-level system. Fig. (19) shows all the possible configuration. Since the partition function is summation of the Boltzmann factor of all accessible configuration, we can simply rewrite the total partition function as sum of the partial partition function in this example.

$$Z_3(\beta) = e^{-3\beta\epsilon_0} Z_0^*(\beta) + e^{-2\beta\epsilon_0} Z_1^*(\beta) + e^{-\beta\epsilon_0} Z_2^*(\beta) + Z_3^*(\beta). \tag{5.40}$$

3. Moments of Occupation Number in Condensate State of the Weakly Interacting Bose Gas

Since the partition function has been constructed on quasi-particles, not particles, the moments of the particles should derive from them of quasi-particles. More explicitly, moments of particles in condensate state will be calculated from them of quasi-particles in excited states.

The only one connecting relation between ground state and excited states is the number conserving relation, that is

$$n_0 = a_0^\dagger a_0 = N - \sum_{\mathbf{k}\neq 0} a_{\mathbf{k}}^\dagger a_{\mathbf{k}} = N - \sum_{\mathbf{k}\neq 0} \beta_{\mathbf{k}}^\dagger \beta_{\mathbf{k}} \tag{5.41}$$

where $\beta_{\mathbf{k}} = \beta_0^\dagger a_{\mathbf{k}}$. On this section, we will use $\mathbf{k}$ and $\mathbf{k}'$ notation instead of μ for specifying the state for clarity.

a. Average

The expectation value for the occupation number of the condensate state is

$$\langle n_0 \rangle = \langle a_0^\dagger a_0 \rangle = N - \sum_{\mathbf{k}\neq 0} \langle a_{\mathbf{k}}^\dagger a_{\mathbf{k}} \rangle = N - \sum_{\mathbf{k}\neq 0} \langle \beta_{\mathbf{k}}^\dagger \beta_{\mathbf{k}} \rangle. \tag{5.42}$$

Since the density operator is represented in terms of the Bogoliubov-transformed quasi-particle operators, the operator also should be represented in the quasi-particle basis $b_{\mathbf{k}}^\dagger$ and $b_{\mathbf{k}}$ to get the thermodynamic average. Furthermore, by Bogoliubov transformation $\mathbf{k}$ and $-\mathbf{k}$ states are correlated and should be considered simultaneously for the calculation.

The expectation value for the occupation number in quasi-particle basis is

$$\langle \beta_{\mathbf{k}}^\dagger \beta_{\mathbf{k}} \rangle = (u_{\mathbf{k}}^2 + v_{\mathbf{k}}^2)\overline{n}_{\mathbf{k}} + v_{\mathbf{k}}^2, \tag{5.43}$$

where

$$\overline{n}_{\mathbf{k}} = \sum_{n=1}^{N} e^{-n\beta\epsilon_{\mathbf{k}}} \frac{Z_{N-n}}{Z_N}. \tag{5.44}$$

Here, we used the equal average of the occupation number for the energy-degenerate state. The derivation are shown in Appendix in detail.

The usual way to calculate the occupation number in canonical ensemble in BEC is that $\left\langle n_{\mathbf{k}} \right\rangle \cong \frac{1}{e^{-\beta\epsilon_{\mathbf{k}}}-1}$ as the approximate value in canonical ensemble, because in grand canonical ensemble it is well-known that the chemical potential is almost zero at lower temperature. [24]

In Eq. (5.43), the second term $v_{\mathbf{k}}^2$ in right side is independent of the occupation number of the quasi-particle, which is considered as quantum effect [32], which shows the depletion in the condensate state even at $T = 0$. Since the interactions in the system gives some excitation, and the excited states are occupied even at $T = 0$.

Near $T \approx 0.4 - 0.6T_c$, the interacting Bose gas has larger condensation than that of ideal Bose gas. It suggests that the interacting Bose gas is more ordered system, which is known as "attraction in momentum space" [33].

The average number in condensate states in interacting Bose Gas shows the usual predicted behavior: non-vanishing fluctuation in zero temperature and slightly higher condensation in intermediate temperature compared with that in ideal Bose gas, and smoothly transition into the higher temperature over the critical temperature. The reason to show good behavior over extended into the higher temperature is that taking the average for the number operator in strict way from the probability which can be calculated from the partition function.

b. Variance

Similar way we can apply this probability to higher moments, especially to variance. Since the quantum mechanics requires the four-point probability in calculation of the variance, let's try extend the concept to cover these things.

Let's start with the explicit definition of the variance. The number operator for the condensate state is

$$\hat{n}_0 = \hat{a}_0^\dagger \hat{a}_0 = N - \sum_{\mathbf{k}\neq 0} \hat{a}_{\mathbf{k}}^\dagger \hat{a}_{\mathbf{k}}, \tag{5.45}$$

and the difference is

$$\delta\hat{n}_0 = \hat{a}_0^\dagger \hat{a}_0 - \left\langle \hat{a}_0^\dagger \hat{a}_0 \right\rangle = \sum_{\mathbf{k}\neq 0} \left(\left\langle \hat{a}_{\mathbf{k}}^\dagger \hat{a}_{\mathbf{k}} \right\rangle - \hat{a}_{\mathbf{k}}^\dagger \hat{a}_{\mathbf{k}} \right). \tag{5.46}$$

The variance is

$$\begin{aligned}\left\langle (\delta\hat{n}_0)^2 \right\rangle &= \sum_{\mathbf{k},\mathbf{k}'\neq 0} \left\langle \left(\left\langle \hat{a}^\dagger_{\mathbf{k}} \hat{a}_{\mathbf{k}} \right\rangle - \hat{a}^\dagger_{\mathbf{k}} \hat{a}_{\mathbf{k}} \right) \left(\left\langle \hat{a}^\dagger_{\mathbf{k}'} \hat{a}_{\mathbf{k}'} \right\rangle - \hat{a}^\dagger_{\mathbf{k}'} \hat{a}_{\mathbf{k}'} \right) \right\rangle \\ &= \sum_{\mathbf{k},\mathbf{k}'\neq 0} \left\{ \left\langle \hat{a}^\dagger_{\mathbf{k}} \hat{a}_{\mathbf{k}} \hat{a}^\dagger_{\mathbf{k}'} \hat{a}_{\mathbf{k}'} \right\rangle - \left\langle \hat{a}^\dagger_{\mathbf{k}} \hat{a}_{\mathbf{k}} \right\rangle \left\langle \hat{a}^\dagger_{\mathbf{k}'} \hat{a}_{\mathbf{k}'} \right\rangle \right\} . \end{aligned} \tag{5.47}$$

In the quasi-particle basis $\hat{\beta}^\dagger_{\mathbf{k}}$ and $\hat{\beta}_{\mathbf{k}}$

$$\left\langle (\delta\hat{n}_0)^2 \right\rangle = \sum_{\mathbf{k},\mathbf{k}'\neq 0} \left\{ \left\langle \hat{\beta}^\dagger_{\mathbf{k}} \hat{\beta}_{\mathbf{k}} \hat{\beta}^\dagger_{\mathbf{k}'} \hat{\beta}_{\mathbf{k}'} \right\rangle - \left\langle \hat{\beta}^\dagger_{\mathbf{k}} \hat{\beta}_{\mathbf{k}} \right\rangle \left\langle \hat{\beta}^\dagger_{\mathbf{k}'} \hat{\beta}_{\mathbf{k}'} \right\rangle \right\} .$$

The explicit evaluation in quasi-particle basis is shown in Appendix J.

Especially, when $\mathbf{k} \neq \mathbf{k}'$ and $\mathbf{k} \neq -\mathbf{k}'$, the cross correlation $\left\langle \hat{\beta}^\dagger_{\mathbf{k}} \hat{\beta}_{\mathbf{k}} \hat{\beta}^\dagger_{\mathbf{k}'} \hat{\beta}_{\mathbf{k}'} \right\rangle$ is not vanished, which was neglected in other papers since the cross correlation between two different states was considered vanished due to the statistical independence. This expectation values play a significant role to reduce the fluctuation at larger temperature. [34, 35]

The results for the variance show the explicit depletion at $T = 0$. At low interaction $an^{1/3} = 0.05$, the result is very similar to that of CNB5, only slightly different near maximum of the variance.

c. 3rd Moment

The usual mean field theory cannot calculate any higher moment since the correlation effects are averaged out. However, the partition function method makes it possible to calculate the 3rd moment. The explicit forms are shown in the appendix.

The nonzero value of 3rd moment means that the fluctuation inside the BEC phenomena is non-Gaussian type. [27]

4. Comments for the Canonical Ensemble

In these calculations, we specify the condition of the fixed total number of particles using the canonical ensemble, and use the operator form of moments in occupation number explicitly to calculate all the statistics. Usually, the quasi-particle description seems to be applicable for the very low temperature, where the occupation number of condensate state is comparable to the total number of particles, and it is believed to give divergent result for higher temperature. However, the shortcoming of the divergence doesn't come from this quasi-particle transformation. It is the usual grand canonical ensemble which is used for simple formalism and calculation. If we apply the canonical ensemble in this system, we can get the finite result whose values converges into that of ideal bose gas in higher temperature, even in 3rd moment.

CHAPTER VI

SUMMARY

In Chapter II, a single-photon confined in a volume V satisfies a simple equation of states $PV = n\hbar\Omega$, and the heat engine with a single-photon has the Carnot efficiency like the classical ideal gas.

In Chapter III, the complex Schrödinger equation for the multi-electron atoms is simplified into the algebraic equation by the application of the dimensional scaling. Furthermore, the electron configuration was calculated and showed similar structure that were predicted by quantum mechanics. Especially, the atomic structure for the ground state of the Carbon atom is shown to the tetrahedral structure with (sp^3)-hybridization.

In Chapter IV, the hydrogen molecule, the simplest neutral molecule, has treated by the two-center molecular orbit, and calculated the binding energy of hydrogen molecule as 4.7eV, which is comparable to the experimental value 4.74eV.

In Chapter V, a weakly interacting Bose gas with N particles was considered using the application of the partition function. Within Bogoliubov transformation, we've calculated all possible correlation function for 2nd or 3rd centered moment of the occupation numberto investigate the fluctuation of the condensate state. Depletion of the condensate state, cross-over from low temperatures into high temperatures, and non-gaussian feature of the residing fluctuation.

Here, we've used un-traditional method such as dimensional scaling to traditional method such as quantum field theory. Though we've only considered the physical properties of the simple systems, the applicable ranges of these methods will be expanded.

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APPENDIX A

LAPLACIAN IN HYPER-SPHERICAL COORDINATES

Here we show the explicit form of the Laplacian in the hyper-spherical coordinates. From the definition of hyper-spherical coordinate (3.5), let's try to calculate the scaling factors. The definitions for them are

$$h_0^2 = \sum_{j=1}^{D} \left(\frac{\partial x_j}{\partial r} \right)^2 , \tag{A.1}$$

$$h_k^2 = \sum_{j=1}^{D} \left(\frac{\partial x_j}{\partial \theta_k} \right)^2 \tag{A.2}$$

and

$$h = \prod_{j=0}^{D-1} h_j . \tag{A.3}$$

Explicitly,

$$\begin{aligned}
h_0 &= 1, \\
h_1 &= r \sin\theta_2 \sin\theta_3 \cdots \sin\theta_{D-1}, \\
h_2 &= r \sin\theta_3 \sin\theta_4 \cdots \sin\theta_{D-1}, \\
&\ \vdots \\
h_k &= r \sin\theta_{k+1} \sin\theta_{k+2} \cdots \sin\theta_{D-1}, \\
&\ \vdots \\
h_{D-2} &= r \sin\theta_{D-1}, \\
h_{D-1} &= r, \\
h &= r^{D-1} \sin\theta_2 \sin^2\theta_3 \sin^3\theta_4 \cdots \sin^{k-1}\theta_k \cdots \sin^{D-1}\theta_{D-1}.
\end{aligned} \tag{A.4}$$

The D-dimensional Laplacian now becomes

$$\begin{aligned}\nabla_D^2 =&\frac{1}{r^{D-1}}\frac{\partial}{\partial r}r^{D-1}\frac{\partial}{\partial r}\\&+\frac{1}{r^2}\sum_{k=1}^{D-2}\frac{1}{\sin^2\theta_{k+1}\sin^2\theta_{k+2}\cdots\sin^2\theta_{D-1}}\left\{\frac{1}{\sin^{k-1}\theta_k}\frac{\partial}{\partial\theta_k}\sin^{k-1}\theta_k\frac{\partial}{\partial\theta_k}\right\}\\&+\frac{1}{r^2}\left\{\frac{1}{\sin^{D-2}\theta_{D-1}}\frac{\partial}{\partial\theta_{D-1}}\sin^{D-2}\theta_{D-1}\frac{\partial}{\partial\theta_{D-1}}\right\}.\end{aligned}\tag{A.5}$$

Define the generalized orbital angular momentum operators by

$$\begin{aligned}L_1^2 &= -\frac{\partial^2}{\partial\theta_1^2},\\L_2^2 &= -\frac{1}{\sin\theta_2}\frac{\partial}{\partial\theta_2}\sin\theta_2\frac{\partial}{\partial\theta_2}+\frac{L_1^2}{\sin^2\theta_2},\\&\vdots\\L_k^2 &= -\frac{1}{\sin^{k-1}\theta_k}\frac{\partial}{\partial\theta_k}\sin^{k-1}\theta_k\frac{\partial}{\partial\theta_k}+\frac{L_{k-1}^2}{\sin^2\theta_k}.\end{aligned}\tag{A.6}$$

Then we have (3.7) with

$$K_{D-1}(r)=\frac{1}{r^{D-1}}\frac{\partial}{\partial r}\left(r^{D-1}\frac{\partial}{\partial r}\right).\tag{A.7}$$

APPENDIX B

SEPARATION OF VARIABLES FOR THE H_2^+-LIKE SCHRÖDINGER EQUATION

Let us consider (4.4). Here we show how to separate the variables through the use of the ellipsoidal (or, prolate spheroidal) coordinates.

$$\begin{aligned}
x &= \frac{R}{2}\sqrt{(\lambda^2-1)(1-\mu^2)}\cos\phi, \\
y &= \frac{R}{2}\sqrt{(\lambda^2-1)(1-\mu^2)}\sin\phi, \\
z &= \frac{R}{2}\lambda\mu.
\end{aligned} \tag{B.1}$$

Note the coordinates λ, μ and ϕ are orthogonal, and we have the first fundamental form

$$\mathrm{d}s^2 = \mathrm{d}x^2 + \mathrm{d}y^2 + \mathrm{d}z^2 = h_\lambda^2 \mathrm{d}\lambda^2 + h_\mu^2 \mathrm{d}\mu^2 + h_\phi^2 \mathrm{d}\phi^2, \tag{B.2}$$

where

$$h_\lambda^2 = \left(\frac{\partial x}{\partial \lambda}\right)^2 + \left(\frac{\partial y}{\partial \lambda}\right)^2 + \left(\frac{\partial z}{\partial \lambda}\right)^2 = \frac{R^2}{4}\frac{1-\mu^2}{\lambda^2-1}, \tag{B.3}$$

$$h_\mu^2 = \left(\frac{\partial x}{\partial \mu}\right)^2 + \left(\frac{\partial y}{\partial \mu}\right)^2 + \left(\frac{\partial z}{\partial \mu}\right)^2 = \frac{R^2}{4}\frac{\lambda^2-1}{1-\mu^2}, \tag{B.4}$$

$$h_\phi^2 = \left(\frac{\partial x}{\partial \phi}\right)^2 + \left(\frac{\partial y}{\partial \phi}\right)^2 + \left(\frac{\partial z}{\partial \phi}\right)^2 = \frac{R^2}{4}(\lambda^2-1)(1-\mu^2). \tag{B.5}$$

Thus

$$\begin{aligned}\nabla^2\Psi &= \frac{1}{h_\lambda h_\mu h_\phi}\left[\frac{\partial}{\partial\lambda}\left(\frac{h_\mu h_\phi}{h_\lambda}\frac{\partial}{\partial\lambda}\Psi\right)+\frac{\partial}{\partial\mu}\left(\frac{h_\lambda h_\phi}{h_\mu}\frac{\partial}{\partial\mu}\Psi\right)+\frac{\partial}{\partial\phi}\left(\frac{h_\lambda h_\mu}{h_\phi}\frac{\partial}{\partial\phi}\Psi\right)\right]\\ &= \frac{4}{R^2(\lambda^2-\mu^2)}\left\{\frac{\partial}{\partial\lambda}\left[(\lambda^2-1)\frac{\partial}{\partial\lambda}\right]+\frac{\partial}{\partial\mu}\left[(1-\mu^2)\frac{\partial}{\partial\mu}\right]\right.\\ &\qquad\left.+\frac{\lambda^2-\mu^2}{(\lambda^2-1)(1-\mu^2)}\frac{\partial^2}{\partial\phi^2}\right\}\Psi. \end{aligned} \tag{B.6}$$

Note that through the coordinate transformation (B.1), we have

$$\begin{cases}\lambda = \frac{r_a+r_b}{R},\\ \mu = \frac{r_a-r_b}{R},\end{cases} \qquad \text{equivalently,} \qquad \begin{cases} r_a = \frac{R}{2}(\lambda+\mu),\\ r_b = \frac{R}{2}(\lambda-\mu).\end{cases} \tag{B.7}$$

Also, we have $\lambda \leq 1$, $-1 \geq \mu \geq 1$. Write

$$\Psi = \Lambda(\lambda)M(\mu)\Phi(\phi). \tag{B.8}$$

$\Phi(\phi)$ must be periodic with period 2π. Therefore

$$\Phi(\phi) = e^{im\phi}, \qquad m = 0, \pm1, \pm2, \ldots. \tag{B.9}$$

Substitute (B.6), (B.8) and (B.9) into (4.4), and then divide by $e^{im\phi}$:

$$\begin{aligned}&-\frac{1}{2}\frac{4}{R^2(\lambda^2-\mu^2)}\left\{\frac{\partial}{\partial\lambda}\left[(\lambda^2-1)\frac{\partial}{\partial\lambda}\Lambda\right]M+\frac{\partial}{\partial\mu}\left[(1-\mu^2)\frac{\partial}{\partial\mu}M\right]\Lambda\right.\\ &\qquad\left.-\frac{(\lambda^2-\mu^2)m^2}{(\lambda^2-1)(1-\mu^2)}\Lambda M\right\}-\frac{2}{R}\frac{Z_a}{\lambda-\mu}\Lambda M-\frac{2}{R}\frac{Z_b}{\lambda+\mu}\Lambda M+\frac{Z_aZ_b}{R}\Lambda M\\ &= E\Lambda M.\end{aligned} \tag{B.10}$$

Further multiplying every term by $-\frac{R^2}{2}(\lambda^2-\mu^2)$, we obtain

$$\begin{aligned}&\frac{\partial}{\partial\lambda}\left[(\lambda^2-1)\frac{\partial}{\partial\lambda}\Lambda\right]M+\frac{\partial}{\partial\mu}\left[(1-\mu^2)\frac{\partial}{\partial\mu}M\right]\Lambda-\frac{\lambda^2-\mu^2}{(\lambda^2-1)(1-\mu^2)}\Lambda M\\ &+\left[RZ_a(\lambda+\mu)+RZ_b(\lambda-\mu)-\left(\frac{RZ_aZ_b}{2}-\frac{R^2E}{2}\right)(\lambda^2-\mu^2)\right]\Lambda M = 0.\end{aligned} \tag{B.11}$$

Set

$$p^2 = \frac{1}{2}(-R^2E + RZ_aZ_b) > 0. \tag{B.12}$$

We have $p^2 > 0$ here due to the fact that we are mainly interested in the electronic states that are bound states, i.e., not ionized.

Let the constant of separation of variables be A. Then from (B.11) and (B.12) we obtain (4.38) and (4.39).

APPENDIX C

ASYMPTOTIC EXPANSION AS $\lambda \to 1$

The proof of (4.45) is given in this appendix. Multiply (4.40) by $(\lambda-1)/(\lambda+1)$ and rewrite it as

$$\begin{aligned} 0 &= (\lambda-1)^2\Lambda''(\lambda) + \frac{2\lambda}{\lambda+1}(\lambda-1)\Lambda'(\lambda) \\ &\quad + \left[\frac{(A+2R_1\lambda-p^2\lambda^2)}{\lambda+1}(\lambda-1) - \frac{m^2}{(\lambda+1)^2}\right]\Lambda(\lambda) \\ &\approx (\lambda-1)^2\Lambda''(\lambda) + (\lambda-1)\Lambda'(\lambda) - \frac{m^2}{4}\Lambda(\lambda), \qquad \text{for } \lambda \approx 1. \end{aligned} \tag{C.1}$$

A differential equation set in the form

$$(x-1)^2y''(x) + (x-1)q(x)y'(x) + r(x)y(x) = 0. \tag{C.2}$$

near $x = 1$, where $q(x)$ and $r(x)$ are analytic functions at $x = 1$, is said to have a *regular singular point* at $x = 1$. The solution's behavior near $x = 1$ hinges largely on the roots ν of the *indicial equation*

$$\nu(\nu-1) + q(1)\nu + r(1) = 0 \tag{C.3}$$

because the solution $y(x)$ of (C.2) is expressible as

$$y(x) = b_1(x-1)^{\nu_1}\sum_{k=0}^{\infty} c_k(x-1)^k + b_2(x-1)^{\nu_2}\sum_{k=0}^{\infty} d_k(x-1)^k \qquad (c_0 = d_0 = 1),$$

where ν_1 and ν_2 are the two roots of the indicial equation (C.3), under the assumptions that

$$\nu_1 > \nu_2, \qquad \nu_1 - \nu_2 \text{ is not a positive integer.} \tag{C.4}$$

However, if (C.4) is violated, then there are two possibilities and two different forms of solutions arise:

(a) $\nu_1 = \nu_2$. Then

$$y(x) = b_1 y_1(x) + b_2 y_2(x), \tag{C.5}$$

where

$$y_1(x) = (x-1)^{\nu_1} \sum_{k=0}^{\infty} c_k (x-1)^k \qquad (c_0 = 1), \tag{C.6}$$

and

$$y_2(x) = (x-1)^{\nu_1} \sum_{k=1}^{\infty} d_k (x-1)^k + [\ln(x-1)] y_1(x) \quad (d_1 = 1). \tag{C.7}$$

Solution y_2 in (C.7) should be discarded because it becomes unbounded at $x = 1$.

(b) $\nu_1 - \nu_2 =$ a positive integer. Then case (a) holds except with the modification that

$$y_2(x) = (x-1)^{\nu_2} \sum_{k=0}^{\infty} d_k (x-1)^k + c[\ln(x-1)] y_1(x)$$

$$(d_0 = 1, c \text{ is a fixed constant but may be0}). \tag{C.8}$$

Applying the above and (C.3) to (C.1):

$$(\lambda-1)^2 \Lambda''(\lambda) + (\lambda-1)\Lambda'(\lambda) - \frac{m^2}{4}\Lambda(\lambda) \approx 0, \tag{C.9}$$

we obtain the indicial equation

$$\nu(\nu-1) + \nu - \frac{m^2}{4} = 0, \tag{C.10}$$

with roots

$$\nu_1 = \frac{|m|}{2}, \qquad \nu_2 = -\frac{|m|}{2} \qquad (m \text{ is non-zero integer}). \tag{C.11}$$

Thus either

$$\nu_1 = \nu_2 \qquad (\text{ when } m = 0)$$

or

$$\nu_1 - \nu_2 = |m| = \text{ a positive integer }, \qquad \text{where } m \neq 0.$$

Again, we see that solution y_2 in (C.8) must be discarded because it becomes unbounded at $x = 1$. Thus, from (C.6) and (C.9), we have

$$\Lambda(\lambda) \approx (\lambda - 1)^{|m|/2} \sum_{k=0}^{\infty} c_k (\lambda - 1)^k. \tag{C.12}$$

APPENDIX D

HYLLERAAS CORRELATION FACTOR IN CUSP CONDITION

Hylleraas correlation function Eqn. (4.71) was considered first when Hylleraas tried to construct a good wave function to get better energy eigenvalue. Since the situation in H_2 molecule is similar, let's try to calculate the coefficient $\kappa = \frac{1}{2}$ with the cusp condition when $r_{12} \to 0$.

Let's consider the behavior of the Hamiltonian (4.70) and the corresponding wavefunction ψ. As $r_{12} \to 0$, the dominant term in potential is the interaction between both electrons, that is $\frac{1}{r_{12}}$, and we may expand the wavefunction ψ as series of r_{12} with slowly varying coefficients which are functions of r_{a1}, r_{b1}, r_{a2} and r_{b2}. Furthermore, $\nabla_1^2\psi$ will be equal to $\nabla_2^2\psi$ and to ∇_{12}^2.

The Hamiltonian (4.70) for the H_2 molecule is reduced in the limit $r_{12} \to 0$.

$$\left(-\nabla_{12}^2 + \frac{1}{r_{12}}\right)\psi = \tilde{E}\psi \tag{D.1}$$

with $\tilde{E} = E + \frac{Z_a}{r_{a1}} + \frac{Z_b}{r_{b1}} + \frac{Z_a}{r_{a2}} + \frac{Z_b}{r_{b2}} - \frac{Z_a Z_b}{R}$. Eqn. (D.1) seems a hydrogen-like Schrödinger equation with repulsive potential, and has the solution as the increasing exponential function is $e^{r_{12}/2}$.

$$\left(-\nabla_{12}^2 + \frac{1}{r_{12}}\right)e^{r_{12}/2} = -\frac{1}{4}e^{r_{12}/2}. \tag{D.2}$$

By expanding this exponential function, the correlation factor to the first order should be

$$1 + \frac{1}{2}r_{12} \tag{D.3}$$

in exact solution of the Schrödinger equation with this correlation repulsion between two electrons.

APPENDIX E

DERIVATION OF CHARACTERISTIC FUNCTION USING WINGER FUNCTION

In this appendix, we will show how to derive the characteristic function in CNB3 [27] using Wigner function[30].

In the interacting Bose gas which is described in CNB3, two modes $\mathbf{k}$ and $-\mathbf{k}$ are intermixed to make dressed modes, so that these two modes are simultaneously treated in the density operator and the characteristic function. The definitions are

$$\rho^{(2)}_{\pm\mathbf{k}} = (1-e^{-\epsilon})^2 e^{-\epsilon(\hat{b}^\dagger_{\mathbf{k}}\hat{b}_{\mathbf{k}}+\hat{b}^\dagger_{-\mathbf{k}}\hat{b}_{-\mathbf{k}})} \tag{E.1}$$

from Eq. (66) in CNB3, and

$$\Theta_{\pm\mathbf{k}}(u) = \mathrm{Tr}\Big[e^{iu(\beta^\dagger_{\mathbf{k}}\beta_{\mathbf{k}}+\beta^\dagger_{-\mathbf{k}}\beta_{-\mathbf{k}})}\rho^{(2)}_{\pm\mathbf{k}}\Big] \tag{E.2}$$

from Eq. (68) in CNB3.

First, we will calculate the Wigner functions for the density operator and for the Kernel $e^{iua^\dagger a}$ in characteristic function for single mode. And, we will calculate them in two mode $\pm\mathbf{k}$. Finally, we will prove the identity in the Wigner function with Bogoliubov transformation, which simplifies the whole calculation in two mode.

Wigner function of density operator in single mode

In canonical ensemble the definition for the density operator is

$$\rho = \frac{e^{-H/k_BT}}{\mathrm{Tr}[e^{-H/k_BT}]}. \tag{E.3}$$

The Hamiltonian for the single mode oscillator is

$$H = \hbar\nu(a^\dagger a + \tfrac{1}{2}), \tag{E.4}$$

and the corresponding density operator is

$$\begin{aligned}
\rho_\epsilon^{(1)} &= \frac{1}{\sum_j e^{-j\epsilon}} \sum_n e^{-n\epsilon} |n\rangle\langle n| \\
&= \left(1 - e^{-\epsilon}\right) \sum_n e^{-\epsilon a^\dagger a} |n\rangle\langle n| \\
&= \left(1 - e^{-\epsilon}\right) e^{-\epsilon a^\dagger a}
\end{aligned} \tag{E.5}$$

with $\epsilon = \frac{\hbar\nu}{k_B T}$. The density operator will be diagonalized and normalizable.

$$\left\langle n \left| \rho_\epsilon^{(1)} \right| m \right\rangle = \left(1 - e^{-\epsilon}\right) \langle n \mid m\rangle\, e^{-n\epsilon} = (1 - e^{-\epsilon}) e^{-n\epsilon} \delta_{nm} \tag{E.6}$$

and

$$\sum_{n=0}^{\infty} \left[\rho_\epsilon^{(1)}\right]_{nn} = 1. \tag{E.7}$$

The corresponding Wigner function is

$$\left[\rho_\epsilon^{(1)}\right]_W = \int \frac{d^2\beta}{\pi} e^{\beta\alpha^* - \beta^*\alpha} \mathrm{Tr}\left\{ e^{\beta^* a - \beta a^\dagger} \rho_\epsilon^{(1)} \right\} \tag{E.8}$$

$$= \left(1 - e^{-\epsilon}\right) \int \frac{d^2\beta}{\pi} e^{\beta\alpha^* - \beta^*\alpha} \mathrm{Tr}\left\{ e^{\beta^* a - \beta a^\dagger} e^{-\epsilon a^\dagger a} \right\}. \tag{E.9}$$

When we take $A = -\beta a^\dagger$ and $B = \beta^* a$,

$$[A, B] = -\beta\beta^* \left[a^\dagger, a\right] = |\beta|^2. \tag{E.10}$$

The Tr-part in Eq.(E.9) is

$$\begin{aligned}
\mathrm{Tr}\left\{e^{\beta^* a-\beta a^\dagger}e^{-\epsilon a^\dagger a}\right\} &= \sum_n \iint \frac{d^2\zeta d^2\xi}{\pi^2}\left\langle n \mid \zeta\right\rangle \left\langle \zeta \left| e^{-\frac{|\beta|^2}{2}} e^{-\beta a^\dagger} e^{\beta^* a} \right| \xi \right\rangle \left\langle \xi \mid n\right\rangle e^{-n\epsilon} \\
&= \sum_n \iint \frac{d^2\zeta d^2\xi}{\pi^2} e^{-\frac{|\beta|^2}{2}} e^{-\beta\zeta^*} e^{\beta^*\xi} e^{-\frac{|\zeta|^2}{2}} \frac{\zeta^n}{\sqrt{n!}} e^{-\frac{|\xi|^2}{2}} \frac{(\xi^*)^n}{\sqrt{n!}} \left\langle \zeta \mid \xi\right\rangle e^{-n\epsilon} \\
&= e^{-\frac{|\beta|^2}{2}} \iint \frac{d^2\zeta d^2\xi}{\pi^2} e^{-\beta\zeta^*} e^{\beta^*\xi} e^{-|\zeta|^2+\xi\zeta^*-|\xi|^2} e^{e^{-\epsilon}\zeta\xi^*}. \qquad \text{(E.11)}
\end{aligned}$$

Here, we use the following identities.

$$e^{A+B} = e^{-[A,B]/2} e^A e^B \qquad \text{if } \left[[A,B],A\right] = \left[[A,B],B\right] = 0.$$

The integration over ξ is

$$\begin{aligned}
\int \frac{d^2\xi}{\pi} e^{\beta^*\xi} e^{\xi\zeta^*-|\xi|^2} e^{e^{-\epsilon}\zeta\xi^*} &= \int \frac{d^2\xi}{\pi} e^{-|\xi|^2+(\beta^*+\zeta^*)\xi+e^{-\epsilon}\zeta\xi^*} \\
&= \sum_{k_1=0}^{\infty}\sum_{k_2=0}^{\infty} \int \frac{d^2\xi}{\pi} e^{-|\xi|^2} \frac{(\beta^*+\zeta^*)^{k_1}\xi^{k_1}}{k_1!} \frac{(e^{-\epsilon}\zeta)^{k_2}(\xi^*)^{k_2}}{k_2!} \\
&= \sum_{k=0}^{\infty} \frac{\left((\beta^*+\zeta^*)(e^{-\epsilon}\zeta)\right)^k}{k!} = e^{(\beta^*+\zeta^*)(e^{-\epsilon}\zeta)}. \qquad \text{(E.12)}
\end{aligned}$$

Then,

$$\begin{aligned}
\mathrm{Tr}\left\{e^{\beta^* a-\beta a^\dagger}e^{-\epsilon a^\dagger a}\right\} &= e^{-\frac{|\beta|^2}{2}} \int \frac{d^2\zeta}{\pi} e^{-\beta\zeta^*-|\zeta|^2} e^{(\beta^*+\zeta^*)(e^{-\epsilon}\zeta)} \\
&= e^{-\frac{|\beta|^2}{2}} \int \frac{d^2\zeta}{\pi} e^{-(1-e^{-\epsilon})|\zeta|^2-\beta\zeta^*+\beta^* e^{-\epsilon}\zeta} \\
&= e^{-\frac{|\beta|^2}{2}} \int \frac{d^2 Z}{(1-e^{-\epsilon})\pi} e^{-|Z|^2-\frac{\beta}{\sqrt{1-e^{-\epsilon}}}Z^*+\frac{\beta^* e^{-\epsilon}}{\sqrt{1-e^{-\epsilon}}}Z} \\
&= e^{-\frac{|\beta|^2}{2}} \frac{e^{-|\beta|^2\frac{e^{-\epsilon}}{1-e^{-\epsilon}}}}{(1-e^{-\epsilon})} = \frac{1}{(1-e^{-\epsilon})} e^{-\frac{(1+e^{-\epsilon})}{2(1-e^{-\epsilon})}|\beta|^2} \\
&= \frac{1}{(1-e^{-\epsilon})} e^{-\frac{1}{2\tanh\frac{\epsilon}{2}}|\beta|^2}. \qquad \text{(E.13)}
\end{aligned}$$

The Wigner function for the single-mode is

$$\begin{aligned}\left[\rho_\epsilon^{(1)}\right]_W &= \frac{1}{\pi}\int d^2\beta\, e^{\beta\alpha^*-\beta^*\alpha} e^{-\frac{1}{2\tanh\frac{\epsilon}{2}}|\beta|^2} \\ &= 2\tanh\tfrac{\epsilon}{2} e^{-2\tanh\frac{\epsilon}{2}\alpha^*\alpha}. \end{aligned} \tag{E.14}$$

The normalization can be easily checked.

$$\mathrm{Tr}\left\{\rho_\epsilon^{(1)}\right\} = 1 = \int \frac{d^2\alpha}{\pi}\left[\rho_\epsilon^{(1)}\right]_W \tag{E.15}$$

by changing $\alpha = x + iy$ and $\alpha^* = x - iy$ with $\mathrm{d}^2\alpha = \mathrm{d}x\mathrm{d}y$.

For the Kernel $e^{iua^\dagger a}$, the corresponding Wigner function can be calculate by replacing ϵ into $-iu$ in Eq. (E.9).

$$\begin{aligned}\left[e^{iua^\dagger a}\right]_W &= \frac{1}{1-e^{iu}} 2\tanh\tfrac{-iu}{2} e^{-2\tanh\frac{-iu}{2}\alpha^*\alpha} \\ &= \frac{1}{1-e^{iu}}(-2i)\tan\tfrac{u}{2} e^{2i\tan\frac{u}{2}\alpha^*\alpha} \\ &= e^{-i\frac{u}{2}}\sec(u/2) e^{2i\tan\frac{u}{2}\alpha^*\alpha} \end{aligned} \tag{E.16}$$

with $\tanh(iz) = i\tan(z)$.

Wigner function in two mode

In interacting system, the density operator in two (quasi)-mode $\pm\mathbf{k}$ is

$$\rho_{\pm\mathbf{k}}^{(2)} = (1-e^{-\epsilon})^2 e^{-\epsilon(\hat{b}_{\mathbf{k}}^\dagger \hat{b}_{\mathbf{k}} + \hat{b}_{-\mathbf{k}}^\dagger \hat{b}_{-\mathbf{k}})}, \tag{E.17}$$

with $\epsilon = E_{\mathbf{k}}/kT$. And, we will generalize the characteristic function by taking two parameters u and v for each mode. The generalized characteristic function $\Theta_{\pm\mathbf{k}}(u,v)$ is

$$\Theta_{\pm\mathbf{k}}(u,v) = \mathrm{Tr}\left[e^{iu\beta_{\mathbf{k}}^\dagger\beta_{\mathbf{k}} + iv\beta_{-\mathbf{k}}^\dagger\beta_{-\mathbf{k}}}\rho_{\pm\mathbf{k}}^{(2)}\right] = \left\langle e^{iu\beta_{\mathbf{k}}^\dagger\beta_{\mathbf{k}} + iv\beta_{-\mathbf{k}}^\dagger\beta_{-\mathbf{k}}}\right\rangle, \tag{E.18}$$

Both operators $\beta_{\pm\mathbf{k}}$ and $b_{\pm\mathbf{k}}$ are connected by the Bogoliubov transformation.

$$\beta_{\mathbf{k}} = u_{\mathbf{k}} b_{\mathbf{k}} - v_{\mathbf{k}} b^{\dagger}_{-\mathbf{k}}, \qquad \beta^{\dagger}_{\mathbf{k}} = u_{\mathbf{k}} b^{\dagger}_{\mathbf{k}} - v_{\mathbf{k}} b_{-\mathbf{k}}, \tag{E.19}$$

$$\beta_{-\mathbf{k}} = u_{\mathbf{k}} b_{-\mathbf{k}} - v_{\mathbf{k}} b^{\dagger}_{\mathbf{k}}, \qquad \beta^{\dagger}_{-\mathbf{k}} = u_{\mathbf{k}} b^{\dagger}_{-\mathbf{k}} - v_{\mathbf{k}} b_{\mathbf{k}}. \tag{E.20}$$

with $u^2_{\mathbf{k}} - v^2_{\mathbf{k}} = 1$.

The two-mode characteristic function [31] is

$$\Theta_{\pm\mathbf{k}}(u,v) = \int \frac{\mathrm{d}^2\alpha}{\pi} \int \frac{\mathrm{d}^2\beta}{\pi} \left[e^{iu\beta^{\dagger}_{\mathbf{k}}\beta_{\mathbf{k}} + iv\beta^{\dagger}_{-\mathbf{k}}\beta_{-\mathbf{k}}}\right]_W \left[\rho^{(2)}_{\pm\mathbf{k}}\right]_W, \tag{E.21}$$

with

$$\begin{aligned}\left[e^{iu\beta^{\dagger}_{\mathbf{k}}\beta_{\mathbf{k}} + iv\beta^{\dagger}_{-\mathbf{k}}\beta_{-\mathbf{k}}}\right]_W &= \left(e^{-i\frac{u}{2}} \sec\tfrac{u}{2} e^{2i\alpha^*\alpha\tan\frac{u}{2}}\right)\left(e^{-i\frac{v}{2}} \sec\tfrac{v}{2} e^{2i\beta^*\beta\tan\frac{v}{2}}\right) \\ &= e^{-i(u+v)/2} \sec\tfrac{u}{2} \sec\tfrac{v}{2} e^{2i\alpha^*\alpha\tan\frac{u}{2} + 2i\beta^*\beta\tan\frac{v}{2}}.\end{aligned} \tag{E.22}$$

Eq. (E.21) will be derived below.

Since the density operator is defined in terms of $b_{\pm\mathbf{k}}$, we need following identity for Wigner function: if $G(A^{\dagger}, A) = F(\mu a^{\dagger} + \nu a, \sigma a + \tau a^{\dagger})$, then their Wigner functions satisfy $G_W(\alpha^*, \alpha) = F_W(\mu\alpha^* + \nu\alpha, \sigma\alpha + \tau\alpha^*)$, which will be also proved. The Wigner function for two-mode density operator is

$$\begin{aligned}\left[\rho^{(2)}_{\pm\mathbf{k}}\right]_W &= 4\tanh^2\left(\tfrac{\epsilon}{2}\right) e^{-2\tanh\frac{\epsilon}{2}[(\alpha^* u_{\mathbf{k}} - \beta v_{\mathbf{k}})(\alpha u_{\mathbf{k}} - \beta^* v_{\mathbf{k}}) + (\beta^* u_{\mathbf{k}} - \alpha v_{\mathbf{k}})(\beta u_{\mathbf{k}} - \alpha^* v_{\mathbf{k}})]} \\ &= 4\tanh^2\left(\frac{\epsilon}{2}\right) e^{-2[(\alpha^*\alpha + \beta^*\beta)(u^2_{\mathbf{k}} + v^2_{\mathbf{k}}) - (\alpha^*\beta^* + \beta\alpha)(2u_{\mathbf{k}}v_{\mathbf{k}})]\tanh\frac{\epsilon}{2}}.\end{aligned}$$

The characteristic function is

$$
\begin{aligned}
&\Theta_{\pm\mathbf{k}}(u,v)\\
&= 4e^{-i(u+v)/2}\sec\tfrac{u}{2}\sec\tfrac{v}{2}\tanh^2\frac{\epsilon}{2}\int\frac{\mathrm{d}^2\beta}{\pi}e^{-2[(u_{\mathbf{k}}^2+v_{\mathbf{k}}^2)\tanh\frac{\epsilon}{2}-i\tan\frac{v}{2}]|\beta|^2}\\
&\quad\times\int\frac{\mathrm{d}^2\alpha}{\pi}e^{-2[(u_{\mathbf{k}}^2+v_{\mathbf{k}}^2)\tanh\frac{\epsilon}{2}-i\tan\frac{u}{2}]|\alpha|^2+2(\alpha\beta+\alpha^*\beta^*)(2u_{\mathbf{k}}v_{\mathbf{k}})\tanh\frac{\epsilon}{2}}\\
&= 4e^{-i(u+v)/2}\sec\tfrac{u}{2}\sec\tfrac{v}{2}\tanh^2\frac{\epsilon}{2}\int\frac{\mathrm{d}^2\beta}{\pi}e^{-2[(u_{\mathbf{k}}^2+v_{\mathbf{k}}^2)\tanh\frac{\epsilon}{2}-i\tan\frac{v}{2}]|\beta|^2}\\
&\quad\times\frac{e^{\frac{8u_{\mathbf{k}}v_{\mathbf{k}}\tanh^2\frac{\epsilon}{2}}{[(u_{\mathbf{k}}^2+v_{\mathbf{k}}^2)\tanh\frac{\epsilon}{2}-i\tan\frac{u}{2}]}|\beta|^2}}{2[(u_{\mathbf{k}}^2+v_{\mathbf{k}}^2)\tanh\frac{\epsilon}{2}-i\tan\frac{u}{2}]}\\
&= \frac{4e^{-i(u+v)/2}\sec\frac{u}{2}\sec\frac{v}{2}\tanh^2\frac{\epsilon}{2}}{2\Big[(u_{\mathbf{k}}^2+v_{\mathbf{k}}^2)\tanh\frac{\epsilon}{2}-i\tan\frac{u}{2}\Big]\Big[2[(u_{\mathbf{k}}^2+v_{\mathbf{k}}^2)\tanh\frac{\epsilon}{2}-i\tan\frac{v}{2}]-\frac{8u_{\mathbf{k}}^2v_{\mathbf{k}}^2\tanh^2\frac{\epsilon}{2}}{[(u_{\mathbf{k}}^2+v_{\mathbf{k}}^2)\tanh\frac{\epsilon}{2}-i\tan\frac{u}{2}]}\Big]}\\
&= \frac{e^{-i(u+v)/2}\sec\frac{u}{2}\sec\frac{v}{2}\tanh^2\frac{\epsilon}{2}}{[(u_{\mathbf{k}}^2+v_{\mathbf{k}}^2)\tanh\frac{\epsilon}{2}-i\tan\frac{u}{2}][(u_{\mathbf{k}}^2+v_{\mathbf{k}}^2)\tanh\frac{\epsilon}{2}-i\tan\frac{v}{2}]-4u_{\mathbf{k}}^2v_{\mathbf{k}}^2\tanh^2\frac{\epsilon}{2}}\\
&= \frac{e^{-i(u+v)/2}\sec\frac{u}{2}\sec\frac{v}{2}\tanh^2\frac{\epsilon}{2}}{\tanh^2\frac{\epsilon}{2}-i(\tan\frac{u}{2}+\tan\frac{v}{2})(u_{\mathbf{k}}^2+v_{\mathbf{k}}^2)\tanh\frac{\epsilon}{2}-\tan\frac{u}{2}\tan\frac{v}{2}}.
\end{aligned}
\tag{E.23}
$$

With the following two identities,

$$\tanh\Big(\frac{\epsilon}{2}\Big)=\frac{e^{\epsilon/2}-e^{-\epsilon/2}}{e^{\epsilon/2}+e^{-\epsilon/2}}=\frac{e^{\epsilon}-1}{e^{\epsilon}+1},\tag{E.24}$$

and,

$$i\tan\tfrac{u}{2}=\tanh\Big(i\frac{u}{2}\Big)=\frac{e^{iu}-1}{e^{iu}+1},\tag{E.25}$$

we will get the characteristic function

$$
\begin{aligned}
&\Theta_{\pm\mathbf{k}}(u,v)\\
&= \frac{e^{-i(u+v)/2}\sec\frac{u}{2}\sec\frac{v}{2}(e^{\epsilon}-1)^2}{(e^{\epsilon}-1)^2 - i(\tan\frac{u}{2}+\tan\frac{v}{2})(u_{\mathbf{k}}^2+v_{\mathbf{k}}^2)(e^{\epsilon}-1)(e^{\epsilon}+1) - \tan\frac{u}{2}\tan\frac{v}{2}(e^{\epsilon}+1)^2}\\
&= \frac{\sec\frac{u}{2}\sec\frac{v}{2}(e^{\epsilon}-1)^2(e^{iu/2}+e^{-iu/2})(e^{iv/2}+e^{-iv/2})}{\left[\begin{array}{l}(e^{\epsilon}-1)^2(e^{iu}+1)(e^{iv}+1) - 2(e^{iu+iv}-1)(u_{\mathbf{k}}^2+v_{\mathbf{k}}^2)(e^{2\epsilon}-1)\\ \qquad +(e^{iu}-1)(e^{iv}-1)(e^{\epsilon}+1)^2\end{array}\right]}\\
&= \frac{4(e^{\epsilon}-1)^2}{\left[\begin{array}{l}(e^{\epsilon}-1)^2(e^{iu}+1)(e^{iv}+1) - 2(e^{iu+iv}-1)(u_{\mathbf{k}}^2+v_{\mathbf{k}}^2)(e^{2\epsilon}-1)\\ \qquad +(e^{iu}-1)(e^{iv}-1)(e^{\epsilon}+1)^2\end{array}\right]}.
\end{aligned}
\tag{E.26}
$$

If we define

$$
Y_{\pm} = \frac{u_{\mathbf{k}}e^{\epsilon} \pm v_{\mathbf{k}}}{u_{\mathbf{k}} \pm v_{\mathbf{k}}e^{\epsilon}},
\tag{E.27}
$$

we will get

$$
Y_{+}Y_{-} = \frac{(u_{\mathbf{k}}^2 e^{2\epsilon} - v_{\mathbf{k}}^2)}{(u_{\mathbf{k}}^2 - v_{\mathbf{k}}^2 e^{2\epsilon})},
\tag{E.28}
$$

$$
Y_{+} + Y_{-} = \frac{(u_{\mathbf{k}}e^{\epsilon}+v_{\mathbf{k}})(u_{\mathbf{k}}-v_{\mathbf{k}}e^{\epsilon}) + (u_{\mathbf{k}}e^{\epsilon}-v_{\mathbf{k}})(u_{\mathbf{k}}+v_{\mathbf{k}}e^{\epsilon})}{(u_{\mathbf{k}}+v_{\mathbf{k}}e^{\epsilon})(u_{\mathbf{k}}-v_{\mathbf{k}}e^{\epsilon})} = \frac{2e^{\epsilon}}{(u_{\mathbf{k}}^2 - v_{\mathbf{k}}^2 e^{2\epsilon})},
\tag{E.29}
$$

$$
Y_{\pm} - 1 = \frac{u_{\mathbf{k}}e^{\epsilon} \pm v_{\mathbf{k}}}{u_{\mathbf{k}} \pm v_{\mathbf{k}}e^{\epsilon}} - 1 = \frac{u_{\mathbf{k}}e^{\epsilon} \pm v_{\mathbf{k}} - u_{\mathbf{k}} \mp v_{\mathbf{k}}e^{\epsilon}}{u_{\mathbf{k}} \pm v_{\mathbf{k}}e^{\epsilon}} = \frac{(e^{\epsilon}-1)(u_{\mathbf{k}} \mp v_{\mathbf{k}})}{u_{\mathbf{k}} \pm v_{\mathbf{k}}e^{\epsilon}},
\tag{E.30}
$$

$$
(Y_{+}-1)(Y_{-}-1) = \frac{(e^{\epsilon}-1)^2}{u_{\mathbf{k}}^2 - v_{\mathbf{k}}^2 e^{2\epsilon}}.
\tag{E.31}
$$

Using $Y_\pm$, we can simplify Eq. (E.26) furthermore.

$$\begin{aligned}\Theta_{\pm\mathbf{k}}(u,v) &= \frac{2(e^{\epsilon}-1)^2}{\left[\begin{array}{c}\big\{(e^{2\epsilon}+1)+(u_{\mathbf{k}}^2+v_{\mathbf{k}}^2)(e^{2\epsilon}-1)\big\}-2e^{\epsilon}(e^{iu}+e^{iv})\\ +\big\{(e^{2\epsilon}+1)-(u_{\mathbf{k}}^2+v_{\mathbf{k}}^2)(e^{2\epsilon}-1)\big\}e^{iu+iv}\end{array}\right]}\\ &= \frac{(e^{\epsilon}-1)^2}{(u_{\mathbf{k}}^2e^{2\epsilon}-v_{\mathbf{k}}^2)-e^{\epsilon}(e^{iu}+e^{iv})+(u_{\mathbf{k}}^2-v_{\mathbf{k}}^2e^{2\epsilon})e^{iu+iv}}\\ &= \frac{(Y_+-1)(Y_--1)}{Y_+Y_- - \frac{1}{2}(Y_++Y_-)(e^{iu}+e^{iv})+e^{iu+iv}}\\ &= \frac{2(Y_+-1)(Y_--1)}{(Y_+-e^{iu})(Y_--e^{iv})+(Y_--e^{iu})(Y_+-e^{iv})}. \end{aligned} \tag{E.32}$$

Trace for two multiplied operators in terms of Wigner function

Let's begin with the definition of the Wigner function. In one degree of freedom system with the rescaled position q and the conjugate momentum p with $\big[q,p\big]=i$, the Wigner function for operator $F(q,p)$ is [31]

$$F_W(q',p') \equiv \int \mathrm{d}y\,\langle q'-\tfrac{y}{2}|F(q,p)|q'+\tfrac{y}{2}\rangle e^{ip'y}. \tag{E.33}$$

The equivalence of above equation to Eq. (E.8) is easily shown by comparing with Eq. (3.3.14) and Eq. (3.4.12) in [5].

By the identity $\int \mathrm{d}q''|q''\rangle\langle q''| = \int \mathrm{d}p''|p''\rangle\langle p''| = 1$ and $\langle q'|p'\rangle = \frac{1}{\sqrt{2\pi}}e^{ip'q'}$,

$$\begin{aligned}F_W(q',p') &= \int \mathrm{d}y\mathrm{d}q''\mathrm{d}p''\,\langle q'-\tfrac{y}{2}|q''\rangle\langle q''|F(q,p)|p''\rangle\langle p''|q'+\tfrac{y}{2}\rangle e^{ip'y}\\ &= 2\int \mathrm{d}q''\mathrm{d}p''\,\langle q''|F(q,p)|p''\rangle\langle p''|2q'-q''\rangle e^{i2p'(q'-q'')}\\ &= \int \mathrm{d}q''\mathrm{d}p''\,\langle q''|F(q,p)|p''\rangle\langle p''|q''\rangle 2e^{i2(p'-p'')(q'-q'')}. \end{aligned} \tag{E.34}$$

Similarly,

$$F_W(q',p') = \int \mathrm{d}q''\mathrm{d}p''\,\langle p''|F(q,p)|q''\rangle\langle q''|p''\rangle 2e^{-i2(p'-p'')(q'-q'')}. \tag{E.35}$$

By introducing the Schwinger's notation,

$$e^{A;B} = \sum_{n=0}^{\infty} \frac{1}{n!} A^n B^n, \tag{E.36}$$

the exponential terms simplifies into

$$\langle p''|q''\rangle e^{i2(p'-p'')(q'-q'')} = \langle p''|e^{2i(p-p');(q-q')}|q''\rangle \tag{E.37}$$

and

$$\langle q''|p''\rangle e^{-i2(p'-p'')(q'-q'')} = \langle q''|e^{-2i(q-q');(p-p')}|p''\rangle. \tag{E.38}$$

We can rewrite the Wigner function.

$$\begin{align} F_W(q',p') &= \mathrm{Tr}[F(q,p)2e^{2i(p-p');(q-q')}] \tag{E.39} \\ &= \mathrm{Tr}[F(q,p)2e^{-2i(q-q');(p-p')}]. \tag{E.40} \end{align}$$

And, we can conclude that

$$2e^{2i(p-p');(q-q')} = 2e^{-2i(q-q');(p-p')}. \tag{E.41}$$

Furthermore, by inversion we can write the operator $F(q,p)$ in terms of Wigner function.

$$\begin{align} F(q,p) &= \int \frac{\mathrm{d}q'\mathrm{d}p'}{2\pi} F_W(q',p') 2e^{2i(p-p');(q-q')} \tag{E.42} \\ &= \int \frac{\mathrm{d}q'\mathrm{d}p'}{2\pi} F_W(q',p') 2e^{-2i(q-q');(p-p')}. \tag{E.43} \end{align}$$

From Eq. (E.43), the trace of multiplication of two operators is

$$\begin{aligned}
&\mathrm{Tr}[F(q,p)G(q,p)]\\
&= \mathrm{Tr}[\int \frac{\mathrm{d}q'\mathrm{d}p'}{\pi} F_W(q',p')e^{-2i(q-q');(p-p')} \int \frac{\mathrm{d}q''\mathrm{d}p''}{\pi} G_W(q'',p'')e^{-2i(q-q'');(p-p'')}]\\
&= \int \frac{\mathrm{d}q'\mathrm{d}p'}{\pi} \int \frac{\mathrm{d}q''\mathrm{d}p''}{\pi} F_W(q',p')G_W(q'',p'')\mathrm{Tr}[e^{-2i(q-q');(p-p')}e^{-2i(q-q'');(p-p'')}]\\
&= \int \frac{\mathrm{d}q'\mathrm{d}p'}{2\pi} F_W(q',p')G_W(q',p'),
\end{aligned} \tag{E.44}$$

where

$$\begin{aligned}
&\mathrm{Tr}[e^{-2i(q-q');(p-p')}e^{-2i(q-q'');(p-p'')}]\\
&= \int \frac{\mathrm{d}q'''\mathrm{d}p'''}{2\pi} e^{-2i(q'''-q')(p'''-p')}e^{2i(p'''-p'')(q'''-q'')}\\
&= \int \frac{\mathrm{d}q'''\mathrm{d}p'''}{2\pi} e^{2i(q'''(p'-p'')+p'''(q'-q'')-p'q'+p''q'')}\\
&= \frac{\pi}{2}\delta(p'-p'')\delta(q'-q'').
\end{aligned} \tag{E.45}$$

So, the trace of two operators can be written in terms of each Wigner function.

Wigner function of function with Bogoliubov-transformed operators

For the single-mode,

$$\begin{aligned}
F_W(\alpha^*,\alpha) &= \int \frac{d^2\beta}{\pi} e^{\beta\alpha^*-\beta^*\alpha}\mathrm{Tr}\left\{e^{\beta^* a-\beta a^\dagger}F(a^\dagger,a)\right\}\\
&= \int \frac{d^2\beta}{\pi} \mathrm{Tr}\left\{e^{\beta^*(a-\alpha)-\beta(a^\dagger-\alpha^*)}F(a^\dagger,a)\right\}\\
&= \int \frac{d^2\beta}{\pi} \mathrm{Tr}\left\{e^{\alpha a^\dagger-\alpha^* a}e^{\beta^* a-\beta a^\dagger}e^{\alpha^* a-\alpha a^\dagger}F(a^\dagger,a)\right\}\\
&= 2\mathrm{Tr}\left\{e^{\alpha a^\dagger-\alpha^* a}Se^{\alpha^* a-\alpha a^\dagger}F(a^\dagger,a)\right\}
\end{aligned} \tag{E.46}$$

with the reflection operator

$$S = \int \frac{d^2\beta}{2\pi} e^{\beta^* a - \beta a^\dagger}. \tag{E.47}$$

Here, we used the following identities.

$$e^{\alpha a^\dagger - \alpha^* a} a^\dagger e^{\alpha^* a - \alpha a^\dagger} = a^\dagger - \alpha^*, \tag{E.48}$$

$$e^{\alpha a^\dagger - \alpha^* a} a e^{\alpha^* a - \alpha a^\dagger} = a - \alpha. \tag{E.49}$$

The proof for above identities are simple. For any nonnegative integer n,

$$a^\dagger a^n = a^n a^\dagger - n a^{n-1}, \tag{E.50}$$

$$a (a^\dagger)^n = (a^\dagger)^n a + n (a^\dagger)^{n-1}, \tag{E.51}$$

$$a^\dagger e^{\alpha^* a} = a^\dagger \sum_{n=0}^{\infty} \frac{(\alpha^*)^n}{n!} a^n = \sum_{n=0}^{\infty} \frac{(\alpha^*)^n}{n!} (a^n a^\dagger - n a^{n-1}) = e^{\alpha^* a}(a^\dagger - \alpha^*), \tag{E.52}$$

and

$$a e^{-\alpha a^\dagger} = e^{-\alpha a^\dagger}(a - \alpha). \tag{E.53}$$

The properties of the reflection operator S are :

$$S^\dagger = S = S^{-1}, \tag{E.54}$$

since

$$\begin{aligned} S^\dagger &= \int \frac{\mathrm{d}\beta^* \mathrm{d}\beta}{2\pi} e^{\beta a^\dagger - \beta^* a} = S^{-1} \\ &= \int \frac{\mathrm{d}(-\beta^*)\mathrm{d}(-\beta)}{2\pi} e^{-\beta a^\dagger + \beta^* a} = S \qquad (\beta \to -\beta, \quad \beta^* \to -\beta^*). \end{aligned}$$

And, the name of S is from the following property.

$$S^{-1} a^\dagger S = -a^\dagger, \qquad S^{-1} a S = -a. \tag{E.55}$$

The proof is

$$
\begin{aligned}
aS &= a\int \frac{\mathrm{d}^2\beta}{2\pi} e^{\beta^* a - \beta a^\dagger} \\
&= \int \frac{\mathrm{d}^2\beta}{2\pi} e^{|\beta|^2/2} e^{\beta^* a} a e^{-\beta a^\dagger} \\
&= \int \frac{\mathrm{d}^2\beta}{2\pi} e^{|\beta|^2/2} e^{\beta^* a} a \int \frac{\mathrm{d}^2\alpha}{\pi} |\alpha\rangle\langle\alpha| e^{-\beta a^\dagger} \\
&= \int \frac{\mathrm{d}^2\beta}{2\pi} \int \frac{\mathrm{d}^2\alpha}{\pi} e^{|\beta|^2/2} e^{\beta^*\alpha} \alpha e^{-\beta\alpha^*} |\alpha\rangle\langle\alpha| \\
&= \int \frac{-\mathrm{d}^2\beta}{2\pi} \int \frac{-\mathrm{d}^2\alpha}{\pi} e^{-|\beta|^2/2} e^{\beta^*\alpha} (-\alpha) e^{-\beta\alpha^*} |\alpha\rangle\langle\alpha| \qquad (\beta^* \to -\beta^* \& \alpha \to -\alpha) \\
&= \int \frac{\mathrm{d}^2\beta}{2\pi} \int \frac{\mathrm{d}^2\alpha}{\pi} e^{-|\beta|^2/2} e^{-\beta\alpha^*} |\alpha\rangle\langle\alpha| e^{\beta^*\alpha} (-\alpha) \\
&= \int \frac{\mathrm{d}^2\beta}{2\pi} e^{-|\beta|^2/2} e^{-\beta a^\dagger} e^{\beta^* a} (-a) \\
&= -Sa.
\end{aligned} \tag{E.56}
$$

The Bogoliubov transformed operator $G(a^\dagger, a)$ can be written in terms of the linear similarity operator V.

$$G(a^\dagger, a) = F(\mu a^\dagger + \nu a, \sigma a + \tau a^\dagger) = V^{-1} F(a^\dagger, a) V, \tag{E.57}$$

with

$$V = e^{\frac{\tau}{2\mu}(a^\dagger)^2} \mu^{-a^\dagger a} e^{-\frac{\nu}{2\mu} a^2}. \tag{E.58}$$

The form of V can easily verified by

$$\begin{aligned}
a^\dagger V &= a^\dagger e^{\frac{\tau}{2\mu}(a^\dagger)^2}\mu^{-a^\dagger a}e^{-\frac{\nu}{2\mu}a^2} \\
&= e^{\frac{\tau}{2\mu}(a^\dagger)^2}a^\dagger\sum\frac{(-\ln\mu)^n}{n!}(a^\dagger a)^n e^{-\frac{\nu}{2\mu}a^2} \\
&= e^{\frac{\tau}{2\mu}(a^\dagger)^2}\sum\frac{(-\ln\mu)^n}{n!}(a^\dagger a-1)^n a^\dagger e^{-\frac{\nu}{2\mu}a^2} \\
&= e^{\frac{\tau}{2\mu}(a^\dagger)^2}e^{-\ln\mu(a^\dagger a-1)}\sum\frac{\left(-\frac{\nu}{2\mu}\right)^n}{n!}(a^{2n}a^\dagger-2na^{2n-1}) \\
&= V\mu(a^\dagger-(-\frac{\nu}{\mu})a) = V(\mu a^\dagger+\nu a),
\end{aligned} \tag{E.59}$$

and

$$\begin{aligned}
aV &= \sum\frac{\left(\frac{\tau}{2\mu}\right)^n}{n!}((a^\dagger)^{2n}a+2n(a^\dagger)^{2n-1})\mu^{-a^\dagger a}e^{-\frac{\nu}{2\mu}a^2} \\
&= e^{\frac{\tau}{2\mu}(a^\dagger)^2}(a+\frac{\tau}{\mu}a^\dagger)\sum\frac{(-\ln\mu)^n}{n!}(a^\dagger a)^n e^{-\frac{\nu}{2\mu}a^2} \\
&= e^{\frac{\tau}{2\mu}(a^\dagger)^2}\left(\sum\frac{(-\ln\mu)^n}{n!}(a^\dagger a+1)^n a+\mu^{-a^\dagger a}\tau a^\dagger\right)e^{-\frac{\nu}{2\mu}a^2} \\
&= e^{\frac{\tau}{2\mu}(a^\dagger)^2}\mu^{-a^\dagger a}e^{-\frac{\nu}{2\mu}a^2}(\frac{1}{\mu}a+\tau\left(a^\dagger+\frac{\nu}{\mu}a\right)) \\
&= V(\sigma a+\tau a^\dagger).
\end{aligned} \tag{E.60}$$

Since V consists of ${a^\dagger}^2$, $a^\dagger a$, and a^2,

$$S^{-1}VS = V \quad \rightarrow \quad VS = SV \quad \rightarrow \quad V^{-1}SV = S. \tag{E.61}$$

The Wigner function for $G(a^\dagger, a)$ is

$$\begin{aligned} G_W(\alpha^*, \alpha) &= 2\mathrm{Tr}\left\{e^{\alpha a^\dagger - \alpha^* a} S e^{\alpha^* a - \alpha a^\dagger} G(a^\dagger, a)\right\} \\ &= 2\mathrm{Tr}\left\{e^{\alpha a^\dagger - \alpha^* a} V^{-1} S V e^{\alpha^* a - \alpha a^\dagger} V^{-1} F(a^\dagger, a) V\right\} \\ &= 2\mathrm{Tr}\left\{V e^{\alpha a^\dagger - \alpha^* a} V^{-1} S V e^{\alpha^* a - \alpha a^\dagger} V^{-1} F(a^\dagger, a)\right\} \\ &= 2\mathrm{Tr}\left\{e^{-(\mu\alpha^* + \nu\alpha)a + (\sigma\alpha + \tau\alpha^*)a^\dagger} S e^{(\mu\alpha^* + \nu\alpha)a - (\sigma\alpha + \tau\alpha^*)a^\dagger} F(a^\dagger, a)\right\} \\ &= F_W(\mu\alpha^* + \nu\alpha, \sigma\alpha + \tau\alpha^*). \end{aligned} \tag{E.62}$$

So, the Wigner function of Bogoliubov transformed operator is given by the Wigner function with transformed argument.

For the general n-dimensional cases, we can define the operator and corresponding complex c-numbers.

$$\begin{aligned} \vec{a} &= (a_1^\dagger, a_1, a_2^\dagger, a_2, \cdots\cdots, a_n^\dagger, a_n), \\ \vec{\alpha} &= (\alpha_1^*, \alpha_1, \alpha_2^*, \alpha_2, \cdots\cdots, \alpha_n^*, \alpha_n). \end{aligned} \tag{E.63}$$

The n-dimensional displacement and reflection operators are

$$\Pi_{k=1}^n e^{\alpha_k^* a_k - \alpha_k a_k^\dagger} = e^{\vec{\alpha} K \vec{a}^T}, \qquad S = \int \frac{d^{2n}\beta}{(2\pi)^n} e^{\vec{\beta} K \vec{a}^T}, \tag{E.64}$$

with the $2n \times 2n$ block matrix K.

$$K = \left(\begin{array}{cc|c|cc} 0 & -1 & & & \\ 1 & 0 & & & \\ \hline & & \ddots & & \\ \hline & & & 0 & -1 \\ & & & 1 & 0 \end{array}\right) = -K^T = -K^{-1}, \tag{E.65}$$

since

$$KK^{-1} = K(-K) = \left(\begin{array}{cc|cc} 0 & -1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ \hline 0 & 0 & 0 & -1 \\ 0 & 0 & 1 & 0 \end{array}\right)\left(\begin{array}{cc|cc} 0 & 1 & 0 & 0 \\ -1 & 0 & 0 & 0 \\ \hline 0 & 0 & 0 & 1 \\ 0 & 0 & -1 & 0 \end{array}\right) = \left(\begin{array}{cc|cc} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ \hline 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{array}\right)$$

.

Wigner function in n-dimension is

$$F_W(\vec{\alpha}) = 2^n \mathrm{tr}\left\{e^{-\vec{\alpha}K\vec{a}^T} S e^{\vec{\alpha}K\vec{a}^T} F(\vec{a})\right\}. \tag{E.66}$$

Let's consider the linear similarity transformation in n dimension.

$$V^{-1}\vec{a}V = \vec{a}\mathbf{V}, \qquad V\vec{a}V^{-1} = \vec{a}\mathbf{V}^{-1}, \tag{E.67}$$

where $\mathbf{V}$ is a $2n \times 2n$ matrix restricted by

$$\mathbf{V}K\mathbf{V}^T = K \tag{E.68}$$

which is the analog of $\mu\sigma - \nu\tau = 1$. V is also the exponential of a bilinear form of $\vec{a}$. Then,

$$G(\vec{a}) = V^{-1}F(\vec{a})V = F(\vec{a}\mathbf{V}) \tag{E.69}$$

and its corresponding Winger function is

$$\begin{aligned} G_W(\vec{\alpha}) &= 2^n \mathrm{tr}\left\{V e^{-\vec{\alpha}K\vec{a}^T} V^{-1} S V e^{\vec{\alpha}K\vec{a}^T} V^{-1} F(\vec{a})\right\} \\ &= 2^n \mathrm{tr}\left\{e^{-\vec{\alpha}\mathbf{V}K\vec{a}^T} S e^{\vec{\alpha}\mathbf{V}K\vec{a}^T} F(\vec{a})\right\} \\ &= F_W(\vec{\alpha}\mathbf{V}). \end{aligned} \tag{E.70}$$

The relation is also valid for n-dimensional case.

APPENDIX F

PARTICLE STATISTICS FROM THE PARTITION FUNCTION FORMALISM IN CANONICAL ENSEMBLE

One-state Probability

In quantum statistical theory with second quantization formalism, the system can be described by the distribution of the occupation number in all accessible quantum states. And, this distribution is described by the proper probability function.

Let's start with the simplest probability function for the occupation number in single quantum state. The probability of m particle in the μ-th state is

$$\begin{aligned} P(n_\mu = m) &= \langle \delta(n_\mu - m) \rangle \\ &= \langle \Theta(n_\mu - m) \rangle - \langle \Theta(n_\mu - (m+1)) \rangle. \end{aligned} \tag{F.1}$$

The δ-function is the Kronecker-delta, which has one when the argument is zero and zero otherwise, and Θ is the step-function, which has one for a non-negative argument and zero for negative.

In the system which we want to describe, since the total number of particles is fixed, we will use the canonical ensemble to evaluate the thermal quantities. And, the probability function is also considered as a conditional probability with fixed total number

$$P(n_\mu = m) \quad \rightarrow \quad P(n_\mu = m|N). \tag{F.2}$$

This probability function $P(n_\mu = m|N)$ can evaluated through the partition function Z_N in equilibrium state.

The partition function for the canonical ensemble with N-particle is

$$Z_N = \sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} \cdots e^{-\beta \sum_{\{\nu\}} \epsilon_\nu n_\nu} \delta(N - \sum_{\{\nu\}} n_\nu) \tag{F.3}$$

where index ν covers all accessible states and n_ν, the occupation number of particles in ν-th state, runs from 0 to infinity for bosons, and $\beta = (k_B T)^{-1}$. Here, δ-function makes sure that there're only N particles in the system. And, let's take $Z_0 = 1$ for convenience.

The probability that the system has over m particle in μ-th state is

$$\begin{aligned} P(n_\mu \geq m|N) &= \langle \Theta(n_\mu - m) \rangle \\ &= \frac{1}{Z_N} \sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} \cdots \sum_{n_\mu=n}^{\infty} \cdots e^{-\beta \sum_{\{\nu\}} \epsilon_\nu n_\nu} \delta(N - \sum_{\{\nu\}} n_\nu). \end{aligned} \tag{F.4}$$

By replacing $n_\mu \to m + n_\mu$,

$$\begin{aligned} P(n_\mu \geq m|N) &= \frac{e^{-m\beta\epsilon_\mu}}{Z_N} \sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} \cdots \sum_{n_\mu=0}^{\infty} \cdots e^{-\beta \sum_{\{\nu\}} \epsilon_\nu n_\nu} \delta(N - m - \sum_{\{\nu\}} n_\nu) \\ &= e^{-m\beta\epsilon_\mu} \frac{Z_{N-m}}{Z_N}. \end{aligned} \tag{F.5}$$

Finally, we will get

$$\begin{aligned} P(n_\mu = m|N) &= P(n_\mu \geq m|N) - P(n_\mu \geq m+1|N) \\ &= e^{-m\beta\epsilon_\mu} \frac{Z_{N-m}}{Z_N} - e^{-(m+1)\beta\epsilon_\mu} \frac{Z_{N-m-1}}{Z_N}. \end{aligned} \tag{F.6}$$

Average for the Occupation Number and the Recursion Relation

The average for the function $f(n_\mu)$ of the occupation number n_μ is

$$\begin{aligned}\langle f(n_\mu)\rangle &= \sum_{m=0}^{N} f(m)P(n_\mu = m|N) \\ &= \frac{1}{Z_N}\sum_{m=0}^{N}\left\{f(m)e^{-m\beta\epsilon_\mu}Z_{N-m} - f(m)e^{-(m+1)\beta\epsilon_\mu}Z_{N-m-1}\right\} \\ &= \frac{1}{Z_N}\left\{\sum_{m=0}^{N} f(m)e^{-m\beta\epsilon_\mu}Z_{N-m} - \sum_{m=1}^{N} f(m-1)e^{-m\beta\epsilon_\mu}Z_{N-m}\right\} \\ &= \sum_{m=1}^{N}\left\{f(m) - f(m-1)\right\}e^{-m\beta\epsilon_\mu}\frac{Z_{N-m}}{Z_N} + f(0), \qquad \text{(F.7)}\end{aligned}$$

with the convention $Z_{-1} = 0$.

For the average of the occupation number in μ-state, $f(n_\mu) = n_\mu$ and

$$\langle n_\mu\rangle = \sum_{m=1}^{N} e^{-m\beta\epsilon_\mu}\frac{Z_{N-m}}{Z_N}. \qquad \text{(F.8)}$$

Since the fixed total number of particles is just the summation of the occupation number in each state,

$$N = \sum_\mu \langle n_\mu\rangle = \sum_{m=1}^{N}\sum_\mu e^{-m\beta\epsilon_\mu}\frac{Z_{N-m}}{Z_N} = \frac{1}{Z_N}\sum_{m=1}^{N} Z_1(m\beta)Z_{N-m}. \qquad \text{(F.9)}$$

The final recursion relation is

$$Z_N(\beta) = \frac{1}{N}\sum_{m=1}^{N} Z_1(m\beta)Z_{N-m}(\beta). \qquad \text{(F.10)}$$

For the convenience in the recursive relation, let's take $Z_m = 0$ for negative integer m.

Two-state Probability and 2nd Moment

Similar to the one-state probability, we can define the two-state probability function.

$$\begin{aligned}
&P(n_\mu = m, n_\nu = n|N) \\
&= \langle \delta(n_\mu - m)\delta(n_\nu - n)\rangle \\
&= \langle \big(\Theta(n_\mu - m) - \Theta(n_\mu - m - 1)\big)\delta(n_\nu - n)\rangle \\
&= \langle \Theta(n_\mu - m)\delta(n_\nu - n)\rangle - \langle \Theta(n_\mu - m - 1)\big)\delta(n_\nu - n)\rangle \\
&= \langle \Theta(n_\mu - m)\big(\Theta(n_\nu - n) - \Theta(n_\nu - n - 1)\big)\rangle \\
&\qquad - \langle \Theta(n_\mu - m - 1)\big(\Theta(n_\nu - n) - \Theta(n_\nu - n - 1)\big)\rangle \\
&= \langle \Theta(n_\mu - m)\Theta(n_\nu - n)\rangle - \langle \Theta(n_\mu - m)\Theta(n_\nu - n - 1)\big)\rangle \\
&\qquad - \langle \Theta(n_\mu - m - 1)\Theta(n_\nu - n)\rangle + \langle \Theta(n_\mu - m - 1)\Theta(n_\nu - n - 1)\big)\rangle.
\end{aligned} \tag{F.11}$$

The expression for the probability that μ-state has more than m and ν-state has more than n is

$$\begin{aligned}
P(n_\mu \geq m, n_\nu \geq n|N) &= \langle \Theta(n_\mu - m)\Theta(n_\nu - n)\rangle \\
&= \frac{1}{Z_N}\sum_{n_1=0}^{\infty}\sum_{n_2=0}^{\infty}\cdots\sum_{n_\mu=m}^{\infty}\cdots\sum_{n_\nu=n}^{\infty}\cdots e^{-\beta\sum_{\{\xi\}}\epsilon_\xi n_\xi}\delta(N - \sum_{\{\xi\}} n_\xi).
\end{aligned} \tag{F.12}$$

By replacing $n_\mu \to m + n_\mu$ and $n_\nu \to n + n_\nu$,

$$\begin{aligned}
&P(n_\mu \geq m, n_\nu \geq n|N) \\
&= \frac{e^{-m\beta\epsilon_\mu}e^{-n\beta\epsilon_\nu}}{Z_N}\sum_{n_1=0}^{\infty}\sum_{n_2=0}^{\infty}\cdots\sum_{n_\mu=0}^{\infty}\cdots\sum_{n_\nu=0}^{\infty}\cdots e^{-\beta\sum_{\{\xi\}}\epsilon_\xi n_\xi}\delta(N - m - n - \sum_{\{\xi\}} n_\xi) \\
&= e^{-m\beta\epsilon_\mu - n\beta\epsilon_\nu}\frac{Z_{N-m-n}}{Z_N}.
\end{aligned} \tag{F.13}$$

The two-state probability with fixed n particles in the ν-th state is

$$\begin{aligned}
P(n_\mu \geq m, n_\nu = n|N) &= \langle \Theta(n_\mu - m)\delta(n_\nu - n)\rangle \\
&= \langle \Theta(n_\mu - m)\Theta(n_\nu - n)\rangle - \langle \Theta(n_\mu - m)\Theta(n_\nu - n - 1))\rangle \\
&= e^{-m\beta\epsilon_\mu - n\beta\epsilon_\nu}\frac{Z_{N-m-n}}{Z_N} - e^{-m\beta\epsilon_\mu-(n+1)\beta\epsilon_\nu}\frac{Z_{N-m-n-1}}{Z_N}. \quad \text{(F.14)}
\end{aligned}$$

Finally, the two-state probability of m particles in the μ-th state and n particles in the ν-th state is

$$\begin{aligned}
&P(n_\mu = m, n_\nu = n|N) = \langle \delta(n_\mu - m)\delta(n_\nu - n)\rangle \\
&= P(n_\mu \geq m, n_\nu = n|N) - P(n_\mu \geq m+1, n_\nu = n|N) \\
&= [P(n_\mu \geq m, n_\nu \geq n|N) - P(n_\mu \geq m, n_\nu \geq n+1|N)] \\
&\quad - [P(n_\mu \geq m+1, n_\nu \geq n|N) - P(n_\mu \geq m+1, n_\nu \geq n+1|N)] \\
&= e^{-m\beta\epsilon_\mu - n\beta\epsilon_\nu}\frac{Z_{N-m-n}}{Z_N} - e^{-m\beta\epsilon_\mu-(n+1)\beta\epsilon_\nu}\frac{Z_{N-m-n-1}}{Z_N} \\
&\quad - e^{-(m+1)\beta\epsilon_\mu - n\beta\epsilon_\nu}\frac{Z_{N-m-n-1}}{Z_N} + e^{-(m+1)\beta\epsilon_\mu-(n+1)\beta\epsilon_\nu}\frac{Z_{N-m-n-2}}{Z_N}. \qquad \text{(F.15)}
\end{aligned}$$

From this two-state probability, the following average can be calculated.

$$
\begin{aligned}
&\langle f(n_\mu) g(n_\nu) \rangle \\
&= \sum_{m=0}^{N} \sum_{n=0}^{N} f(m) g(n) P(n_\mu = m, n_\nu = n | N)
\end{aligned}
\tag{F.16}
$$

$$
\begin{aligned}
&= \frac{1}{Z_N} \sum_{m=0}^{N} f(m) e^{-m\beta\epsilon_\mu} \\
&\qquad\qquad \times \left\{ \sum_{n=0}^{N} g(n) \Big(e^{-n\beta\epsilon_\nu} Z_{N-m-n} - e^{-(n+1)\beta\epsilon_\nu} Z_{N-m-n-1} \Big) \right\} \\
&\quad - \frac{1}{Z_N} \sum_{m=0}^{N} f(m) e^{-(m+1)\beta\epsilon_\mu} \\
&\qquad\qquad \times \left\{ \sum_{n=0}^{N} g(n) \Big(e^{-n\beta\epsilon_\nu} Z_{N-m-n-1} - e^{-(n+1)\beta\epsilon_\nu} Z_{N-m-n-2} \Big) \right\} \\
&= \frac{1}{Z_N} \sum_{m=0}^{N} f(m) e^{-m\beta\epsilon_\mu} \\
&\qquad\qquad \times \left\{ \sum_{n=1}^{N} \big(g(n) - g(n-1) \big) e^{-n\beta\epsilon_\nu} Z_{N-m-n} + g(0) \right\} \\
&\quad - \frac{1}{Z_N} \sum_{m=0}^{N} f(m) e^{-(m+1)\beta\epsilon_\mu} \\
&\qquad\qquad \times \left\{ \sum_{n=1}^{N} \big(g(n) - g(n-1) \big) e^{-n\beta\epsilon_\nu} Z_{N-m-1-n} + g(0) \right\} \\
&= \sum_{m=1}^{N} \sum_{n=1}^{N} \big(f(m) - f(m-1) \big) \big(g(n) - g(n-1) \big) e^{-m\beta\epsilon_\mu - n\beta\epsilon_\nu} \frac{Z_{N-m-n}}{Z_N} \\
&\quad - f(0) \sum_{n=1}^{N} \big(g(n) - g(n-1) \big) e^{-n\beta\epsilon_\nu} \frac{Z_{N-n}}{Z_N} \\
&\quad - g(0) \sum_{m=1}^{N} \big(f(m) - f(m-1) \big) e^{-m\beta\epsilon_\mu} \frac{Z_{N-m}}{Z_N} \\
&\quad + f(0) g(0) \frac{1}{Z_N}.
\end{aligned}
\tag{F.17}
$$

Reduction into Single Summation

Usually, a double summation is needed for the expectation value of the correlation function between two states, because the occupation numbers for both states are counted. However, for the correlation function of the above types, given in Eq. (F.16), we can reduce that into single summation.

By simplification of the polynomial function $(f(m)-f(m-1))(g(n)-g(n-1))$ in Eq. (F.17), the the general form can be written as the sum of the following terms with proper x_μ and x_ν.

$$\begin{aligned}&\sum_{m=1}^{N}\sum_{n=1}^{N} m^{x_\mu} n^{x_\nu} e^{-m\beta\epsilon_\mu - n\beta\epsilon_\nu}\frac{Z_{N-m-n}}{Z_N}\\ &= \left(e^{-\beta\epsilon_\mu}\frac{\partial}{\partial\left(e^{-\beta\epsilon_\mu}\right)}\right)^{x_\mu}\left(e^{-\beta\epsilon_\nu}\frac{\partial}{\partial\left(e^{-\beta\epsilon_\nu}\right)}\right)^{x_\nu}\sum_{m=1}^{N}\sum_{n=1}^{N} e^{-m\beta\epsilon_\mu - n\beta\epsilon_\nu}\frac{Z_{N-m-n}}{Z_N}\end{aligned} \tag{F.18}$$

with nonnegative integers x_μ and x_ν. And,

$$\begin{aligned}\sum_{m=1}^{N}\sum_{n=1}^{N} e^{-m\beta\epsilon_\mu - n\beta\epsilon_\nu}\frac{Z_{N-m-n}}{Z_N} &= \sum_{m=1}^{N-1}\sum_{n=1}^{N-m} e^{-m\beta\epsilon_\mu - n\beta\epsilon_\nu}\frac{Z_{N-m-n}}{Z_N}\\ &= \sum_{T=2}^{N}\sum_{m=1}^{T-1} e^{-m\beta\epsilon_\mu-(T-m)\beta\epsilon_\nu}\frac{Z_{N-T}}{Z_N}\\ &= \sum_{T=2}^{N}\frac{e^{-\beta\epsilon_\nu}\left(e^{-\beta\epsilon_\mu}\right)^T - e^{-\beta\epsilon_\mu}\left(e^{-\beta\epsilon_\nu}\right)^T}{e^{-\beta\epsilon_\mu}-e^{-\beta\epsilon_\nu}}\frac{Z_{N-T}}{Z_N}.\end{aligned} \tag{F.19}$$

Since the double summation is reduced into the single summation, the actual calculation time is also reduced from N^2 order to N order.

In degenerate case ($\epsilon_\mu = \epsilon_\nu$),

$$\begin{aligned}&\sum_{m=1}^{N}\sum_{n=1}^{N} m^{x_\mu} n^{x_\nu} e^{-m\beta\epsilon_\mu - n\beta\epsilon_\nu}\frac{Z_{N-m-n}}{Z_N}\\ &= \sum_{T=2}^{N}\left[\sum_{m=1}^{T-1} m^{x_\mu}(T-m)^{x_\nu}\right] e^{-T\beta\epsilon_\mu}\frac{Z_{N-T}}{Z_N}.\end{aligned} \tag{F.20}$$

In the simplest degenerate case with $x_\mu = 0$ and $x_\nu = 0$,

$$\sum_{m=1}^{N}\sum_{n=1}^{N} e^{-m\beta\epsilon_\mu - n\beta\epsilon_\nu}\frac{Z_{N-m-n}}{Z_N} = \sum_{T=2}^{N}(T-1)e^{-T\beta\epsilon_\mu}\frac{Z_{N-T}}{Z_N}. \tag{F.21}$$

When $x_\mu = 1$ and $x_\nu = 0$,

$$\begin{aligned}
&\sum_{m=1}^{N}\sum_{n=1}^{N} m e^{-m\beta\epsilon_\mu - n\beta\epsilon_\nu}\frac{Z_{N-m-n}}{Z_N} = \left(e^{-\beta\epsilon_\mu}\frac{\partial}{\partial\left(e^{-\beta\epsilon_\mu}\right)}\right)\sum_{m=1}^{N}\sum_{n=1}^{N} e^{-m\beta\epsilon_\mu - n\beta\epsilon_\nu}\frac{Z_{N-m-n}}{Z_N} \\
&= e^{-\beta\epsilon_\mu}e^{-\beta\epsilon_\nu}\sum_{T=2}^{N}\left[\frac{T\left(e^{-\beta\epsilon_\mu}\right)^{T-1}}{e^{-\beta\epsilon_\mu} - e^{-\beta\epsilon_\nu}} - \frac{\left(e^{-\beta\epsilon_\mu}\right)^{T} - \left(e^{-\beta\epsilon_\nu}\right)^{T}}{\left(e^{-\beta\epsilon_\mu} - e^{-\beta\epsilon_\nu}\right)^{2}}\right]\frac{Z_{N-T}}{Z_N},
\end{aligned} \tag{F.22}$$

and for the degenerate case

$$\begin{aligned}
\sum_{m=1}^{N}\sum_{n=1}^{N} m e^{-m\beta\epsilon_\mu - n\beta\epsilon_\nu}\frac{Z_{N-m-n}}{Z_N} &= \sum_{T=2}^{N}\left(\sum_{m=1}^{T-1} m\right)e^{-T\beta\epsilon_\mu}\frac{Z_{N-T}}{Z_N} \\
&= \sum_{T=2}^{N}\tfrac{1}{2}(T-1)Te^{-T\beta\epsilon_\mu}\frac{Z_{N-T}}{Z_N}.
\end{aligned} \tag{F.23}$$

When $x_\mu = 2$ and $x_\nu = 0$,

$$\begin{aligned}
&\sum_{m=1}^{N}\sum_{n=1}^{N} m^2 e^{-m\beta\epsilon_\mu - n\beta\epsilon_\nu}\frac{Z_{N-m-n}}{Z_N} = \left(e^{-\beta\epsilon_\mu}\frac{\partial}{\partial\left(e^{-\beta\epsilon_\mu}\right)}\right)^2\sum_{m=1}^{N}\sum_{n=1}^{N} e^{-m\beta\epsilon_\mu - n\beta\epsilon_\nu}\frac{Z_{N-m-n}}{Z_N} \\
&= \sum_{T=2}^{N}\left[T^2\frac{e^{-\beta\epsilon_\nu}\left(e^{-\beta\epsilon_\mu}\right)^{T}}{e^{-\beta\epsilon_\mu} - e^{-\beta\epsilon_\nu}} - 2T\frac{e^{-\beta\epsilon_\nu}\left(e^{-\beta\epsilon_\mu}\right)^{T+1}}{(e^{-\beta\epsilon_\mu} - e^{-\beta\epsilon_\nu})^2}\right. \\
&\qquad \left. + \frac{e^{-\beta\epsilon_\mu}e^{-\beta\epsilon_\nu}\left(e^{-\beta\epsilon_\mu} + e^{-\beta\epsilon_\nu}\right)\left\{\left(e^{-\beta\epsilon_\mu}\right)^{T} - \left(e^{-\beta\epsilon_\nu}\right)^{T}\right\}}{\left(e^{-\beta\epsilon_\mu} - e^{-\beta\epsilon_\nu}\right)^{3}}\right]\frac{Z_{N-T}}{Z_N},
\end{aligned} \tag{F.24}$$

and for the degenerate case

$$\begin{aligned}
\sum_{m=1}^{N}\sum_{n=1}^{N} m^2 e^{-m\beta\epsilon_\mu - n\beta\epsilon_\nu}\frac{Z_{N-m-n}}{Z_N} &= \sum_{T=2}^{N}\left(\sum_{m=1}^{T-1} m^2\right)e^{-T\beta\epsilon_\mu}\frac{Z_{N-T}}{Z_N} \\
&= \sum_{T=2}^{N}\tfrac{1}{6}(T-1)T(2T-1)e^{-T\beta\epsilon_\mu}\frac{Z_{N-T}}{Z_N}.
\end{aligned} \tag{F.25}$$

When $x_\mu = 1$ and $x_\nu = 1$,

$$
\begin{aligned}
&\sum_{m=1}^{N}\sum_{n=1}^{N} mn e^{-m\beta\epsilon_\mu - n\beta\epsilon_\nu} \frac{Z_{N-m-n}}{Z_N} \\
&= \left(e^{-\beta\epsilon_\mu} \frac{\partial}{\partial\left(e^{-\beta\epsilon_\mu}\right)}\right)\left(e^{-\beta\epsilon_\nu} \frac{\partial}{\partial\left(e^{-\beta\epsilon_\nu}\right)}\right) \sum_{m=1}^{N}\sum_{n=1}^{N} e^{-m\beta\epsilon_\mu - n\beta\epsilon_\nu} \frac{Z_{N-m-n}}{Z_N} \\
&= \frac{e^{-\beta\epsilon_\mu} e^{-\beta\epsilon_\nu}}{\left(e^{-\beta\epsilon_\mu} - e^{-\beta\epsilon_\nu}\right)^2} \sum_{T=2}^{N} \Bigg[T\Big\{\left(e^{-\beta\epsilon_\mu}\right)^T + \left(e^{-\beta\epsilon_\nu}\right)^T\Big\} \\
&\qquad\qquad - \frac{e^{-\beta\epsilon_\mu} + e^{-\beta\epsilon_\mu}}{e^{-\beta\epsilon_\mu} - e^{-\beta\epsilon_\nu}} \Big\{\left(e^{-\beta\epsilon_\mu}\right)^T - \left(e^{-\beta\epsilon_\nu}\right)^T\Big\}\Bigg] \frac{Z_{N-T}}{Z_N},
\end{aligned}
\tag{F.26}
$$

and for the degenerate case

$$
\begin{aligned}
\sum_{m=1}^{N}\sum_{n=1}^{N} mn e^{-m\beta\epsilon_\mu - n\beta\epsilon_\nu} \frac{Z_{N-m-n}}{Z_N} &= \sum_{T=2}^{N} \left(\sum_{m=1}^{T-1} m(T-m)\right) e^{-T\beta\epsilon_\mu} \frac{Z_{N-T}}{Z_N} \\
&= \sum_{T=2}^{N} \tfrac{1}{6}(T-1)T(T+1) e^{-T\beta\epsilon_\mu} \frac{Z_{N-T}}{Z_N}.
\end{aligned}
\tag{F.27}
$$

Cross Correlation Between Two States

The simplest form for the 2nd-order moment is cross correlation between two different states, or $f(n_\mu) = n_\mu$ and $g(n_\nu) = n_\nu$.

$$
\begin{aligned}
\langle n_\mu n_\nu \rangle &= \sum_{m=0}^{N}\sum_{n=0}^{N} mnP(n_\mu = m, n_\nu = n|N) = \sum_{m=1}^{N}\sum_{n=1}^{N} e^{-m\beta\epsilon_\mu - n\beta\epsilon_\nu} \frac{Z_{N-m-n}}{Z_N} \\
&= \sum_{T=2}^{N} \frac{e^{-\beta\epsilon_\nu}\left(e^{-\beta\epsilon_\mu}\right)^T - e^{-\beta\epsilon_\mu}\left(e^{-\beta\epsilon_\nu}\right)^T}{e^{-\beta\epsilon_\mu} - e^{-\beta\epsilon_\nu}} \frac{Z_{N-T}}{Z_N}.
\end{aligned}
\tag{F.28}
$$

For the degenerate case ($\epsilon_\mu = \epsilon_\nu$),

$$
\begin{aligned}
\langle n_\mu n_\nu \rangle &= \sum_{m=0}^{N}\sum_{n=0}^{N} mnP(n_\mu = m, n_\nu = n|N) = \sum_{m=1}^{N}\sum_{n=1}^{N} e^{-m\beta\epsilon_\mu - n\beta\epsilon_\nu} \frac{Z_{N-m-n}}{Z_N} \\
&= \sum_{T=2}^{N}\sum_{m=1}^{T-1} e^{-T\beta\epsilon_\mu} \frac{Z_{N-T}}{Z_N} = \sum_{T=2}^{N} (T-1) e^{-T\beta\epsilon_\mu} \frac{Z_{N-T}}{Z_N}.
\end{aligned}
\tag{F.29}
$$

n-state probability

Similar to the one-state probability,

$$P(\{n_\mu = l_\mu\}|N) = \left\langle \prod_\mu \delta(n_\mu - l_\mu) \right\rangle . \tag{F.30}$$

By replacing the δ-function into substraction of two Θ-function, the n-state probability can be written as linear combination of probability which has occupation number $n_\mu \geq l_\mu$.

$$P(\{n_\mu = l_\mu\}|N) = \left\langle \big(\Theta(n_\mu - l_\mu) - \Theta(n_\mu - (l_\mu + 1))\big) \prod_{\nu \neq \mu} \delta(n_\nu - l_\nu) \right\rangle . \tag{F.31}$$

After replacing the δ-function into Θ-function, we will get the following probability.

$$\begin{aligned} P(\{n_\mu \geq l_\mu\}|N) &= \left\langle \prod_\nu \Theta(n_\nu - l_\nu) \right\rangle \\ &= \frac{1}{Z_N} \sum_{n_1=l_1}^{\infty} \sum_{n_2=l_2}^{\infty} \cdots \sum_{n_\mu=l_\mu}^{\infty} \cdots e^{-\beta \sum_{\{\xi\}} \epsilon_\xi n_\xi} \delta(N - \sum_{\{\xi\}} n_\xi). \end{aligned} \tag{F.32}$$

By replacing $n_\mu \to n_\mu + l_\mu$,

$$\begin{aligned} P(\{n_\mu \geq l_\mu\}|N) &= \frac{e^{-\beta \sum_{\xi=1}^{\infty} l_\xi \epsilon_\xi}}{Z_N} \sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} \cdots \sum_{n_\mu=0}^{\infty} e^{-\beta \sum_{\{\xi\}} \epsilon_\xi n_\xi} \delta(N - \sum_{\{\xi\}} (n_\xi + l_\xi)) \\ &= e^{-\beta \sum_{\{\xi\}} l_\xi \epsilon_\xi} \frac{Z_{N - \sum_{\{\xi\}} l_\xi}}{Z_N}. \end{aligned} \tag{F.33}$$

The probability with fixed l_ν particles in the ν-th state is calculated through the difference between probability with more $P(n_\nu \geq l_\nu)$ and $P(n_\nu \geq l_\nu + 1)$.

$$P\big(n_\nu = l_\nu, \cdots\big) = P\big(n_\nu \geq l_\nu, \cdots\big) - P\big(n_\nu \geq l_\nu + 1, \cdots\big). \tag{F.34}$$

For n-state probability, the explicit form is the sum of these differences with proper signs. For 3-state probability, the explicit form is

$$\begin{aligned}
&P\big(n_1 = l_1, n_2 = l_2, n_3 = l_3\big) \\
=&P\big(n_1 = l_1, n_2 = l_2, n_3 \geq l_3\big) - P\big(n_1 = l_1, n_2 = l_2, n_3 \geq l_3 + 1\big) \\
=&P\big(n_1 = l_1, n_2 \geq l_2, n_3 \geq l_3\big) - P\big(n_1 = l_1, n_2 \geq l_2 + 1, n_3 \geq l_3\big) \\
&- P\big(n_1 = l_1, n_2 \geq l_2, n_3 \geq l_3 + 1\big) + P\big(n_1 = l_1, n_2 \geq l_2 + 1, n_3 \geq l_3 + 1\big) \\
=&P\big(n_1 \geq l_1, n_2 \geq l_2, n_3 \geq l_3\big) - P\big(n_1 \geq l_1 + 1, n_2 \geq l_2, n_3 \geq l_3\big) \\
&- P\big(n_1 \geq l_1, n_2 \geq l_2 + 1, n_3 \geq l_3\big) + P\big(n_1 \geq l_1 + 1, n_2 \geq l_2 + 1, n_3 \geq l_3\big) \\
&- P\big(n_1 \geq l_1, n_2 \geq l_2, n_3 \geq l_3 + 1\big) + P\big(n_1 \geq l_1 + 1, n_2 \geq l_2, n_3 \geq l_3 + 1\big) \\
&+ P\big(n_1 \geq l_1, n_2 \geq l_2 + 1, n_3 \geq l_3 + 1\big) - P\big(n_1 \geq l_1 + 1, n_2 \geq l_2 + 1, n_3 \geq l_3 + 1\big).
\end{aligned} \tag{F.35}$$

The expectation value for the general polynomial-type function of the occupation number is

$$\begin{aligned}
&\langle f_1(n_{\mu_1}) f_2(n_{\mu_2}) \cdots \rangle = \sum_{l_1=0}^{N} \sum_{l_2=0}^{N} \cdots \Big[f_1(l_1) f_2(l_2) \cdots \Big] P(\{n_\mu = l_\mu\} \,| N) \\
&= \sum_{l_1=0}^{N} \sum_{l_2=0}^{N} \cdots \Big[f_1(l_1) f_2(l_2) \cdots \Big] \Big(P(n_1 \geq l_1, \{n_\mu = l_\mu; \mu = 2, 3 \cdots\} \,| N) \\
&\qquad - P(n_1 \geq l_1 + 1, \{n_\mu = l_\mu; \mu = 2, 3 \cdots\} \,| N) \Big) \\
&= \sum_{l_1=0}^{N} \sum_{l_2=0}^{N} \cdots \Big[f_1(l_1) f_2(l_2) \cdots \Big] P(n_1 \geq l_1, \{n_\mu = l_\mu; \mu = 2, 3 \cdots\} \,| N) \\
&\quad - \sum_{l_1=1}^{N} \sum_{l_2=0}^{N} \cdots \Big[f_1(l_1 - 1) f_2(l_2) \cdots \Big] P(n_1 \geq l_1, \{n_\mu = l_\mu; \mu = 2, 3 \cdots\} \,| N) \\
&= \sum_{l_1=1}^{N} \Big\{ f_1(l_1) - f_1(l_1 - 1) \Big\} \sum_{l_2=0}^{N} \cdots \Big[f_2(l_2) \cdots \Big] P(n_{\mu_1} \geq l_1, \{n_\mu = l_\mu; \mu = 2, 3, \cdots\} \,| N) \\
&\quad + f_1(0) \sum_{l_2=0}^{N} \cdots \Big[f_2(l_2) \cdots \Big] P(n_{\mu_1} \geq l_1, \{n_\mu = l_\mu; \mu = 2, 3, \cdots\} \,| N).
\end{aligned} \tag{F.36}$$

After repeating similar procedure for other states, the final form will be

$$\begin{aligned}&\langle f_1(n_{\mu_1})f_2(n_{\mu_2})\cdots\rangle\\&=\sum_{l_1=1}^{N}\Big\{f_1(l_1)-f_1(l_1-1)\Big\}\sum_{l_2=1}^{N}\Big\{f_2(l_2)-f_2(l_2-1)\Big\}\cdots P(\{n_\mu\geq l_\mu\}\,|N)\end{aligned}\tag{F.37}$$

when $f_i(l_i=0)=0$. Since every summation starts from 1 and the total sum of l_i is N, the ranges for the summation should be shifted. For n-state expectation value,

$$\begin{aligned}\langle f_1(n_{\mu_1})f_2(n_{\mu_2})\cdots\rangle=&\sum_{l_1=1}^{r_1}\Big\{f_1(l_1)-f_1(l_1-1)\Big\}\sum_{l_2=1}^{r_2}\Big\{f_2(l_2)-f_2(l_2-1)\Big\}\\&\sum_{l_3=1}^{r_3}\Big\{f_2(l_2)-f_2(l_2-1)\Big\}\cdots P(\{n_\mu\geq l_\mu\}\,|N)\end{aligned}\tag{F.38}$$

where $r_1=N-n+1$, $r_2=N-n+2-l_1$, $r_3=N-n+3-l_1-l_2$, and etc.

Now, we can rearrange the terms to make single summation.

$$\langle f_1(n_{\mu_1})f_2(n_{\mu_2})\cdots\rangle=\sum_{T=n}^{N}F(e^{-\mu_1},e^{-\mu_2},\cdots)\frac{Z_{N-T}}{Z_N}.\tag{F.39}$$

Since the reduction into single summation depends on the actual form of the function and degeneracy, the procedure for each case should be evaluated case by case. Anyway, the reduction into single summation means the reduction of calculation time. Let's show the example explicitly by starting in 3-state expectation.

$$\begin{aligned}
\langle n_{\mu_1} n_{\mu_2} n_{\mu_3} \rangle &= \sum_{l_1=1}^{N-2} \sum_{l_2=1}^{N-1-l_1} \sum_{l_3=1}^{N-l_1-l_2} \left(e^{-\beta\epsilon_1}\right)^{l_1} \left(e^{-\beta\epsilon_2}\right)^{l_2} \left(e^{-\beta\epsilon_3}\right)^{l_3} \frac{Z_{N-l_1-l_2-l_3}}{Z_N} \\
&= \sum_{l_1=1}^{N-2} \left(e^{-\beta\epsilon_1}\right)^{l_1} \sum_{T_1=2}^{N-l_1} \frac{e^{-\beta\epsilon_3}\left(e^{-\beta\epsilon_2}\right)^{T_1} - e^{-\beta\epsilon_2}\left(e^{-\beta\epsilon_3}\right)^{T_1}}{e^{-\beta\epsilon_2} - e^{-\beta\epsilon_3}} \frac{Z_{N-l_1-T_1}}{Z_N} \\
&= \sum_{T=3}^{N} \sum_{l_1=1}^{T-2} \left(e^{-\beta\epsilon_1}\right)^{l_1} \frac{e^{-\beta\epsilon_3}\left(e^{-\beta\epsilon_2}\right)^{T-l_1} - e^{-\beta\epsilon_2}\left(e^{-\beta\epsilon_3}\right)^{T-l_1}}{e^{-\beta\epsilon_2} - e^{-\beta\epsilon_3}} \frac{Z_{N-T}}{Z_N} \\
&= \sum_{T=3}^{N} \left[\frac{e^{-\beta\epsilon_2} e^{-\beta\epsilon_3}}{e^{-\beta\epsilon_2} - e^{-\beta\epsilon_3}} \frac{e^{-\beta\epsilon_2}\left(e^{-\beta\epsilon_1}\right)^{T-1} - e^{-\beta\epsilon_1}\left(e^{-\beta\epsilon_2}\right)^{T-1}}{e^{-\beta\epsilon_1} - e^{-\beta\epsilon_2}} \right. \\
&\qquad \left. - \frac{e^{-\beta\epsilon_2} e^{-\beta\epsilon_3}}{e^{-\beta\epsilon_2} - e^{-\beta\epsilon_3}} \frac{e^{-\beta\epsilon_3}\left(e^{-\beta\epsilon_1}\right)^{T-1} - e^{-\beta\epsilon_1}\left(e^{-\beta\epsilon_3}\right)^{T-1}}{e^{-\beta\epsilon_1} - e^{-\beta\epsilon_3}} \right] \frac{Z_{N-T}}{Z_N} \\
&= \sum_{T=3}^{N} \left[\frac{e^{-\beta\epsilon_2} e^{-\beta\epsilon_3} \left(e^{-\beta\epsilon_1}\right)^{T}}{\left(e^{-\beta\epsilon_1} - e^{-\beta\epsilon_2}\right)\left(e^{-\beta\epsilon_1} - e^{-\beta\epsilon_3}\right)} + \frac{e^{-\beta\epsilon_3} e^{-\beta\epsilon_1} \left(e^{-\beta\epsilon_2}\right)^{T}}{\left(e^{-\beta\epsilon_2} - e^{-\beta\epsilon_3}\right)\left(e^{-\beta\epsilon_2} - e^{-\beta\epsilon_1}\right)} \right. \\
&\qquad \left. + \frac{e^{-\beta\epsilon_1} e^{-\beta\epsilon_2} \left(e^{-\beta\epsilon_3}\right)^{T}}{\left(e^{-\beta\epsilon_3} - e^{-\beta\epsilon_1}\right)\left(e^{-\beta\epsilon_3} - e^{-\beta\epsilon_2}\right)} \right] \frac{Z_{N-T}}{Z_N}. \qquad \text{(F.40)}
\end{aligned}$$

For degenerate case where $\epsilon_1 = \epsilon_2 = \epsilon_3$,

$$\begin{aligned}
\langle n_{\mu_1} n_{\mu_2} n_{\mu_3} \rangle &= \sum_{l_1=1}^{N-2} \sum_{l_2=1}^{N-1-l_1} \sum_{l_3=1}^{N-l_1-l_2} \left(e^{-\beta\epsilon_1}\right)^{l_1} \left(e^{-\beta\epsilon_2}\right)^{l_2} \left(e^{-\beta\epsilon_3}\right)^{l_3} \frac{Z_{N-l_1-l_2-l_3}}{Z_N} \\
&= \sum_{T=3}^{N} \sum_{l_1=1}^{T-2} \sum_{l_2=1}^{T-1-l_1} \left(e^{-\beta\epsilon_1}\right)^{T} \frac{Z_{N-T}}{Z_N} \\
&= \sum_{T=3}^{N} \sum_{l_1=1}^{T-2} \left(T-1-l_1\right) \left(e^{-\beta\epsilon_1}\right)^{T} \frac{Z_{N-T}}{Z_N} \\
&= \sum_{T=3}^{N} \left((T-1)(T-2) - \tfrac{1}{2}(T-2)(T-1)\right) \left(e^{-\beta\epsilon_1}\right)^{T} \frac{Z_{N-T}}{Z_N} \\
&= \sum_{T=3}^{N} \frac{(T-1)(T-2)}{2} \left(e^{-\beta\epsilon_1}\right)^{T} \frac{Z_{N-T}}{Z_N}. \qquad \text{(F.41)}
\end{aligned}$$

Or, for $\epsilon_1 \neq \epsilon_2 = \epsilon_3$,

$$\begin{aligned}
&\langle n_{\mu_1} n_{\mu_2} n_{\mu_3} \rangle \\
&= \sum_{l_1=1}^{N-2} \sum_{l_2=1}^{N-1-l_1} \sum_{l_3=1}^{N-l_1-l_2} \left(e^{-\beta\epsilon_1}\right)^{l_1} \left(e^{-\beta\epsilon_2}\right)^{l_2+l_3} \frac{Z_{N-l_1-l_2-l_3}}{Z_N} \\
&= \sum_{l_1=1}^{N-2} \left(e^{-\beta\epsilon_1}\right)^{l_1} \sum_{T_1=2}^{N-l_1} \sum_{l_2=1}^{T_1-1} \left(e^{-\beta\epsilon_2}\right)^{T_1} \frac{Z_{N-l_1-T_1}}{Z_N} \\
&= \sum_{l_1=1}^{N-2} \left(e^{-\beta\epsilon_1}\right)^{l_1} \sum_{T_1=2}^{N-l_1} (T_1-1) \left(e^{-\beta\epsilon_2}\right)^{T_1} \frac{Z_{N-l_1-T_1}}{Z_N} \\
&= \left(e^{-\beta\epsilon_2} \frac{\partial}{\partial\left(e^{-\beta\epsilon_2}\right)} - 1 \right) \sum_{l_1=1}^{N-2} \sum_{T_1=2}^{N-l_1} \left(e^{-\beta\epsilon_1}\right)^{l_1} \left(e^{-\beta\epsilon_2}\right)^{T_1} \frac{Z_{N-l_1-T_1}}{Z_N} \\
&= \left(e^{-\beta\epsilon_2} \frac{\partial}{\partial\left(e^{-\beta\epsilon_2}\right)} - 1 \right) \sum_{T=3}^{N} \sum_{l_1=1}^{T-2} \left(e^{-\beta\epsilon_1}\right)^{l_1} \left(e^{-\beta\epsilon_2}\right)^{T-l_1} \frac{Z_{N-T}}{Z_N} \\
&= \left(e^{-\beta\epsilon_2} \frac{\partial}{\partial\left(e^{-\beta\epsilon_2}\right)} - 1 \right) \sum_{T=3}^{N} \frac{\left(e^{-\beta\epsilon_2}\right)^2 \left(e^{-\beta\epsilon_1}\right)^{T-1} - e^{-\beta\epsilon_1} \left(e^{-\beta\epsilon_2}\right)^{T}}{e^{-\beta\epsilon_1} - e^{-\beta\epsilon_2}} \frac{Z_{N-T}}{Z_N} \\
&= \sum_{T=3}^{N} \left[(T-1) \frac{e^{-\beta\epsilon_1} \left(e^{-\beta\epsilon_2}\right)^{T}}{e^{-\beta\epsilon_2} - e^{-\beta\epsilon_1}} + \frac{\left(e^{-\beta\epsilon_2}\right)^2 \left(e^{-\beta\epsilon_1}\right)^{T} - e^{-\beta\epsilon_1} \left(e^{-\beta\epsilon_2}\right)^{T+1}}{\left(e^{-\beta\epsilon_1} - e^{-\beta\epsilon_2}\right)^2} \right] \frac{Z_{N-T}}{Z_N}.
\end{aligned} \tag{F.42}$$

Similarly, for $\epsilon_1 = \epsilon_2 \neq \epsilon_3$,

$$\begin{aligned}
&\langle n_{\mu_1} n_{\mu_2} n_{\mu_3} \rangle \\
&= \sum_{T=3}^{N} \left[(T-1) \frac{e^{-\beta\epsilon_3} \left(e^{-\beta\epsilon_1}\right)^{T}}{e^{-\beta\epsilon_1} - e^{-\beta\epsilon_3}} + \frac{\left(e^{-\beta\epsilon_1}\right)^2 \left(e^{-\beta\epsilon_3}\right)^{T} - e^{-\beta\epsilon_3} \left(e^{-\beta\epsilon_1}\right)^{T+1}}{\left(e^{-\beta\epsilon_3} - e^{-\beta\epsilon_1}\right)^2} \right] \frac{Z_{N-T}}{Z_N}.
\end{aligned}$$

APPENDIX G

OCCUPATION NUMBER IN QUASI-PARTICLE BASIS AND COMMUTATION RELATION

The number operator in quasi-particle basis is

$$\begin{aligned}
\beta_{\mathbf{k}}^{\dagger}\beta_{\mathbf{k}} &= a_{\mathbf{k}}^{\dagger}\beta_0\beta_0^{\dagger}a_{\mathbf{k}} \\
&= a_{\mathbf{k}}^{\dagger}(1+n_0)^{-1/2}a_0a_0^{\dagger}(1+n_0)^{-1/2}a_{\mathbf{k}} \\
&= a_{\mathbf{k}}^{\dagger}(1+n_0)^{-1/2}(1+n_0)(1+n_0)^{-1/2}a_{\mathbf{k}} \\
&= a_{\mathbf{k}}^{\dagger}a_{\mathbf{k}} \\
&= n_{\mathbf{k}}. \qquad \text{(G.1)}
\end{aligned}$$

So, the distribution of the occupation number in quasi-particle basis is same to that in particle basis.

The commutation relation is

$$\begin{aligned}
\left[\beta_{\mathbf{k}}, \beta_{\mathbf{k}'}^{\dagger}\right] &= \left[\beta_0^{\dagger}a_{\mathbf{k}}, a_{\mathbf{k}'}^{\dagger}\beta_0\right] \\
&= \left[a_0^{\dagger}(1+n_0)^{-1/2}a_{\mathbf{k}}, a_{\mathbf{k}'}^{\dagger}(1+n_0)^{-1/2}a_0\right] \\
&= a_0^{\dagger}(1+n_0)^{-1/2}a_{\mathbf{k}}a_{\mathbf{k}'}^{\dagger}(1+n_0)^{-1/2}a_0 - a_{\mathbf{k}'}^{\dagger}(1+n_0)^{-1/2}a_0a_0^{\dagger}(1+n_0)^{-1/2}a_{\mathbf{k}} \\
&= a_0^{\dagger}(1+n_0)^{-1}a_0a_{\mathbf{k}}a_{\mathbf{k}'}^{\dagger} - a_{\mathbf{k}'}^{\dagger}(1+n_0)^{-1/2}(1+n_0)(1+n_0)^{-1/2}a_{\mathbf{k}} \\
&= a_0^{\dagger}a_0n_0^{-1}a_{\mathbf{k}}a_{\mathbf{k}'}^{\dagger} - a_{\mathbf{k}'}^{\dagger}a_{\mathbf{k}} \\
&= \delta_{\mathbf{k},\mathbf{k}'}. \qquad \text{(G.2)}
\end{aligned}$$

However, for the ground state

$$\begin{aligned}\left[\beta_0, \beta_0^\dagger\right] &= \beta_0\beta_0^\dagger - \beta_0^\dagger\beta_0 \\ &= (1+n_0)^{-1/2}a_0a_0^\dagger(1+n_0)^{-1/2} - a_0^\dagger(1+n_0)^{-1/2}(1+n_0)^{-1/2}a_0 \\ &= 0. \end{aligned} \tag{G.3}$$

So, the commutation relation for the quasi-particle basis is same to that of the particle basis except the ground state. And, we cannot construct the number state for the ground state of the quasi-particle.

APPENDIX H

REPRESENTATION OF THE DENSITY OPERATOR IN A WEAKLY INTERACTING BOSE GAS

In the interacting bose gas with finite number of particles, the density operator in Fock space $\mathcal{F}_a$ spanned by $\hat{n}_{\mathbf{k}} = \hat{a}^{\dagger}_{\mathbf{k}}\hat{a}_{\mathbf{k}}$ can be represented with all possible combinations of occupation number of particles in bra and ket state.

$$\rho_{\text{Int}} = \sum_{\{n_\mu\},\{m_\mu\}} P(\{n_\mu\},\{m_\mu\}|N)|\{n_\mu\}\rangle\langle\{m_\mu\}|, \tag{H.1}$$

where $\{n_\mu\}$ and $\{m_\mu\}$ are the distribution of particles in each state. Here, $n_\mu(m_\mu)$ is the occupation number of particles in μ ket(bra)-state, and

$$\hat{n}_{\mathbf{k}}|\{n_\mu\}\rangle = \hat{a}^{\dagger}_{\mathbf{k}}\hat{a}_{\mathbf{k}}|\{n_\mu\}\rangle = n_\mu|\{n_\mu\}\rangle, \tag{H.2}$$

$$\langle\{m_\mu\}|\hat{m}_{\mathbf{k}} = \langle\{m_\mu\}|\hat{a}^{\dagger}_{\mathbf{k}}\hat{a}_{\mathbf{k}} = m_\mu\langle\{m_\mu\}|. \tag{H.3}$$

The condition for the finite total number of particles is

$$\sum_\mu n_\mu = \sum_\mu m_\mu = N. \tag{H.4}$$

Following the second quantization notation, we can rewrite the ket state with creation operator $a^{\dagger}_{\mathbf{k}}$.

$$|\{n_\mu\}\rangle = \prod_\mu \left(\frac{1}{\sqrt{n_\mu!}}(\hat{a}^{\dagger}_\mu)^{n_\mu}\right)|0\rangle. \tag{H.5}$$

When we replace the a-operator in terms of $\hat{\beta}_{\mathbf{k}}$ and $\hat{\beta}^{\dagger}_{\mathbf{k}}$,

$$\hat{a}_\mu = \hat{\beta}_0\hat{\beta}_\mu \qquad \text{with} \quad \hat{\beta}_0 = (1+\hat{n}_0)^{-1/2}a_0, \tag{H.6}$$

$$\hat{a}^{\dagger}_\mu = \hat{\beta}^{\dagger}_\mu\hat{\beta}^{\dagger}_0 \qquad \text{with} \quad \hat{\beta}^{\dagger}_0 = a^{\dagger}_0(1+\hat{n}_0)^{-1/2}, \tag{H.7}$$

the ground state should be considered separately.

$$|\{n_\mu\}\rangle = \prod_{\mu\neq 0}\left\{\frac{1}{\sqrt{n_\mu!}}\left(\hat{\beta}^\dagger_\mu \hat{a}^\dagger_0\big(\hat{a}^\dagger_0\hat{a}_0+1\big)^{-1/2}\right)^{n_\mu}\right\}|n_0,\{0\}_{\text{exc}}\rangle, \tag{H.8}$$

where $\{0\}_{\text{exc}}$ is all the excited states. Because $\hat{a}^\dagger_0\big(\hat{a}^\dagger_0\hat{a}_0+1\big)^{-1/2}$ operator with $\hat{\beta}^\dagger_\mu$ creates one more particle in the ground state,

$$\hat{a}^\dagger_0\big(\hat{a}^\dagger_0\hat{a}_0+1\big)^{-1/2}\big|n_0=n\big\rangle = \hat{a}^\dagger_0\frac{1}{\sqrt{n+1}}\big|n_0=n\big\rangle = \big|n_0=n+1\big\rangle, \tag{H.9}$$

the form of the ket-state becomes

$$|\{n_\mu\}\rangle = \big|n_0=N,\{\mathbf{n}_\mu\}\big\rangle. \tag{H.10}$$

where

$$\hat{\mathbf{n}}_\mu\big|\mathbf{n}_\mu\big\rangle = \hat{\beta}^\dagger_\mu\hat{\beta}_\mu\big|\mathbf{n}_\mu\big\rangle = \mathbf{n}_\mu\big|\mathbf{n}_\mu\big\rangle \tag{H.11}$$

for the excited state, and

$$\sum_{\mu\neq 0}\mathbf{n}_\mu = M. \tag{H.12}$$

By separating the ground state and rewriting the ket-state in terms of $\hat{\beta}^\dagger_\mu$ operator,

$$\begin{aligned} |\{n_\mu\}\rangle &= \prod_{\mu\neq 0}\left\{\frac{1}{\sqrt{n_\mu!}}\left(\hat{\beta}^\dagger_\mu\right)^{n_\mu}\right\}\big|n_0=N,\{0\}_{\text{exc}}\big\rangle & \text{(H.13)}\\ &= \prod_{\mu\neq 0}\left\{\frac{1}{\sqrt{n_\mu!}}\left(u_{\mathbf{k}}\hat{b}^\dagger_{\mathbf{k}}+v_{\mathbf{k}}\hat{b}_{-\mathbf{k}}\right)^{n_\mu}\right\}\big|n_0=N,\{0\}_{\text{exc}}\big\rangle. & \text{(H.14)}\end{aligned}$$

Eq. (H.14) is the ket-state which is represented in Fock space $\mathcal{F}_b$ which is spanned by $\hat{n}_{\mathbf{k}} = \hat{b}^\dagger_{\mathbf{k}}b_{\mathbf{k}}$ state. Here, the maximum number of quasi-particles which are created in the configuration is same to total number of particles in excited state, even though the states with less number of quasi-particles are created. For each state in $\mathcal{F}_a$, the corresponding state in $\mathcal{F}_b$ will have that the maximum number of quasi-particle is $N - n_0(N - m_0)$ for ket(bra)-state.

Since the approximate Hamiltonian in $b_{\mathbf{k}}$ and $b^\dagger_{\mathbf{k}}$ basis is in diagonal form, that is similar to the non-interacting boson, all excited state in $\mathcal{F}_b$ is statistically independent. And the possible configuration in the density operator in this basis should be diagonal in equilibrium : the ket-state and the corresponding bra-state should be dual to each other. Finally, we can write the density operator as

$$\rho_{\text{Int}} = \sum_{M=0}^{N} P(n_0 = N - M|N) \sum_{\{n_\mu\}_b} P(\{n_\mu\}_b|M)|\{n_\mu\}_b\rangle\langle\{n_\mu\}_b|. \qquad \text{(H.15)}$$

Eq. (H.15) is the density operator in terms of the number of condensate particle n_0 and the occupation number $\{n_\mu\}_b$ of Bogoliubov transformed $b_{\mathbf{k}}$ and $b^\dagger_{\mathbf{k}}$ operator. Here, n_μ is the number of Bogoliubov transformed quasi-particle in μ-state, and its sum $\sum_{\mu\neq 0} n_\mu$ should be M to make sure that the total number of quasi-particle is $M = N - n_0$.

APPENDIX I

SUMMATION OF PARTIAL PARTITION FUNCTION

This appendix is about the proof of the Eq. (5.39).

The total configurations seem to be divided into distinguishable set of configurations according to the proper parameter, for example, the occupation number of one-state. However, the division of the partition function in CE for boson is not trivial.

Let's assume that ν-state with energy ϵ_ν is in-accessible. Since we can divide the total configuration as the occupation number in that state, we might write down the partition function as sum of partial partition function.

$$Z_N(\beta) = \sum_{n=0}^{N} e^{-(N-n)\beta\epsilon_\nu} Z_n^*(\beta) \tag{I.1}$$

where Z_N is the partition function for the whole states with N particles and Z_n^* is the partial partition function with the states except ν-state.

Since the definition for $Z_n^*(\beta)$ is

$$Z_n^* = \sum_{n_1=0}^{\infty}\sum_{n_2=0}^{\infty}\cdots\sum_{n_{\nu-1}=0}^{\infty}\sum_{n_{\nu+1}=0}^{\infty}\cdots\ \exp\Big\{-\beta\sum_{\{\mu\neq\nu\}}\epsilon_\mu n_\mu\Big\}\,\delta\Big(n-\sum_{\{\mu\neq\nu\}}n_\mu\Big), \tag{I.2}$$

the recursive relation for $Z_N(\beta)$ is also applicable to $Z_n^*(\beta)$:

$$Z_n^*(\beta) = \frac{1}{n}\sum_{k=1}^{n} Z_1^*(k\beta) Z_{n-k}^*(\beta). \tag{I.3}$$

Now, let's prove the relation between $Z_N(\beta)$ and $Z_n^*(\beta)$ explicitly with the mathematical induction. For the system with a single particle,

$$Z_1(\beta) = \sum_{\{\mu \neq \nu\}} e^{-\beta\epsilon_\mu}, \tag{I.4}$$

$$Z_1^*(\beta) = \sum_{\{\mu \neq \nu\}} e^{-\beta\epsilon_\mu} = Z_1(\beta) - e^{-\beta\epsilon_\nu}. \tag{I.5}$$

To simplify the proof, let's choose ν-state as ground state with $\epsilon_0 = 0$. Then, for the single particle case,

$$Z_1(\beta) = 1 + Z_1^*(\beta). \tag{I.6}$$

For two-particle case,

$$\begin{aligned} Z_2(\beta) &= \frac{1}{2}\big(Z_1(\beta)Z_1(\beta) + Z_1(2\beta)Z_0(\beta)\big) = \frac{1}{2}\Big\{\big(1 + Z_1^*(\beta)\big)^2 + \big(1 + Z_1^*(2\beta)\big)\Big\} \\ &= \frac{1}{2}\Big\{2 + 2Z_1^*(\beta) + \big(Z_1^*(\beta)\big)^2 + Z_1^*(2\beta)\Big\} \\ &= 1 + Z_1^*(\beta) + \frac{1}{2}\Big\{\big(Z_1^*(\beta)\big)^2 + Z_1^*(2\beta)\Big\} \\ &= 1 + Z_1^*(\beta) + Z_2^*(\beta). \end{aligned} \tag{I.7}$$

If we assume that

$$Z_N(\beta) = \sum_{n=0}^{N} Z_n^*(\beta), \tag{I.8}$$

then

$$
\begin{aligned}
&Z_{N+1}(\beta)\\
&= \frac{1}{N+1}\sum_{n=1}^{N+1} Z_1(n\beta)Z_{N+1-n}(\beta) = \frac{1}{N+1}\sum_{n=1}^{N+1}\left\{1+Z_1^*(n\beta)\right\} Z_{N+1-n}(\beta)\\
&= \frac{1}{N+1}\\
&\times \left[\begin{array}{rrllllll}
\{1 & +Z_1^*(\beta)\} & \{Z_N^*(\beta) & +Z_{N-1}^*(\beta) & +\cdots & +Z_3^*(\beta) & +Z_2^*(\beta) & \\
 & & & & & & +Z_1^*(\beta) & +1\} \\
+\{1 & +Z_1^*(2\beta)\} & \left\{Z_{N-1}^*(\beta)\right. & +Z_{N-2}^*(\beta) & +\cdots & +Z_2^*(\beta) & +Z_1^*(\beta) & +1\} \\
+\{1 & +Z_1^*(3\beta)\} & \left\{Z_{N-2}^*(\beta)\right. & +Z_{N-3}^*(\beta) & +\cdots & +Z_1^*(\beta) & +1\} & \\
 & & \cdots & & & & & \\
+\{1 & +Z_1^*((N-1)\beta)\} & \{Z_2^*(\beta) & +Z_1^*(\beta) & +1\} & & & \\
+\{1 & +Z_1^*(N\beta)\} & \{Z_1^*(\beta) & +1\} & & & & \\
+\{1 & +Z_1^*((N+1)\beta)\} & & & & & &
\end{array} \right]
\end{aligned}
$$

$$
= \frac{1}{N+1}\sum_{k=0}^{N}(N+1-k)Z_k^*(\beta) + \frac{1}{N+1}\sum_{k=1}^{N+1} kZ_k^*(\beta) \tag{I.9}
$$

$$
= \sum_{k=0}^{N+1} Z_k^*(\beta). \qquad\qquad (Q.E.D.) \tag{I.10}
$$

The first term 1 in $Z_1(n\beta) = 1 + Z_1^*(n\beta)$ gives the first term in Eq. (I.9), and the second term $Z_1^*(n\beta)$ gives the second term in Eq. (I.9).

APPENDIX J

STATISTICS IN INTERACTING BOSE GAS

Average

The occupation number in quasi-particle basis is

$$\begin{aligned}
\langle\hat\beta^\dagger_{\mathbf{k}}\hat\beta_{\mathbf{k}}\rangle &= \Big\langle(u_{\mathbf{k}}\hat b^\dagger_{\mathbf{k}}+v_{\mathbf{k}}\hat b_{-\mathbf{k}})(u_{\mathbf{k}}\hat b_{\mathbf{k}}+v_{\mathbf{k}}\hat b^\dagger_{-\mathbf{k}})\Big\rangle\\
&= u^2_{\mathbf{k}}\Big\langle\hat b^\dagger_{\mathbf{k}}\hat b_{\mathbf{k}}\Big\rangle + u_{\mathbf{k}}v_{\mathbf{k}}\Big\langle\hat b^\dagger_{\mathbf{k}}\hat b^\dagger_{-\mathbf{k}}\Big\rangle + v_{\mathbf{k}}u_{\mathbf{k}}\Big\langle\hat b_{-\mathbf{k}}\hat b_{\mathbf{k}}\Big\rangle + v^2_{\mathbf{k}}\Big\langle\hat b_{-\mathbf{k}}\hat b^\dagger_{-\mathbf{k}}\Big\rangle\\
&= u^2_{\mathbf{k}}\mathrm{Tr}\big(\rho_{\mathrm{Int}}\hat b^\dagger_{\mathbf{k}}\hat b_{\mathbf{k}}\big) + u_{\mathbf{k}}v_{\mathbf{k}}\mathrm{Tr}\big(\rho_{\mathrm{Int}}\hat b^\dagger_{\mathbf{k}}\hat b^\dagger_{-\mathbf{k}}\big) + v_{\mathbf{k}}u_{\mathbf{k}}\mathrm{Tr}\big(\rho_{\mathrm{Int}}\hat b_{-\mathbf{k}}\hat b_{\mathbf{k}}\big) + v^2_{\mathbf{k}}\mathrm{Tr}\big(\rho_{\mathrm{Int}}\hat b_{-\mathbf{k}}\hat b^\dagger_{-\mathbf{k}}\big)\\
&= u^2_{\mathbf{k}}\mathrm{Tr}\big(\rho_{\mathrm{Int}}\hat b^\dagger_{\mathbf{k}}\hat b_{\mathbf{k}}\big) + v^2_{\mathbf{k}}\mathrm{Tr}\big(\rho_{\mathrm{Int}}\hat b_{-\mathbf{k}}\hat b^\dagger_{-\mathbf{k}}\big)\\
&= u^2_{\mathbf{k}}\sum_{M=0}^{N}P(n_0=N-M|N)\sum_{n=0}^{M}P(n_{\mathbf{k}}=n|M)\big\langle n_{\mathbf{k}}=n|\hat b^\dagger_{\mathbf{k}}\hat b_{\mathbf{k}}|n_{\mathbf{k}}=n\big\rangle\\
&\quad + v^2_{\mathbf{k}}\sum_{M=0}^{N}P(n_0=N-M|N)\sum_{n=0}^{M}P(n_{-\mathbf{k}}=n|M)\big\langle n_{-\mathbf{k}}=n|\hat b_{-\mathbf{k}}\hat b^\dagger_{-\mathbf{k}}|n_{-\mathbf{k}}=n\big\rangle\\
&= \sum_{M=0}^{N}P(n_0=N-M|N)\sum_{n=0}^{M}P(n_{\mathbf{k}}=n\mid M)\Big(nu^2_{\mathbf{k}}+(n+1)v^2_{\mathbf{k}}\Big)\\
&= (u^2_{\mathbf{k}}+v^2_{\mathbf{k}})\overline{n}_{\mathbf{k}}+v^2_{\mathbf{k}} \qquad (J.1)
\end{aligned}$$

with

$$\overline{n}_{\mathbf{k}} = \sum_{M=0}^{N}P(n_0=N-M|N)\sum_{n=0}^{M}nP(n_{\mathbf{k}}=n\mid M). \qquad (J.2)$$

Here, we used $P(n_{-\mathbf{k}}=n|M)=P(n_{\mathbf{k}}=n|M)$.

Similar to the case of ideal gas, we can simplify Eq. (J.2).

$$
\begin{aligned}
\overline{n}_{\mathbf{k}} &= \sum_{M=0}^{N} P(n_0 = N-M|N) \sum_{n=0}^{M} nP(n_{\mathbf{k}} = n \mid M) \\
&= \sum_{M=0}^{N} \frac{Z_M - Z_{M-1}}{Z_N} \sum_{n=0}^{M} n \left(e^{-n\beta\epsilon_\mu} \frac{Z^*_{M-n}}{Z^*_M} - e^{-(n+1)\beta\epsilon_\mu} \frac{Z^*_{M-n-1}}{Z^*_M} \right) \\
&= \sum_{M=0}^{N} \frac{Z^*_M}{Z_N} \sum_{n=1}^{M} e^{-n\beta\epsilon_\mu} \frac{Z^*_{M-n}}{Z^*_M} \\
&= \sum_{n=1}^{N} \sum_{M=n}^{N} e^{-n\beta\epsilon_\mu} \frac{Z^*_{M-n}}{Z_N} \\
&= \sum_{n=1}^{N} e^{-n\beta\epsilon_\mu} \frac{Z_{N-n}}{Z_N}.
\end{aligned} \tag{J.3}
$$

The final form seems to be same in ideal case.

Variance

After applying the Bogoliubov transformation, the average for the 4-operator is

$$
\begin{aligned}
\left\langle \hat{\beta}^\dagger_{\mathbf{k}} \hat{\beta}_{\mathbf{k}} \hat{\beta}^\dagger_{\mathbf{k}'} \hat{\beta}_{\mathbf{k}'} \right\rangle =& \left\langle (u_{\mathbf{k}} \hat{b}^\dagger_{\mathbf{k}} + v_{\mathbf{k}} \hat{b}_{-\mathbf{k}})(u_{\mathbf{k}} \hat{b}_{\mathbf{k}} + v_{\mathbf{k}} \hat{b}^\dagger_{-\mathbf{k}})(u_{\mathbf{k}'} \hat{b}^\dagger_{\mathbf{k}'} + v_{\mathbf{k}'} \hat{b}_{-\mathbf{k}'})(u_{\mathbf{k}'} \hat{b}_{\mathbf{k}'} + v_{\mathbf{k}'} \hat{b}^\dagger_{-\mathbf{k}'}) \right\rangle \\
=& \quad u^2_{\mathbf{k}} u^2_{\mathbf{k}'} \left\langle \hat{b}^\dagger_{\mathbf{k}} \hat{b}_{\mathbf{k}} \hat{b}^\dagger_{\mathbf{k}'} \hat{b}_{\mathbf{k}'} \right\rangle + u^2_{\mathbf{k}} u_{\mathbf{k}'} v_{\mathbf{k}'} \left\langle \hat{b}^\dagger_{\mathbf{k}} \hat{b}_{\mathbf{k}} \hat{b}^\dagger_{\mathbf{k}'} \hat{b}^\dagger_{-\mathbf{k}'} \right\rangle \\
& + u^2_{\mathbf{k}} v_{\mathbf{k}'} u_{\mathbf{k}'} \left\langle \hat{b}^\dagger_{\mathbf{k}} \hat{b}_{\mathbf{k}} \hat{b}_{-\mathbf{k}'} \hat{b}_{\mathbf{k}'} \right\rangle + u^2_{\mathbf{k}} v^2_{\mathbf{k}'} \left\langle \hat{b}^\dagger_{\mathbf{k}} \hat{b}_{\mathbf{k}} \hat{b}_{-\mathbf{k}'} \hat{b}^\dagger_{-\mathbf{k}'} \right\rangle \\
& + u_{\mathbf{k}} v_{\mathbf{k}} u^2_{\mathbf{k}'} \left\langle \hat{b}^\dagger_{\mathbf{k}} \hat{b}^\dagger_{-\mathbf{k}} \hat{b}^\dagger_{\mathbf{k}'} \hat{b}_{\mathbf{k}'} \right\rangle + u_{\mathbf{k}} v_{\mathbf{k}} u_{\mathbf{k}'} v_{\mathbf{k}'} \left\langle \hat{b}^\dagger_{\mathbf{k}} \hat{b}^\dagger_{-\mathbf{k}} \hat{b}^\dagger_{\mathbf{k}'} \hat{b}^\dagger_{-\mathbf{k}'} \right\rangle \\
& + u_{\mathbf{k}} v_{\mathbf{k}} v_{\mathbf{k}'} u_{\mathbf{k}'} \left\langle \hat{b}^\dagger_{\mathbf{k}} \hat{b}^\dagger_{-\mathbf{k}} \hat{b}_{-\mathbf{k}'} \hat{b}_{\mathbf{k}'} \right\rangle + u_{\mathbf{k}} v_{\mathbf{k}} v^2_{\mathbf{k}'} \left\langle \hat{b}^\dagger_{\mathbf{k}} \hat{b}^\dagger_{-\mathbf{k}} \hat{b}_{-\mathbf{k}'} \hat{b}^\dagger_{-\mathbf{k}'} \right\rangle \\
& + v_{\mathbf{k}} u_{\mathbf{k}} u^2_{\mathbf{k}'} \left\langle \hat{b}_{-\mathbf{k}} \hat{b}_{\mathbf{k}} \hat{b}^\dagger_{\mathbf{k}'} \hat{b}_{\mathbf{k}'} \right\rangle + v_{\mathbf{k}} u_{\mathbf{k}} u_{\mathbf{k}'} v_{\mathbf{k}'} \left\langle \hat{b}_{-\mathbf{k}} \hat{b}_{\mathbf{k}} \hat{b}^\dagger_{\mathbf{k}'} \hat{b}^\dagger_{-\mathbf{k}'} \right\rangle \\
& + v_{\mathbf{k}} u_{\mathbf{k}} v_{\mathbf{k}'} u_{\mathbf{k}'} \left\langle \hat{b}_{-\mathbf{k}} \hat{b}_{\mathbf{k}} \hat{b}_{-\mathbf{k}'} \hat{b}_{\mathbf{k}'} \right\rangle + v_{\mathbf{k}} u_{\mathbf{k}} v^2_{\mathbf{k}'} \left\langle \hat{b}_{-\mathbf{k}} \hat{b}_{\mathbf{k}} \hat{b}_{-\mathbf{k}'} \hat{b}^\dagger_{-\mathbf{k}'} \right\rangle \\
& + v^2_{\mathbf{k}} u^2_{\mathbf{k}'} \left\langle \hat{b}_{-\mathbf{k}} \hat{b}^\dagger_{-\mathbf{k}} \hat{b}^\dagger_{\mathbf{k}'} \hat{b}_{\mathbf{k}'} \right\rangle + v^2_{\mathbf{k}} u_{\mathbf{k}'} v_{\mathbf{k}'} \left\langle \hat{b}_{-\mathbf{k}} \hat{b}^\dagger_{-\mathbf{k}} \hat{b}^\dagger_{\mathbf{k}'} \hat{b}^\dagger_{-\mathbf{k}'} \right\rangle \\
& + v^2_{\mathbf{k}} v_{\mathbf{k}'} u_{\mathbf{k}'} \left\langle \hat{b}_{-\mathbf{k}} \hat{b}^\dagger_{-\mathbf{k}} \hat{b}_{-\mathbf{k}'} \hat{b}_{\mathbf{k}'} \right\rangle + v^2_{\mathbf{k}} v^2_{\mathbf{k}'} \left\langle \hat{b}_{-\mathbf{k}} \hat{b}^\dagger_{-\mathbf{k}} \hat{b}_{-\mathbf{k}'} \hat{b}^\dagger_{-\mathbf{k}'} \right\rangle .
\end{aligned} \tag{J.4}
$$

When the number of the creation operators is equal to that of the annihilation ones, the average of the 4-operators are contributed to the variance. The terms which have equal number of operators are

$$\begin{aligned}\left\langle \hat{\beta}^{\dagger}_{\mathbf{k}}\hat{\beta}_{\mathbf{k}}\hat{\beta}^{\dagger}_{\mathbf{k}'}\hat{\beta}_{\mathbf{k}'} \right\rangle = \quad & u_{\mathbf{k}}^2 u_{\mathbf{k}'}^2 \left\langle \hat{b}^{\dagger}_{\mathbf{k}}\hat{b}_{\mathbf{k}}\hat{b}^{\dagger}_{\mathbf{k}'}\hat{b}_{\mathbf{k}'} \right\rangle + u_{\mathbf{k}}^2 v_{\mathbf{k}'}^2 \left\langle \hat{b}^{\dagger}_{\mathbf{k}}\hat{b}_{\mathbf{k}}\hat{b}_{-\mathbf{k}'}\hat{b}^{\dagger}_{-\mathbf{k}'} \right\rangle \\ & + u_{\mathbf{k}} v_{\mathbf{k}} v_{\mathbf{k}'} u_{\mathbf{k}'} \left\langle \hat{b}^{\dagger}_{\mathbf{k}}\hat{b}^{\dagger}_{-\mathbf{k}}\hat{b}_{-\mathbf{k}'}\hat{b}_{\mathbf{k}'} \right\rangle + v_{\mathbf{k}} u_{\mathbf{k}} u_{\mathbf{k}'} v_{\mathbf{k}'} \left\langle \hat{b}_{-\mathbf{k}}\hat{b}_{\mathbf{k}}\hat{b}^{\dagger}_{\mathbf{k}'}\hat{b}^{\dagger}_{-\mathbf{k}'} \right\rangle \\ & + v_{\mathbf{k}}^2 u_{\mathbf{k}'}^2 \left\langle \hat{b}_{-\mathbf{k}}\hat{b}^{\dagger}_{-\mathbf{k}}\hat{b}^{\dagger}_{\mathbf{k}'}\hat{b}_{\mathbf{k}'} \right\rangle + v_{\mathbf{k}}^2 v_{\mathbf{k}'}^2 \left\langle \hat{b}_{-\mathbf{k}}\hat{b}^{\dagger}_{-\mathbf{k}}\hat{b}_{-\mathbf{k}'}\hat{b}^{\dagger}_{-\mathbf{k}'} \right\rangle . \qquad \text{(J.5)}\end{aligned}$$

To evaluate each term explicitly, we need the 2-state probability $P(n_\mu, n_\nu|M)$ with $\mu(\nu) = \pm\mathbf{k}, \pm\mathbf{k}'$. For simplicity, let's use the following convention for the occupation number of particles in each state.

$$l = n_{\mathbf{k}}, \quad m = n_{-\mathbf{k}}, \quad p = n_{\mathbf{k}'}, \quad \text{and} \quad q = n_{-\mathbf{k}'}. \qquad \text{(J.6)}$$

Then, the corresponding 1-state and 2-state probabilities are

$$\begin{aligned} P(l|M) &= P(n_{\mathbf{k}} = l|M), \\ P(m|M) &= P(n_{-\mathbf{k}} = m|M), \\ P(l,m|M) &= P(n_{\mathbf{k}} = l, n_{-\mathbf{k}} = m|M), \qquad \text{(J.7)} \\ P(l,p|M) &= P(n_{\mathbf{k}} = l, n_{\mathbf{k}'} = p|M), \\ &\vdots \end{aligned}$$

Since the total number in excited state is M, the summation for the 2-state is restricted. For example, the ranges are restricted to $l + m \leq M$ in $P(l, m|M)$.

Let's evaluate the expectation value explicitly. When $\mathbf{k}' = \mathbf{k}$,

$$\begin{aligned}
&\left\langle \hat{\beta}^{\dagger}_{\mathbf{k}}\hat{\beta}_{\mathbf{k}}\hat{\beta}^{\dagger}_{\mathbf{k}}\hat{\beta}_{\mathbf{k}} \right\rangle \\
= \;& u_{\mathbf{k}}^4 \left\langle \hat{b}^{\dagger}_{\mathbf{k}}\hat{b}_{\mathbf{k}}\hat{b}^{\dagger}_{\mathbf{k}}\hat{b}_{\mathbf{k}} \right\rangle + u_{\mathbf{k}}^2 v_{\mathbf{k}}^2 \left\langle \hat{b}^{\dagger}_{\mathbf{k}}\hat{b}_{\mathbf{k}}\hat{b}_{-\mathbf{k}}\hat{b}^{\dagger}_{-\mathbf{k}} \right\rangle \\
&+ u_{\mathbf{k}}^2 v_{\mathbf{k}}^2 \left\langle \hat{b}^{\dagger}_{\mathbf{k}}\hat{b}^{\dagger}_{-\mathbf{k}}\hat{b}_{-\mathbf{k}}\hat{b}_{\mathbf{k}} \right\rangle + v_{\mathbf{k}}^2 u_{\mathbf{k}}^2 \left\langle \hat{b}_{-\mathbf{k}}\hat{b}_{\mathbf{k}}\hat{b}^{\dagger}_{\mathbf{k}}\hat{b}^{\dagger}_{-\mathbf{k}} \right\rangle \\
&+ v_{\mathbf{k}}^2 u_{\mathbf{k}}^2 \left\langle \hat{b}_{-\mathbf{k}}\hat{b}^{\dagger}_{-\mathbf{k}}\hat{b}^{\dagger}_{\mathbf{k}}\hat{b}_{\mathbf{k}} \right\rangle + v_{\mathbf{k}}^4 \left\langle \hat{b}_{-\mathbf{k}}\hat{b}^{\dagger}_{-\mathbf{k}}\hat{b}_{-\mathbf{k}}\hat{b}^{\dagger}_{-\mathbf{k}} \right\rangle \\
= \;& u_{\mathbf{k}}^4 \sum_{M=0}^{N} P_M \sum_{l=0}^{M} l^2 P(l|M) + u_{\mathbf{k}}^2 v_{\mathbf{k}}^2 \sum_{M=0}^{N} P_M \sum_{l=0}^{M}\sum_{m=0}^{M-l} l(m+1)P(l,m|M) \\
&+ u_{\mathbf{k}}^2 v_{\mathbf{k}}^2 \sum_{M=0}^{N} P_M \sum_{l=0}^{M}\sum_{m=0}^{M-l} lmP(l,m|M) + v_{\mathbf{k}}^2 u_{\mathbf{k}}^2 \sum_{M=0}^{N} P_M \sum_{l=0}^{M}\sum_{m=0}^{M-l} (l+1)(m+1)P(l,m|M) \\
&+ v_{\mathbf{k}}^2 u_{\mathbf{k}}^2 \sum_{M=0}^{N} P_M \sum_{l=0}^{M}\sum_{m=0}^{M-l} l(m+1)P(l,m|M) + v_{\mathbf{k}}^4 \sum_{M=0}^{N} P_M \sum_{m=0}^{M} (m+1)^2 P(m|M).
\end{aligned} \tag{J.8}$$

The average value from the 2-state probability also can be simplified.

$$\begin{aligned}
\overline{lm} &= \sum_{M=0}^{N} P_M \sum_{l=0}^{M}\sum_{m=0}^{M-l} lmP(l,m|M) = \sum_{M=0}^{N} \frac{Z_M^*}{Z_N} \sum_{l=1}^{M-1}\sum_{m=1}^{M-l} P(n_\mu \geq l, n_\nu \geq m|M) \\
&= \sum_{M=0}^{N} \frac{Z_M^*}{Z_N} \sum_{l=1}^{M-1}\sum_{m=1}^{M-l} e^{-l\beta\epsilon_\mu - m\beta\epsilon_\nu} \frac{Z_{M-l-m}^*}{Z_M^*} = \sum_{l=1}^{N-1}\sum_{M=l+1}^{N}\sum_{m=1}^{M-l} e^{-l\beta\epsilon_\mu - m\beta\epsilon_\nu} \frac{Z_{M-l-m}^*}{Z_N} \\
&= \sum_{l=1}^{N-1}\sum_{m=1}^{N-l}\sum_{M=l+m}^{N} e^{-l\beta\epsilon_\mu - m\beta\epsilon_\nu} \frac{Z_{M-l-m}^*}{Z_N} \\
&= \sum_{l=1}^{N-1}\sum_{m=1}^{N-l} e^{-l\beta\epsilon_\mu - m\beta\epsilon_\nu} \frac{Z_{N-l-m}}{Z_N}.
\end{aligned} \tag{J.9}$$

Similar to 1-state probability, the final form is also same to that in ideal Bose gas.

When $\mathbf{k}' = -\mathbf{k}$,

$$\begin{aligned}
&\left\langle \hat\beta_{\mathbf{k}}^\dagger \hat\beta_{\mathbf{k}} \hat\beta_{-\mathbf{k}}^\dagger \hat\beta_{-\mathbf{k}} \right\rangle \\
= \quad & u_{\mathbf{k}}^2 u_{\mathbf{k}'}^2 \left\langle \hat b_{\mathbf{k}}^\dagger \hat b_{\mathbf{k}} \hat b_{-\mathbf{k}}^\dagger \hat b_{-\mathbf{k}} \right\rangle + u_{\mathbf{k}}^2 v_{\mathbf{k}'}^2 \left\langle \hat b_{\mathbf{k}}^\dagger \hat b_{\mathbf{k}} \hat b_{\mathbf{k}} \hat b_{\mathbf{k}}^\dagger \right\rangle \\
& + u_{\mathbf{k}} v_{\mathbf{k}} v_{\mathbf{k}'} u_{\mathbf{k}'} \left\langle \hat b_{\mathbf{k}}^\dagger \hat b_{-\mathbf{k}}^\dagger \hat b_{\mathbf{k}} \hat b_{-\mathbf{k}} \right\rangle + v_{\mathbf{k}} u_{\mathbf{k}} u_{\mathbf{k}'} v_{\mathbf{k}'} \left\langle \hat b_{-\mathbf{k}} \hat b_{\mathbf{k}} \hat b_{-\mathbf{k}}^\dagger \hat b_{\mathbf{k}}^\dagger \right\rangle \\
& + v_{\mathbf{k}}^2 u_{\mathbf{k}'}^2 \left\langle \hat b_{-\mathbf{k}} \hat b_{-\mathbf{k}}^\dagger \hat b_{-\mathbf{k}}^\dagger \hat b_{-\mathbf{k}} \right\rangle + v_{\mathbf{k}}^2 v_{\mathbf{k}'}^2 \left\langle \hat b_{-\mathbf{k}} \hat b_{-\mathbf{k}}^\dagger \hat b_{\mathbf{k}} \hat b_{\mathbf{k}}^\dagger \right\rangle \\
= \quad & u_{\mathbf{k}}^4 \sum_{M=0}^{N} P_M \sum_{l=0}^{M} \sum_{m=0}^{M-l} lmP(l,m|M) + u_{\mathbf{k}}^2 v_{\mathbf{k}}^2 \sum_{M=0}^{N} P_M \sum_{l=0}^{M} l(l+1)P(l|M) \\
& + u_{\mathbf{k}}^2 v_{\mathbf{k}}^2 \sum_{M=0}^{N} P_M \sum_{l=0}^{M} \sum_{m=0}^{M-l} lmP(l,m|M) + v_{\mathbf{k}}^2 u_{\mathbf{k}}^2 \sum_{M=0}^{N} P_M \sum_{l=0}^{M} \sum_{m=0}^{M-l} (l+1)(m+1)P(l,m|M) \\
& + v_{\mathbf{k}}^2 u_{\mathbf{k}}^2 \sum_{M=0}^{N} P_M \sum_{m=0}^{M} m(m+1)P(m|M) + v_{\mathbf{k}}^4 \sum_{M=0}^{N} P_M \sum_{l=0}^{M} \sum_{m=0}^{M-l} (l+1)(m+1)P(l,m|M).
\end{aligned} \tag{J.10}$$

Otherwise, that is $\mathbf{k}' \neq \pm\mathbf{k}$,

$$\begin{aligned}
&\left\langle \hat\beta_{\mathbf{k}}^\dagger \hat\beta_{\mathbf{k}} \hat\beta_{\mathbf{k}'}^\dagger \hat\beta_{\mathbf{k}'} \right\rangle \\
= \quad & u_{\mathbf{k}}^2 u_{\mathbf{k}'}^2 \left\langle \hat b_{\mathbf{k}}^\dagger \hat b_{\mathbf{k}} \hat b_{\mathbf{k}'}^\dagger \hat b_{\mathbf{k}'} \right\rangle + u_{\mathbf{k}}^2 v_{\mathbf{k}'}^2 \left\langle \hat b_{\mathbf{k}}^\dagger \hat b_{\mathbf{k}} \hat b_{-\mathbf{k}'} \hat b_{-\mathbf{k}'}^\dagger \right\rangle \\
& + v_{\mathbf{k}}^2 u_{\mathbf{k}'}^2 \left\langle \hat b_{-\mathbf{k}} \hat b_{-\mathbf{k}}^\dagger \hat b_{\mathbf{k}'}^\dagger \hat b_{\mathbf{k}'} \right\rangle + v_{\mathbf{k}}^2 v_{\mathbf{k}'}^2 \left\langle \hat b_{-\mathbf{k}} \hat b_{-\mathbf{k}}^\dagger \hat b_{-\mathbf{k}'} \hat b_{-\mathbf{k}'}^\dagger \right\rangle \\
= \quad & u_{\mathbf{k}}^2 u_{\mathbf{k}'}^2 \sum_{M=0}^{N} P_M \sum_{l=0}^{M} \sum_{p=0}^{M-l} lpP(l,p|M) + u_{\mathbf{k}}^2 v_{\mathbf{k}'}^2 \sum_{M=0}^{N} P_M \sum_{l=0}^{M} \sum_{q=0}^{M-l} l(q+1)P(l,q|M) \\
& + v_{\mathbf{k}}^2 u_{\mathbf{k}'}^2 \sum_{M=0}^{N} P_M \sum_{m=0}^{M} \sum_{p=0}^{M-m} (m+1)pP(l,p|M) \\
& + v_{\mathbf{k}}^2 v_{\mathbf{k}'}^2 \sum_{M=0}^{N} P_M \sum_{m=0}^{M} \sum_{q=0}^{M-m} (m+1)(q+1)P(m,q|M).
\end{aligned} \tag{J.11}$$

Third Moment

For the 3rd moment, we need the expectation value for the 6-operator.

$$\begin{aligned}
&\left\langle \hat{\beta}^\dagger_{\mathbf{k}} \hat{\beta}_{\mathbf{k}} \hat{\beta}^\dagger_{\mathbf{k}'} \hat{\beta}_{\mathbf{k}'} \hat{\beta}^\dagger_{\mathbf{k}''} \hat{\beta}_{\mathbf{k}''} \right\rangle \\
=&\Big\langle (u_{\mathbf{k}} \hat{b}^\dagger_{\mathbf{k}} + v_{\mathbf{k}} \hat{b}_{-\mathbf{k}})(u_{\mathbf{k}} \hat{b}_{\mathbf{k}} + v_{\mathbf{k}} \hat{b}^\dagger_{-\mathbf{k}})(u_{\mathbf{k}'} \hat{b}^\dagger_{\mathbf{k}'} + v_{\mathbf{k}'} \hat{b}_{-\mathbf{k}'})(u_{\mathbf{k}'} \hat{b}_{\mathbf{k}'} + v_{\mathbf{k}'} \hat{b}^\dagger_{-\mathbf{k}'}) \\
&(u_{\mathbf{k}''} \hat{b}^\dagger_{\mathbf{k}''} + v_{\mathbf{k}''} \hat{b}_{-\mathbf{k}''})(u_{\mathbf{k}''} \hat{b}_{\mathbf{k}''} + v_{\mathbf{k}''} \hat{b}^\dagger_{-\mathbf{k}''}) \Big\rangle . \qquad \text{(J.12)}
\end{aligned}$$

The terms which have equal number of creation operators and of annihilation operators can only be contributed to the 3rd moment. So, the remaining terms are

$$\begin{aligned}
&\left\langle \hat{\beta}^\dagger_{\mathbf{k}} \hat{\beta}_{\mathbf{k}} \hat{\beta}^\dagger_{\mathbf{k}'} \hat{\beta}_{\mathbf{k}'} \hat{\beta}^\dagger_{\mathbf{k}''} \hat{\beta}_{\mathbf{k}''} \right\rangle \\
=\;& u^2_{\mathbf{k}} u^2_{\mathbf{k}'} u^2_{\mathbf{k}''} \left\langle \hat{b}^\dagger_{\mathbf{k}} \hat{b}_{\mathbf{k}} \hat{b}^\dagger_{\mathbf{k}'} \hat{b}_{\mathbf{k}'} \hat{b}^\dagger_{\mathbf{k}''} \hat{b}_{\mathbf{k}''} \right\rangle + u^2_{\mathbf{k}} u^2_{\mathbf{k}'} v^2_{\mathbf{k}''} \left\langle \hat{b}^\dagger_{\mathbf{k}} \hat{b}_{\mathbf{k}} \hat{b}^\dagger_{\mathbf{k}'} \hat{b}_{\mathbf{k}'} \hat{b}_{-\mathbf{k}''} \hat{b}^\dagger_{-\mathbf{k}''} \right\rangle \\
&+ u^2_{\mathbf{k}} u_{\mathbf{k}'} v_{\mathbf{k}'} v_{\mathbf{k}''} u_{\mathbf{k}''} \left\langle \hat{b}^\dagger_{\mathbf{k}} \hat{b}_{\mathbf{k}} \hat{b}^\dagger_{\mathbf{k}'} \hat{b}^\dagger_{-\mathbf{k}'} \hat{b}_{-\mathbf{k}''} \hat{b}_{\mathbf{k}''} \right\rangle + u^2_{\mathbf{k}} v_{\mathbf{k}'} u_{\mathbf{k}'} u_{\mathbf{k}''} v_{\mathbf{k}''} \left\langle \hat{b}^\dagger_{\mathbf{k}} \hat{b}_{\mathbf{k}} \hat{b}_{-\mathbf{k}'} \hat{b}_{\mathbf{k}'} \hat{b}^\dagger_{\mathbf{k}''} \hat{b}^\dagger_{-\mathbf{k}''} \right\rangle \\
&+ u^2_{\mathbf{k}} v^2_{\mathbf{k}'} u^2_{\mathbf{k}''} \left\langle \hat{b}^\dagger_{\mathbf{k}} \hat{b}_{\mathbf{k}} \hat{b}_{-\mathbf{k}'} \hat{b}^\dagger_{-\mathbf{k}'} \hat{b}^\dagger_{\mathbf{k}''} \hat{b}_{\mathbf{k}''} \right\rangle + u^2_{\mathbf{k}} v^2_{\mathbf{k}'} v^2_{\mathbf{k}''} \left\langle \hat{b}^\dagger_{\mathbf{k}} \hat{b}_{\mathbf{k}} \hat{b}_{-\mathbf{k}'} \hat{b}^\dagger_{-\mathbf{k}'} \hat{b}_{-\mathbf{k}''} \hat{b}^\dagger_{-\mathbf{k}''} \right\rangle \\
&+ u_{\mathbf{k}} v_{\mathbf{k}} u^2_{\mathbf{k}'} v_{\mathbf{k}''} u_{\mathbf{k}''} \left\langle \hat{b}^\dagger_{\mathbf{k}} \hat{b}^\dagger_{-\mathbf{k}} \hat{b}^\dagger_{\mathbf{k}'} \hat{b}_{\mathbf{k}'} \hat{b}_{-\mathbf{k}''} \hat{b}_{\mathbf{k}''} \right\rangle + u_{\mathbf{k}} v_{\mathbf{k}} v_{\mathbf{k}'} u_{\mathbf{k}'} u^2_{\mathbf{k}''} \left\langle \hat{b}^\dagger_{\mathbf{k}} \hat{b}^\dagger_{-\mathbf{k}} \hat{b}_{-\mathbf{k}'} \hat{b}_{\mathbf{k}'} \hat{b}^\dagger_{\mathbf{k}''} \hat{b}_{\mathbf{k}''} \right\rangle \\
&+ u_{\mathbf{k}} v_{\mathbf{k}} v_{\mathbf{k}'} u_{\mathbf{k}'} v^2_{\mathbf{k}''} \left\langle \hat{b}^\dagger_{\mathbf{k}} \hat{b}^\dagger_{-\mathbf{k}} \hat{b}_{-\mathbf{k}'} \hat{b}_{\mathbf{k}'} \hat{b}_{-\mathbf{k}''} \hat{b}^\dagger_{-\mathbf{k}''} \right\rangle + u_{\mathbf{k}} v_{\mathbf{k}} v^2_{\mathbf{k}'} v_{\mathbf{k}''} u_{\mathbf{k}''} \left\langle \hat{b}^\dagger_{\mathbf{k}} \hat{b}^\dagger_{-\mathbf{k}} \hat{b}_{-\mathbf{k}'} \hat{b}^\dagger_{-\mathbf{k}'} \hat{b}_{-\mathbf{k}''} \hat{b}_{\mathbf{k}''} \right\rangle \\
&+ v_{\mathbf{k}} u_{\mathbf{k}} u^2_{\mathbf{k}'} u_{\mathbf{k}''} v_{\mathbf{k}''} \left\langle \hat{b}_{-\mathbf{k}} \hat{b}_{\mathbf{k}} \hat{b}^\dagger_{\mathbf{k}'} \hat{b}_{\mathbf{k}'} \hat{b}^\dagger_{\mathbf{k}''} \hat{b}^\dagger_{-\mathbf{k}''} \right\rangle + v_{\mathbf{k}} u_{\mathbf{k}} u_{\mathbf{k}'} v_{\mathbf{k}'} u^2_{\mathbf{k}''} \left\langle \hat{b}_{-\mathbf{k}} \hat{b}_{\mathbf{k}} \hat{b}^\dagger_{\mathbf{k}'} \hat{b}^\dagger_{-\mathbf{k}'} \hat{b}^\dagger_{\mathbf{k}''} \hat{b}_{\mathbf{k}''} \right\rangle \\
&+ v_{\mathbf{k}} u_{\mathbf{k}} u_{\mathbf{k}'} v_{\mathbf{k}'} v^2_{\mathbf{k}''} \left\langle \hat{b}_{-\mathbf{k}} \hat{b}_{\mathbf{k}} \hat{b}^\dagger_{\mathbf{k}'} \hat{b}^\dagger_{-\mathbf{k}'} \hat{b}_{-\mathbf{k}''} \hat{b}^\dagger_{-\mathbf{k}''} \right\rangle + v_{\mathbf{k}} u_{\mathbf{k}} v^2_{\mathbf{k}'} u_{\mathbf{k}''} v_{\mathbf{k}''} \left\langle \hat{b}_{-\mathbf{k}} \hat{b}_{\mathbf{k}} \hat{b}_{-\mathbf{k}'} \hat{b}^\dagger_{-\mathbf{k}'} \hat{b}^\dagger_{\mathbf{k}''} \hat{b}^\dagger_{-\mathbf{k}''} \right\rangle \\
&+ v^2_{\mathbf{k}} u^2_{\mathbf{k}'} u^2_{\mathbf{k}''} \left\langle \hat{b}_{-\mathbf{k}} \hat{b}^\dagger_{-\mathbf{k}} \hat{b}^\dagger_{\mathbf{k}'} \hat{b}_{\mathbf{k}'} \hat{b}^\dagger_{\mathbf{k}''} \hat{b}_{\mathbf{k}''} \right\rangle + v^2_{\mathbf{k}} u^2_{\mathbf{k}'} v^2_{\mathbf{k}''} \left\langle \hat{b}_{-\mathbf{k}} \hat{b}^\dagger_{-\mathbf{k}} \hat{b}^\dagger_{\mathbf{k}'} \hat{b}_{\mathbf{k}'} \hat{b}_{-\mathbf{k}''} \hat{b}^\dagger_{-\mathbf{k}''} \right\rangle \\
&+ v^2_{\mathbf{k}} u_{\mathbf{k}'} v_{\mathbf{k}'} v_{\mathbf{k}''} u_{\mathbf{k}''} \left\langle \hat{b}_{-\mathbf{k}} \hat{b}^\dagger_{-\mathbf{k}} \hat{b}^\dagger_{\mathbf{k}'} \hat{b}^\dagger_{-\mathbf{k}'} \hat{b}_{-\mathbf{k}''} \hat{b}_{\mathbf{k}''} \right\rangle + v^2_{\mathbf{k}} v_{\mathbf{k}'} u_{\mathbf{k}'} u_{\mathbf{k}''} v_{\mathbf{k}''} \left\langle \hat{b}_{-\mathbf{k}} \hat{b}^\dagger_{-\mathbf{k}} \hat{b}_{-\mathbf{k}'} \hat{b}_{\mathbf{k}'} \hat{b}^\dagger_{\mathbf{k}''} \hat{b}^\dagger_{-\mathbf{k}''} \right\rangle \\
&+ v^2_{\mathbf{k}} v^2_{\mathbf{k}'} u^2_{\mathbf{k}''} \left\langle \hat{b}_{-\mathbf{k}} \hat{b}^\dagger_{-\mathbf{k}} \hat{b}_{-\mathbf{k}'} \hat{b}^\dagger_{-\mathbf{k}'} \hat{b}^\dagger_{\mathbf{k}''} \hat{b}_{\mathbf{k}''} \right\rangle + v^2_{\mathbf{k}} v^2_{\mathbf{k}'} v^2_{\mathbf{k}''} \left\langle \hat{b}_{-\mathbf{k}} \hat{b}^\dagger_{-\mathbf{k}} \hat{b}_{-\mathbf{k}'} \hat{b}^\dagger_{-\mathbf{k}'} \hat{b}_{-\mathbf{k}''} \hat{b}^\dagger_{-\mathbf{k}''} \right\rangle . \quad \text{(J.13)}
\end{aligned}$$

In 3rd moment calculation, there're 11 different types of terms, which are shown in Table. VI.

For simplicity, let's use the following conventions.

$$n_{\mathbf{k}} = l, n_{-\mathbf{k}} = m, n_{\mathbf{k}'} = p, n_{-\mathbf{k}'} = q, n_{\mathbf{k}''} = r, n_{-\mathbf{k}''} = s. \tag{J.14}$$

Here, we will use an over-line to denote the proper average.

$$\overline{lp} = \sum_{M=0}^{N} \frac{Z_M^*}{Z_N} \sum_{l=0}^{N} \sum_{p=0}^{N} lpP(n_{\mathbf{k}} = l, n_{\mathbf{k}'} = p \mid M). \tag{J.15}$$

Case 1. non-degenerate case where $\mathbf{k} \neq \pm\mathbf{k}' \neq \pm\mathbf{k}''$

$$\begin{aligned}
&\left\langle \hat{\beta}^\dagger_{\mathbf{k}} \hat{\beta}_{\mathbf{k}} \hat{\beta}^\dagger_{\mathbf{k}'} \hat{\beta}_{\mathbf{k}'} \hat{\beta}^\dagger_{\mathbf{k}''} \hat{\beta}_{\mathbf{k}''} \right\rangle \\
= \quad & u_{\mathbf{k}}^2 u_{\mathbf{k}'}^2 u_{\mathbf{k}''}^2 \overline{lpr} + u_{\mathbf{k}}^2 u_{\mathbf{k}'}^2 v_{\mathbf{k}''}^2 \overline{lp(s+1)} \\
& + u_{\mathbf{k}}^2 v_{\mathbf{k}'}^2 u_{\mathbf{k}''}^2 \overline{l(q+1)r} + u_{\mathbf{k}}^2 v_{\mathbf{k}'}^2 v_{\mathbf{k}''}^2 \overline{l(q+1)(s+1)} \\
& + v_{\mathbf{k}}^2 u_{\mathbf{k}'}^2 u_{\mathbf{k}''}^2 \overline{(m+1)pr} + v_{\mathbf{k}}^2 u_{\mathbf{k}'}^2 v_{\mathbf{k}''}^2 \overline{(m+1)p(s+1)} \\
& + v_{\mathbf{k}}^2 v_{\mathbf{k}'}^2 u_{\mathbf{k}''}^2 \overline{(m+1)(q+1)r} + v_{\mathbf{k}}^2 v_{\mathbf{k}'}^2 v_{\mathbf{k}''}^2 \overline{(m+1)(q+1)(s+1)}.
\end{aligned} \tag{J.16}$$

Case 2. $\mathbf{k} = \mathbf{k}' \neq \pm\mathbf{k}''$

$$\begin{aligned}
&\left\langle \hat{\beta}^\dagger_{\mathbf{k}} \hat{\beta}_{\mathbf{k}} \hat{\beta}^\dagger_{\mathbf{k}} \hat{\beta}_{\mathbf{k}} \hat{\beta}^\dagger_{\mathbf{k}''} \hat{\beta}_{\mathbf{k}''} \right\rangle \\
= \quad & u_{\mathbf{k}}^2 u_{\mathbf{k}'}^2 u_{\mathbf{k}''}^2 \overline{l^2 r} + u_{\mathbf{k}}^2 u_{\mathbf{k}'}^2 v_{\mathbf{k}''}^2 \overline{l^2(s+1)} \\
& + u_{\mathbf{k}}^2 v_{\mathbf{k}'}^2 u_{\mathbf{k}''}^2 \overline{l(m+1)r} + u_{\mathbf{k}}^2 v_{\mathbf{k}'}^2 v_{\mathbf{k}''}^2 \overline{l(m+1)(s+1)} \\
& + u_{\mathbf{k}} v_{\mathbf{k}} v_{\mathbf{k}'} u_{\mathbf{k}'} u_{\mathbf{k}''}^2 \overline{lmr} \\
& + u_{\mathbf{k}} v_{\mathbf{k}} v_{\mathbf{k}'} u_{\mathbf{k}'} v_{\mathbf{k}''}^2 \overline{lm(s+1)} \\
& + v_{\mathbf{k}} u_{\mathbf{k}} u_{\mathbf{k}'} v_{\mathbf{k}'} u_{\mathbf{k}''}^2 \overline{(l+1)(m+1)r} \\
& + v_{\mathbf{k}} u_{\mathbf{k}} u_{\mathbf{k}'} v_{\mathbf{k}'} v_{\mathbf{k}''}^2 \overline{(l+1)(m+1)(s+1)} \\
& + v_{\mathbf{k}}^2 u_{\mathbf{k}'}^2 u_{\mathbf{k}''}^2 \overline{l(m+1)r} + v_{\mathbf{k}}^2 u_{\mathbf{k}'}^2 v_{\mathbf{k}''}^2 \overline{l(m+1)(s+1)} \\
& + v_{\mathbf{k}}^2 v_{\mathbf{k}'}^2 u_{\mathbf{k}''}^2 \overline{(m+1)^2 r} + v_{\mathbf{k}}^2 v_{\mathbf{k}'}^2 v_{\mathbf{k}''}^2 \overline{(m+1)^2(s+1)}.
\end{aligned} \tag{J.17}$$

Case 3. $\mathbf{k} = -\mathbf{k}' \neq \pm\mathbf{k}''$

$$
\begin{aligned}
&\left\langle \hat{\beta}^{\dagger}_{\mathbf{k}} \hat{\beta}_{\mathbf{k}} \hat{\beta}^{\dagger}_{-\mathbf{k}} \hat{\beta}_{-\mathbf{k}} \hat{\beta}^{\dagger}_{\mathbf{k}''} \hat{\beta}_{\mathbf{k}''} \right\rangle \\
= \quad & u^2_{\mathbf{k}} u^2_{\mathbf{k}'} u^2_{\mathbf{k}''} \overline{lmr} + u^2_{\mathbf{k}} u^2_{\mathbf{k}'} v^2_{\mathbf{k}''} \overline{lm(s+1)} \\
& + u^2_{\mathbf{k}} v^2_{\mathbf{k}'} u^2_{\mathbf{k}''} \overline{l(l+1)r} + u^2_{\mathbf{k}} v^2_{\mathbf{k}'} v^2_{\mathbf{k}''} \overline{l(l+1)(s+1)} \\
& + u_{\mathbf{k}} v_{\mathbf{k}} v_{\mathbf{k}'} u_{\mathbf{k}'} u^2_{\mathbf{k}''} \overline{lmr} \\
& + u_{\mathbf{k}} v_{\mathbf{k}} v_{\mathbf{k}'} u_{\mathbf{k}'} v^2_{\mathbf{k}''} \overline{lm(s+1)} \\
& + v_{\mathbf{k}} u_{\mathbf{k}} u_{\mathbf{k}'} v_{\mathbf{k}'} u^2_{\mathbf{k}''} \overline{(l+1)(m+1)r} \\
& + v_{\mathbf{k}} u_{\mathbf{k}} u_{\mathbf{k}'} v_{\mathbf{k}'} v^2_{\mathbf{k}''} \overline{(l+1)(m+1)(s+1)} \\
& + v^2_{\mathbf{k}} u^2_{\mathbf{k}'} u^2_{\mathbf{k}''} \overline{m(m+1)r} + v^2_{\mathbf{k}} u^2_{\mathbf{k}'} v^2_{\mathbf{k}''} \overline{m(m+1)(s+1)} \\
& + v^2_{\mathbf{k}} v^2_{\mathbf{k}'} u^2_{\mathbf{k}''} \overline{(l+1)(m+1)r} + v^2_{\mathbf{k}} v^2_{\mathbf{k}'} v^2_{\mathbf{k}''} \overline{(l+1)(m+1)(s+1)}.
\end{aligned}
\tag{J.18}
$$

Case 4. $\mathbf{k} = \mathbf{k}'' \neq \pm\mathbf{k}'$

$$
\begin{aligned}
&\left\langle \hat{\beta}^{\dagger}_{\mathbf{k}} \hat{\beta}_{\mathbf{k}} \hat{\beta}^{\dagger}_{\mathbf{k}'} \hat{\beta}_{\mathbf{k}'} \hat{\beta}^{\dagger}_{\mathbf{k}} \hat{\beta}_{\mathbf{k}} \right\rangle \\
= \quad & u^2_{\mathbf{k}} u^2_{\mathbf{k}'} u^2_{\mathbf{k}''} \overline{l^2 p} + u^2_{\mathbf{k}} u^2_{\mathbf{k}'} v^2_{\mathbf{k}''} \overline{l(m+1)p} \\
& + u^2_{\mathbf{k}} v^2_{\mathbf{k}'} u^2_{\mathbf{k}''} \overline{l^2(q+1)} + u^2_{\mathbf{k}} v^2_{\mathbf{k}'} v^2_{\mathbf{k}''} \overline{l(m+1)(q+1)} \\
& + u_{\mathbf{k}} v_{\mathbf{k}} u^2_{\mathbf{k}'} v_{\mathbf{k}''} u_{\mathbf{k}''} \overline{lmp} \\
& + u_{\mathbf{k}} v_{\mathbf{k}} v^2_{\mathbf{k}'} v_{\mathbf{k}''} u_{\mathbf{k}''} \overline{lm(q+1)} \\
& + v_{\mathbf{k}} u_{\mathbf{k}} u^2_{\mathbf{k}'} u_{\mathbf{k}''} v_{\mathbf{k}''} \overline{(l+1)(m+1)p} \\
& + v_{\mathbf{k}} u_{\mathbf{k}} v^2_{\mathbf{k}'} u_{\mathbf{k}''} v_{\mathbf{k}''} \overline{(l+1)(m+1)(q+1)} \\
& + v^2_{\mathbf{k}} u^2_{\mathbf{k}'} u^2_{\mathbf{k}''} \overline{l(m+1)p} + v^2_{\mathbf{k}} u^2_{\mathbf{k}'} v^2_{\mathbf{k}''} \overline{(m+1)^2 p} \\
& + v^2_{\mathbf{k}} v^2_{\mathbf{k}'} u^2_{\mathbf{k}''} \overline{l(m+1)(q+1)} + v^2_{\mathbf{k}} v^2_{\mathbf{k}'} v^2_{\mathbf{k}''} \overline{(m+1)^2(q+1)}.
\end{aligned}
\tag{J.19}
$$

Case 5. $\mathbf{k} = -\mathbf{k}'' \neq \pm\mathbf{k}'$

$$\begin{aligned}
&\left\langle \hat{\beta}^{\dagger}_{\mathbf{k}}\hat{\beta}_{\mathbf{k}}\hat{\beta}^{\dagger}_{\mathbf{k}'}\hat{\beta}_{\mathbf{k}'}\hat{\beta}^{\dagger}_{-\mathbf{k}}\hat{\beta}_{-\mathbf{k}} \right\rangle \\
= \quad & u^2_{\mathbf{k}}u^2_{\mathbf{k}'}u^2_{\mathbf{k}''}\overline{lmp} + u^2_{\mathbf{k}}u^2_{\mathbf{k}'}v^2_{\mathbf{k}''}\overline{l(l+1)p} \\
&+ u^2_{\mathbf{k}}v^2_{\mathbf{k}'}u^2_{\mathbf{k}''}\overline{lm(q+1)} + u^2_{\mathbf{k}}v^2_{\mathbf{k}'}v^2_{\mathbf{k}''}\overline{l(l+1)(q+1)} \\
&+ u_{\mathbf{k}}v_{\mathbf{k}}u^2_{\mathbf{k}'}v_{\mathbf{k}''}u_{\mathbf{k}''}\overline{lmp} \\
&+ u_{\mathbf{k}}v_{\mathbf{k}}v^2_{\mathbf{k}'}v_{\mathbf{k}''}u_{\mathbf{k}''}\overline{lm(q+1)} \\
&+ v_{\mathbf{k}}u_{\mathbf{k}}u^2_{\mathbf{k}'}u_{\mathbf{k}''}v_{\mathbf{k}''}\overline{(l+1)(m+1)p} \\
&+ v_{\mathbf{k}}u_{\mathbf{k}}v^2_{\mathbf{k}'}u_{\mathbf{k}''}v_{\mathbf{k}''}\overline{(l+1)(m+1)(q+1)} \\
&+ v^2_{\mathbf{k}}u^2_{\mathbf{k}'}u^2_{\mathbf{k}''}\overline{m(m+1)p} + v^2_{\mathbf{k}}u^2_{\mathbf{k}'}v^2_{\mathbf{k}''}\overline{(l+1)(m+1)p} \\
&+ v^2_{\mathbf{k}}v^2_{\mathbf{k}'}u^2_{\mathbf{k}''}\overline{m(m+1)(q+1)} + v^2_{\mathbf{k}}v^2_{\mathbf{k}'}v^2_{\mathbf{k}''}\overline{(l+1)(m+1)(q+1)}. \qquad \text{(J.20)}
\end{aligned}$$

Case 6. $\mathbf{k} = \mathbf{k}' = \mathbf{k}''$

$$\begin{aligned}
&\left\langle \hat{\beta}^{\dagger}_{\mathbf{k}} \hat{\beta}_{\mathbf{k}} \hat{\beta}^{\dagger}_{\mathbf{k}'} \hat{\beta}_{\mathbf{k}'} \hat{\beta}^{\dagger}_{\mathbf{k}''} \hat{\beta}_{\mathbf{k}''} \right\rangle \\
= \quad & u_{\mathbf{k}}^6 \overline{l^3} + u_{\mathbf{k}}^4 v_{\mathbf{k}}^2 \overline{l^2(m+1)} \\
& + u_{\mathbf{k}}^2 u_{\mathbf{k}'} v_{\mathbf{k}'} v_{\mathbf{k}''} u_{\mathbf{k}''} \overline{l^2 m} + u_{\mathbf{k}}^2 v_{\mathbf{k}'} u_{\mathbf{k}'} u_{\mathbf{k}''} v_{\mathbf{k}''} \overline{l(l+1)(m+1)} \\
& + u_{\mathbf{k}}^2 v_{\mathbf{k}'}^2 u_{\mathbf{k}''}^2 \overline{l^2(m+1)} + u_{\mathbf{k}}^2 v_{\mathbf{k}'}^2 v_{\mathbf{k}''}^2 \overline{l(m+1)^2} \\
& + u_{\mathbf{k}} v_{\mathbf{k}} u_{\mathbf{k}'}^2 v_{\mathbf{k}''} u_{\mathbf{k}''} \overline{l(l-1)m} + u_{\mathbf{k}} v_{\mathbf{k}} v_{\mathbf{k}'} u_{\mathbf{k}'} u_{\mathbf{k}''}^2 \overline{l^2 m} \\
& + u_{\mathbf{k}} v_{\mathbf{k}} v_{\mathbf{k}'} u_{\mathbf{k}'} v_{\mathbf{k}''}^2 \overline{lm(m+1)} + u_{\mathbf{k}} v_{\mathbf{k}} v_{\mathbf{k}'}^2 v_{\mathbf{k}''} u_{\mathbf{k}''} \overline{lm^2} \\
& + v_{\mathbf{k}} u_{\mathbf{k}} u_{\mathbf{k}'}^2 u_{\mathbf{k}''} v_{\mathbf{k}''} \overline{(l+1)^2(m+1)} + v_{\mathbf{k}} u_{\mathbf{k}} u_{\mathbf{k}'} v_{\mathbf{k}'} u_{\mathbf{k}''}^2 \overline{l(l+1)(m+1)} \\
& + v_{\mathbf{k}} u_{\mathbf{k}} u_{\mathbf{k}'} v_{\mathbf{k}'} v_{\mathbf{k}''}^2 \overline{(l+1)(m+1)^2} + v_{\mathbf{k}} u_{\mathbf{k}} v_{\mathbf{k}'}^2 u_{\mathbf{k}''} v_{\mathbf{k}''} \overline{(l+1)(m+1)(m+2)} \\
& + v_{\mathbf{k}}^2 u_{\mathbf{k}'}^2 u_{\mathbf{k}''}^2 \overline{l^2(m+1)} + v_{\mathbf{k}}^2 u_{\mathbf{k}'}^2 v_{\mathbf{k}''}^2 \overline{l(m+1)^2} \\
& + v_{\mathbf{k}}^2 u_{\mathbf{k}'} v_{\mathbf{k}'} v_{\mathbf{k}''} u_{\mathbf{k}''} \overline{lm(m+1)} + v_{\mathbf{k}}^2 v_{\mathbf{k}'} u_{\mathbf{k}'} u_{\mathbf{k}''} v_{\mathbf{k}''} \overline{(l+1)(m+1)^2} \\
& + v_{\mathbf{k}}^2 v_{\mathbf{k}'}^2 u_{\mathbf{k}''}^2 \overline{l(m+1)^2} + v_{\mathbf{k}}^2 v_{\mathbf{k}'}^2 v_{\mathbf{k}''}^2 \overline{(m+1)^3}.
\end{aligned} \tag{J.21}$$

Case 7. $\mathbf{k} = \mathbf{k}' = -\mathbf{k}''$

$$\begin{aligned}
&\left\langle \hat{\beta}^{\dagger}_{\mathbf{k}} \hat{\beta}_{\mathbf{k}} \hat{\beta}^{\dagger}_{\mathbf{k}} \hat{\beta}_{\mathbf{k}} \hat{\beta}^{\dagger}_{-\mathbf{k}} \hat{\beta}_{-\mathbf{k}} \right\rangle \\
= \;& u_{\mathbf{k}}^2 u_{\mathbf{k}'}^2 u_{\mathbf{k}''}^2 \overline{l^2 m} + u_{\mathbf{k}}^2 u_{\mathbf{k}'}^2 v_{\mathbf{k}''}^2 \overline{l^2 (l+1)} \\
&+ u_{\mathbf{k}}^2 u_{\mathbf{k}'} v_{\mathbf{k}'} v_{\mathbf{k}''} u_{\mathbf{k}''} \overline{l^2 m} + u_{\mathbf{k}}^2 v_{\mathbf{k}'} u_{\mathbf{k}'} u_{\mathbf{k}''} v_{\mathbf{k}''} \overline{l(l+1)(m+1)} \\
&+ u_{\mathbf{k}}^2 v_{\mathbf{k}'}^2 u_{\mathbf{k}''}^2 \overline{l(m+1)m} + u_{\mathbf{k}}^2 v_{\mathbf{k}'}^2 v_{\mathbf{k}''}^2 \overline{l(m+1)(l+1)} \\
&+ u_{\mathbf{k}} v_{\mathbf{k}} u_{\mathbf{k}'}^2 v_{\mathbf{k}''} u_{\mathbf{k}''} \overline{l(l-1)m} + u_{\mathbf{k}} v_{\mathbf{k}} v_{\mathbf{k}'} u_{\mathbf{k}'} u_{\mathbf{k}''}^2 \overline{l m^2} \\
&+ u_{\mathbf{k}} v_{\mathbf{k}} v_{\mathbf{k}'} u_{\mathbf{k}'} v_{\mathbf{k}''}^2 \overline{l(l+1)m} + u_{\mathbf{k}} v_{\mathbf{k}} v_{\mathbf{k}'}^2 v_{\mathbf{k}''} u_{\mathbf{k}''} \overline{l m^2} \\
&+ v_{\mathbf{k}} u_{\mathbf{k}} u_{\mathbf{k}'}^2 u_{\mathbf{k}''} v_{\mathbf{k}''} \overline{(l+1)^2 (m+1)} + v_{\mathbf{k}} u_{\mathbf{k}} u_{\mathbf{k}'} v_{\mathbf{k}'} u_{\mathbf{k}''}^2 \overline{(l+1)m(m+1)} \\
&+ v_{\mathbf{k}} u_{\mathbf{k}} u_{\mathbf{k}'} v_{\mathbf{k}'} v_{\mathbf{k}''}^2 \overline{(l+1)^2 (m+1)} + v_{\mathbf{k}} u_{\mathbf{k}} v_{\mathbf{k}'}^2 u_{\mathbf{k}''} v_{\mathbf{k}''} \overline{(l+1)(m+1)(m+2)} \\
&+ v_{\mathbf{k}}^2 u_{\mathbf{k}'}^2 u_{\mathbf{k}''}^2 \overline{lm(m+1)} + v_{\mathbf{k}}^2 u_{\mathbf{k}'}^2 v_{\mathbf{k}''}^2 \overline{l(l+1)(m+1)} \\
&+ v_{\mathbf{k}}^2 u_{\mathbf{k}'} v_{\mathbf{k}'} v_{\mathbf{k}''} u_{\mathbf{k}''} \overline{lm(m+1)} + v_{\mathbf{k}}^2 v_{\mathbf{k}'} u_{\mathbf{k}'} u_{\mathbf{k}''} v_{\mathbf{k}''} \overline{(l+1)(m+1)^2} \\
&+ v_{\mathbf{k}}^2 v_{\mathbf{k}'}^2 u_{\mathbf{k}''}^2 \overline{(m+1)^2 m} + v_{\mathbf{k}}^2 v_{\mathbf{k}'}^2 v_{\mathbf{k}''}^2 \overline{(m+1)^2 (l+1)}. \qquad \text{(J.22)}
\end{aligned}$$

Case 8. $\mathbf{k} = -\mathbf{k}' = \mathbf{k}''$

$$\begin{aligned}
&\left\langle \hat{\beta}^{\dagger}_{\mathbf{k}}\hat{\beta}_{\mathbf{k}}\hat{\beta}^{\dagger}_{-\mathbf{k}}\hat{\beta}_{-\mathbf{k}}\hat{\beta}^{\dagger}_{\mathbf{k}}\hat{\beta}_{\mathbf{k}} \right\rangle \\
= \quad & u^2_{\mathbf{k}}u^2_{\mathbf{k}'}u^2_{\mathbf{k}''}\overline{l^2m} + u^2_{\mathbf{k}}u^2_{\mathbf{k}'}v^2_{\mathbf{k}''}\overline{lm(m+1)} \\
& + u^2_{\mathbf{k}}u_{\mathbf{k}'}v_{\mathbf{k}'}v_{\mathbf{k}''}u_{\mathbf{k}''}\overline{l^2m} + u^2_{\mathbf{k}}v_{\mathbf{k}'}u_{\mathbf{k}'}u_{\mathbf{k}''}v_{\mathbf{k}''}\overline{l(l+1)(m+1)} \\
& + u^2_{\mathbf{k}}v^2_{\mathbf{k}'}u^2_{\mathbf{k}''}\overline{l^2(l+1)} + u^2_{\mathbf{k}}v^2_{\mathbf{k}'}v^2_{\mathbf{k}''}\overline{l(l+1)(m+1)} \\
& + u_{\mathbf{k}}v_{\mathbf{k}}u^2_{\mathbf{k}'}v_{\mathbf{k}''}u_{\mathbf{k}''}\overline{lm(m-1)} + u_{\mathbf{k}}v_{\mathbf{k}}v_{\mathbf{k}'}u_{\mathbf{k}'}u^2_{\mathbf{k}''}\overline{l^2m} \\
& + u_{\mathbf{k}}v_{\mathbf{k}}v_{\mathbf{k}'}u_{\mathbf{k}'}v^2_{\mathbf{k}''}\overline{lm(m+1)} + u_{\mathbf{k}}v_{\mathbf{k}}v^2_{\mathbf{k}'}v_{\mathbf{k}''}u_{\mathbf{k}''}\overline{l^2m} \\
& + v_{\mathbf{k}}u_{\mathbf{k}}u^2_{\mathbf{k}'}u_{\mathbf{k}''}v_{\mathbf{k}''}\overline{(l+1)(m+1)^2} + v_{\mathbf{k}}u_{\mathbf{k}}u_{\mathbf{k}'}v_{\mathbf{k}'}u^2_{\mathbf{k}''}\overline{l(l+1)(m+1)} \\
& + v_{\mathbf{k}}u_{\mathbf{k}}u_{\mathbf{k}'}v_{\mathbf{k}'}v^2_{\mathbf{k}''}\overline{(l+1)(m+1)^2} + v_{\mathbf{k}}u_{\mathbf{k}}v^2_{\mathbf{k}'}u_{\mathbf{k}''}v_{\mathbf{k}''}\overline{(l+1)(l+2)(m+1)} \\
& + v^2_{\mathbf{k}}u^2_{\mathbf{k}'}u^2_{\mathbf{k}''}\overline{lm(m+1)} + v^2_{\mathbf{k}}u^2_{\mathbf{k}'}v^2_{\mathbf{k}''}\overline{m(m+1)^2} \\
& + v^2_{\mathbf{k}}u_{\mathbf{k}'}v_{\mathbf{k}'}v_{\mathbf{k}''}u_{\mathbf{k}''}\overline{lm(m+1)} + v^2_{\mathbf{k}}v_{\mathbf{k}'}u_{\mathbf{k}'}u_{\mathbf{k}''}v_{\mathbf{k}''}\overline{(l+1)(m+1)^2} \\
& + v^2_{\mathbf{k}}v^2_{\mathbf{k}'}u^2_{\mathbf{k}''}\overline{l(l+1)(m+1)} + v^2_{\mathbf{k}}v^2_{\mathbf{k}'}v^2_{\mathbf{k}''}\overline{(l+1)(m+1)^2}. \qquad \text{(J.23)}
\end{aligned}$$

Case 9. $\mathbf{k} = -\mathbf{k}' = -\mathbf{k}''$

$$
\begin{aligned}
&\left\langle \hat{\beta}^\dagger_{\mathbf{k}} \hat{\beta}_{\mathbf{k}} \hat{\beta}^\dagger_{-\mathbf{k}} \hat{\beta}_{-\mathbf{k}} \hat{\beta}^\dagger_{-\mathbf{k}} \hat{\beta}_{-\mathbf{k}} \right\rangle \\
= \quad & u_{\mathbf{k}}^2 u_{\mathbf{k}'}^2 u_{\mathbf{k}''}^2 \overline{lm^2} + u_{\mathbf{k}}^2 u_{\mathbf{k}'}^2 v_{\mathbf{k}''}^2 \overline{l(l+1)m} \\
& + u_{\mathbf{k}}^2 u_{\mathbf{k}'} v_{\mathbf{k}'} v_{\mathbf{k}''} u_{\mathbf{k}''} \overline{l^2 m} + u_{\mathbf{k}}^2 v_{\mathbf{k}'} u_{\mathbf{k}'} u_{\mathbf{k}''} v_{\mathbf{k}''} \overline{l(l+1)(m+1)} \\
& + u_{\mathbf{k}}^2 v_{\mathbf{k}'}^2 u_{\mathbf{k}''}^2 \overline{l(l+1)m} + u_{\mathbf{k}}^2 v_{\mathbf{k}'}^2 v_{\mathbf{k}''}^2 \overline{l(l+1)^2} \\
& + u_{\mathbf{k}} v_{\mathbf{k}} u_{\mathbf{k}'}^2 v_{\mathbf{k}''} u_{\mathbf{k}''} \overline{lm(m-1)} + u_{\mathbf{k}} v_{\mathbf{k}} v_{\mathbf{k}'} u_{\mathbf{k}'} u_{\mathbf{k}''}^2 \overline{lm^2} \\
& + u_{\mathbf{k}} v_{\mathbf{k}} v_{\mathbf{k}'} u_{\mathbf{k}'} v_{\mathbf{k}''}^2 \overline{l(l+1)m} + u_{\mathbf{k}} v_{\mathbf{k}} v_{\mathbf{k}'}^2 v_{\mathbf{k}''} u_{\mathbf{k}''} \overline{l^2 m} \\
& + v_{\mathbf{k}} u_{\mathbf{k}} u_{\mathbf{k}'}^2 u_{\mathbf{k}''} v_{\mathbf{k}''} \overline{(l+1)(m+1)^2} + v_{\mathbf{k}} u_{\mathbf{k}} u_{\mathbf{k}'} v_{\mathbf{k}'} u_{\mathbf{k}''}^2 \overline{(l+1)m(m+1)} \\
& + v_{\mathbf{k}} u_{\mathbf{k}} u_{\mathbf{k}'} v_{\mathbf{k}'} v_{\mathbf{k}''}^2 \overline{(l+1)^2(m+1)} + v_{\mathbf{k}} u_{\mathbf{k}} v_{\mathbf{k}'}^2 u_{\mathbf{k}''} v_{\mathbf{k}''} \overline{(l+1)(l+2)(m+1)} \\
& + v_{\mathbf{k}}^2 u_{\mathbf{k}'}^2 u_{\mathbf{k}''}^2 \overline{m^2(m+1)} + v_{\mathbf{k}}^2 u_{\mathbf{k}'}^2 v_{\mathbf{k}''}^2 \overline{(l+1)m(m+1)} \\
& + v_{\mathbf{k}}^2 u_{\mathbf{k}'} v_{\mathbf{k}'} v_{\mathbf{k}''} u_{\mathbf{k}''} \overline{lm(m+1)} + v_{\mathbf{k}}^2 v_{\mathbf{k}'} u_{\mathbf{k}'} u_{\mathbf{k}''} v_{\mathbf{k}''} \overline{(l+1)(m+1)^2} \\
& + v_{\mathbf{k}}^2 v_{\mathbf{k}'}^2 u_{\mathbf{k}''}^2 \overline{(l+1)m(m+1)} + v_{\mathbf{k}}^2 v_{\mathbf{k}'}^2 v_{\mathbf{k}''}^2 \overline{(l+1)^2(m+1)}. \qquad \text{(J.24)}
\end{aligned}
$$

Case 10. $\pm\mathbf{k} \neq \mathbf{k}' = \mathbf{k}''$

$$
\begin{aligned}
&\left\langle \hat{\beta}^\dagger_{\mathbf{k}} \hat{\beta}_{\mathbf{k}} \hat{\beta}^\dagger_{\mathbf{k}'} \hat{\beta}_{\mathbf{k}'} \hat{\beta}^\dagger_{\mathbf{k}'} \hat{\beta}_{\mathbf{k}'} \right\rangle \\
= \quad & u_{\mathbf{k}}^2 u_{\mathbf{k}'}^2 u_{\mathbf{k}''}^2 \overline{lp^2} + u_{\mathbf{k}}^2 u_{\mathbf{k}'}^2 v_{\mathbf{k}''}^2 \overline{lp(q+1)} \\
& + u_{\mathbf{k}}^2 u_{\mathbf{k}'} v_{\mathbf{k}'} v_{\mathbf{k}''} u_{\mathbf{k}''} \overline{lpq} + u_{\mathbf{k}}^2 v_{\mathbf{k}'} u_{\mathbf{k}'} u_{\mathbf{k}''} v_{\mathbf{k}''} \overline{l(p+1)(q+1)} \\
& + u_{\mathbf{k}}^2 v_{\mathbf{k}'}^2 u_{\mathbf{k}''}^2 \overline{lp(q+1)} + u_{\mathbf{k}}^2 v_{\mathbf{k}'}^2 v_{\mathbf{k}''}^2 \overline{l(q+1)^2} \\
& + v_{\mathbf{k}}^2 u_{\mathbf{k}'}^2 u_{\mathbf{k}''}^2 \overline{(m+1)p^2} + v_{\mathbf{k}}^2 u_{\mathbf{k}'}^2 v_{\mathbf{k}''}^2 \overline{(m+1)p(q+1)} \\
& + v_{\mathbf{k}}^2 u_{\mathbf{k}'} v_{\mathbf{k}'} v_{\mathbf{k}''} u_{\mathbf{k}''} \overline{(m+1)pq} + v_{\mathbf{k}}^2 v_{\mathbf{k}'} u_{\mathbf{k}'} u_{\mathbf{k}''} v_{\mathbf{k}''} \overline{(m+1)(p+1)(q+1)} \\
& + v_{\mathbf{k}}^2 v_{\mathbf{k}'}^2 u_{\mathbf{k}''}^2 \overline{(m+1)p(q+1)} + v_{\mathbf{k}}^2 v_{\mathbf{k}'}^2 v_{\mathbf{k}''}^2 \overline{(m+1)(q+1)^2}. \qquad \text{(J.25)}
\end{aligned}
$$

Case 11. $\pm\mathbf{k} \neq \mathbf{k}' = -\mathbf{k}''$

$$\begin{aligned}
&\left\langle \hat{\beta}^{\dagger}_{\mathbf{k}}\hat{\beta}_{\mathbf{k}}\hat{\beta}^{\dagger}_{\mathbf{k}'}\hat{\beta}_{\mathbf{k}'}\hat{\beta}^{\dagger}_{-\mathbf{k}'}\hat{\beta}_{-\mathbf{k}'} \right\rangle \\
= \;& u^2_{\mathbf{k}}u^2_{\mathbf{k}'}u^2_{\mathbf{k}''}\overline{lpq} + u^2_{\mathbf{k}}u^2_{\mathbf{k}'}v^2_{\mathbf{k}''}\overline{lp(p+1)} \\
&+ u^2_{\mathbf{k}}u_{\mathbf{k}'}v_{\mathbf{k}'}v_{\mathbf{k}''}u_{\mathbf{k}''}\overline{lpq} + u^2_{\mathbf{k}}v_{\mathbf{k}'}u_{\mathbf{k}'}u_{\mathbf{k}''}v_{\mathbf{k}''}\overline{l(p+1)(q+1)} \\
&+ u^2_{\mathbf{k}}v^2_{\mathbf{k}'}u^2_{\mathbf{k}''}\overline{lq(q+1)} + u^2_{\mathbf{k}}v^2_{\mathbf{k}'}v^2_{\mathbf{k}''}\overline{l(p+1)(q+1)} \\
&+ v^2_{\mathbf{k}}u^2_{\mathbf{k}'}u^2_{\mathbf{k}''}\overline{(m+1)pq} + v^2_{\mathbf{k}}u^2_{\mathbf{k}'}v^2_{\mathbf{k}''}\overline{(m+1)p(p+1)} \\
&+ v^2_{\mathbf{k}}u_{\mathbf{k}'}v_{\mathbf{k}'}v_{\mathbf{k}''}u_{\mathbf{k}''}\overline{(m+1)pq} + v^2_{\mathbf{k}}v_{\mathbf{k}'}u_{\mathbf{k}'}u_{\mathbf{k}''}v_{\mathbf{k}''}\overline{(m+1)(p+1)(q+1)} \\
&+ v^2_{\mathbf{k}}v^2_{\mathbf{k}'}u^2_{\mathbf{k}''}\overline{(m+1)(q+1)q} + v^2_{\mathbf{k}}v^2_{\mathbf{k}'}v^2_{\mathbf{k}''}\overline{(m+1)(q+1)(p+1)}. \qquad \text{(J.26)}
\end{aligned}$$

Table I. Processes in Carnot cycle with a single photon

	L	$V = LA$	T	$\Omega = \frac{\pi c}{L}$	$\bar{n}$	P
Stage	(mm)	(mm^3)	(K)	($\times 10^{11}$ Hz)		($\times 10^{-12}$ N/m^2 = Pa)
1	1	1	300	9.42	6.15	3.84
2	2	**2**	300	4.72	12.78	2.00
3	3	3	**200**	3.14	12.78	0.89
4	3/2	**3/2**	200	6.28	6.15	1.71

Table II. Table for the shell structure of the multi-electron atoms

notation for state	maximum number of electrons in the state	quantum number
1s	2	$n_i = 1$
2s	2	$n_i = 2$
2p	6	$n_i = 2$
3s	2	$n_i = 3$
3p	6	$n_i = 3$
4s	2	$n_i = 4$
3d	10	$n_i = 3$
4p	6	$n_i = 4$
5s	2	$n_i = 5$
4d	10	$n_i = 3$
	$\vdots$	

Table III. Table for the ground state energy of multi-electron atoms until $Z = 25$

Atomic Number	E(Experiment)	E(Bohr Model)
2(He)	-2.903	-3.06250
3(Li)	-7.478	-7.69046
4(Be)	-14.667	-14.84035
5(B)	-24.652	-24.79358
6(C)	-37.842	-37.81680
7(N)	-54.584	-54.16099
8(O)	-75.059	-74.17799
9(F)	-99.719	-98.05818
10(Ne)	-128.919	-126.05298
11(Na)	-162.233	-158.42380
12(Mg)	-200.026	-195.29550
13(Al)	-242.315	-236.53440
14(Si)	-289.322	-282.23095
15(P)	-341.208	-332.55240
16(S)	-398.601	-387.58611
17(Cl)	-460.102	-447.39648
18(Ar)	-527.494	-512.25169
19(K)	-599.924	-582.12325
20(Ca)	-677.558	-657.12386
21(Sc)	-760.575	-737.47984
22(Ti)	-849.285	-823.40219
23(V)	-943.804	-914.80980
24(Cr)	-1044.315	-1011.84586
25(Mn)	-1150.866	-1114.54139

Table IV. Table for the variational parameters in the wavefunction (The only variational parameter here is the nuclear charge Z^*, and all other parameters are calculated by solving the H_2^+ eigenvalue problem for a variationally best effective charge.)

Parameter	$\Psi^J(1,2)$	$\Psi^J(1,2)f(r_{12})$
Z^*	0.7786	0.9370
p	0.9152	1.0647
a_1	0.0072	0.0096
a_2	0.0004	0.0004
b_2	0.0955	0.1303
b_4	0.0014	0.0026
BE(eV)	3.44	4.60

Parameter	$\Psi^H(1,2)$	$\Psi^H(1,2)f(r_{12})$
Z^*	0.7806	0.9407
p	0.9171	1.0680
A_1	-0.0376	-0.0412
A_2	-0.0045	-0.0043
B_2	0.0959	0.1312
B_4	0.0014	0.0026
BE(eV)	3.46	4.62

Table V. Comparisons among different descriptions to the BEC problem

	Ideal Bose Gas	Weakly Interacting Bose Gas		
Kinds of Entity	Particle	Particle	Quasi-particle	Bogoliubov transformed
Operator	$\hat{a}_{\mathbf{k}}, \hat{a}_{\mathbf{k}}^{\dagger}$	$\hat{a}_{\mathbf{k}}, \hat{a}_{\mathbf{k}}^{\dagger}$	$\hat{\beta}_{\mathbf{k}}, \hat{\beta}_{\mathbf{k}}^{\dagger}$	$\hat{b}_{\mathbf{k}}, \hat{b}_{\mathbf{k}}^{\dagger}$
Diagonalized Hamiltonian	Yes	No		Yes
Diagonal form of Density Operator	Yes	No		Yes
Partition Function	Yes	No		Yes
Access to condensate state	Yes	Yes	No	No

Table VI. 11 different types of terms in the 3rd moment of evaluation

1	non-degenerate case where $\mathbf{k} \neq \pm\mathbf{k}' \neq \pm\mathbf{k}''$
2	$\mathbf{k} = \mathbf{k}' \neq \pm\mathbf{k}''$
3	$\mathbf{k} = -\mathbf{k}' \neq \pm\mathbf{k}''$
4	$\mathbf{k} = \mathbf{k}'' \neq \pm\mathbf{k}'$
5	$\mathbf{k} = -\mathbf{k}'' \neq \pm\mathbf{k}'$
6	$\mathbf{k} = \mathbf{k}' = \mathbf{k}''$
7	$\mathbf{k} = \mathbf{k}' = -\mathbf{k}''$
8	$\mathbf{k} = -\mathbf{k}' = \mathbf{k}''$
9	$\mathbf{k} = -\mathbf{k}' = -\mathbf{k}''$
10	$\pm\mathbf{k} \neq \mathbf{k}' = \mathbf{k}''$
11	$\pm\mathbf{k} \neq \mathbf{k}' = -\mathbf{k}''$

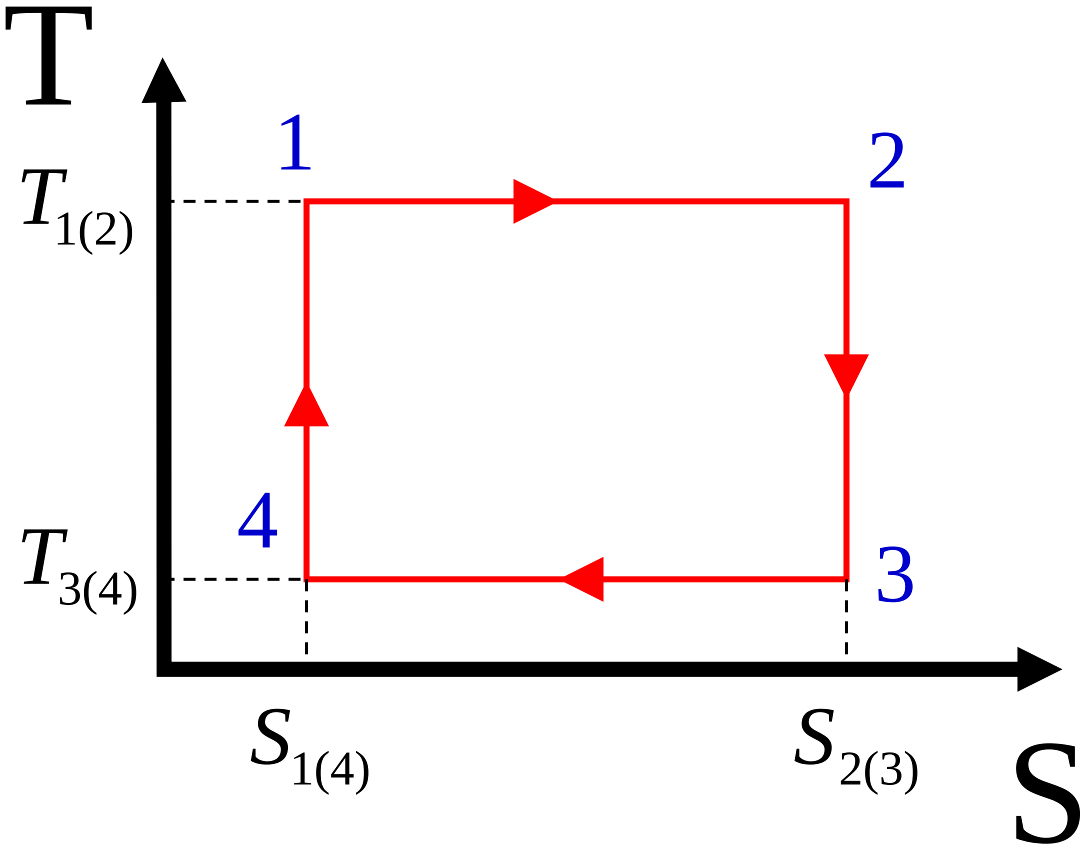

Fig. 1. Carnot cycle diagram in T-S plane : 1 → 2 and 3 → 4 are isothermal process with constant temperature. 2 → 3 and 4 → 1 are adiabatic process with constant entropy.

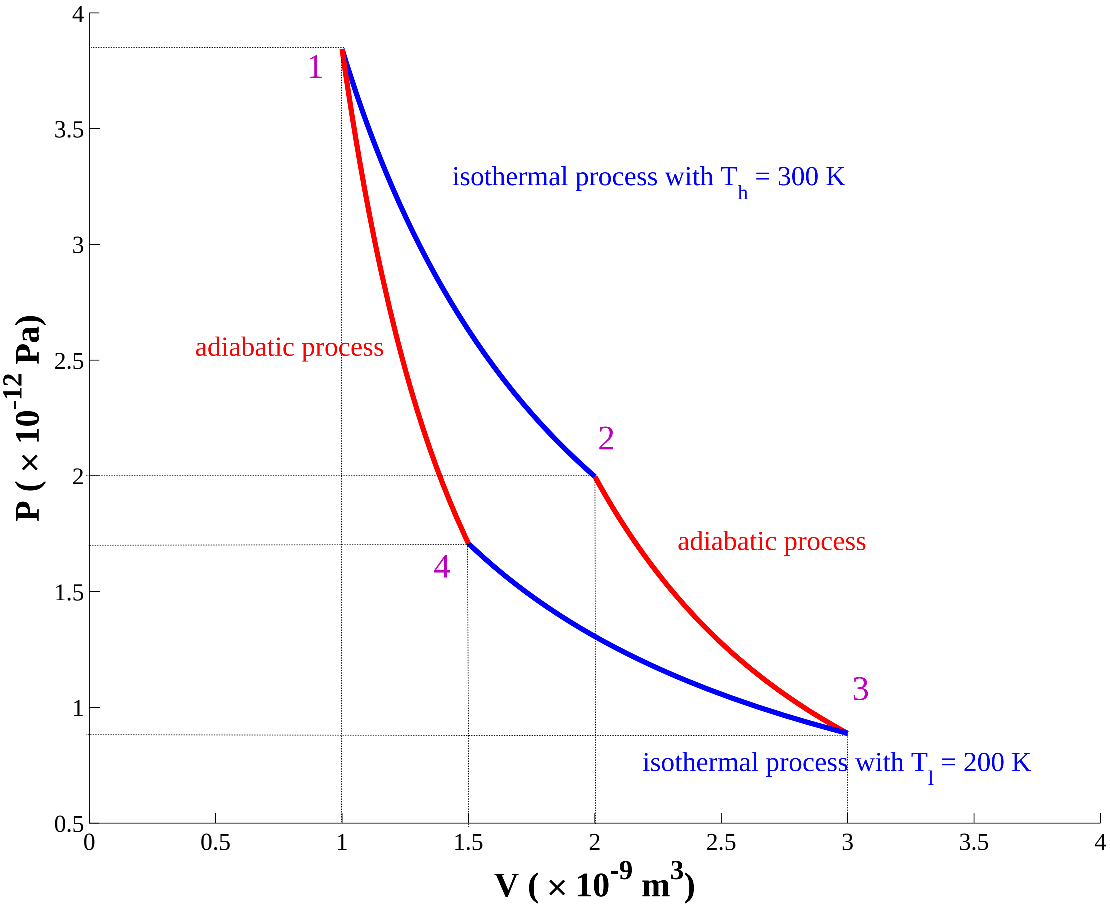

Fig. 2. Diagram in P-V plane for the Carnot cycle with single-photon.

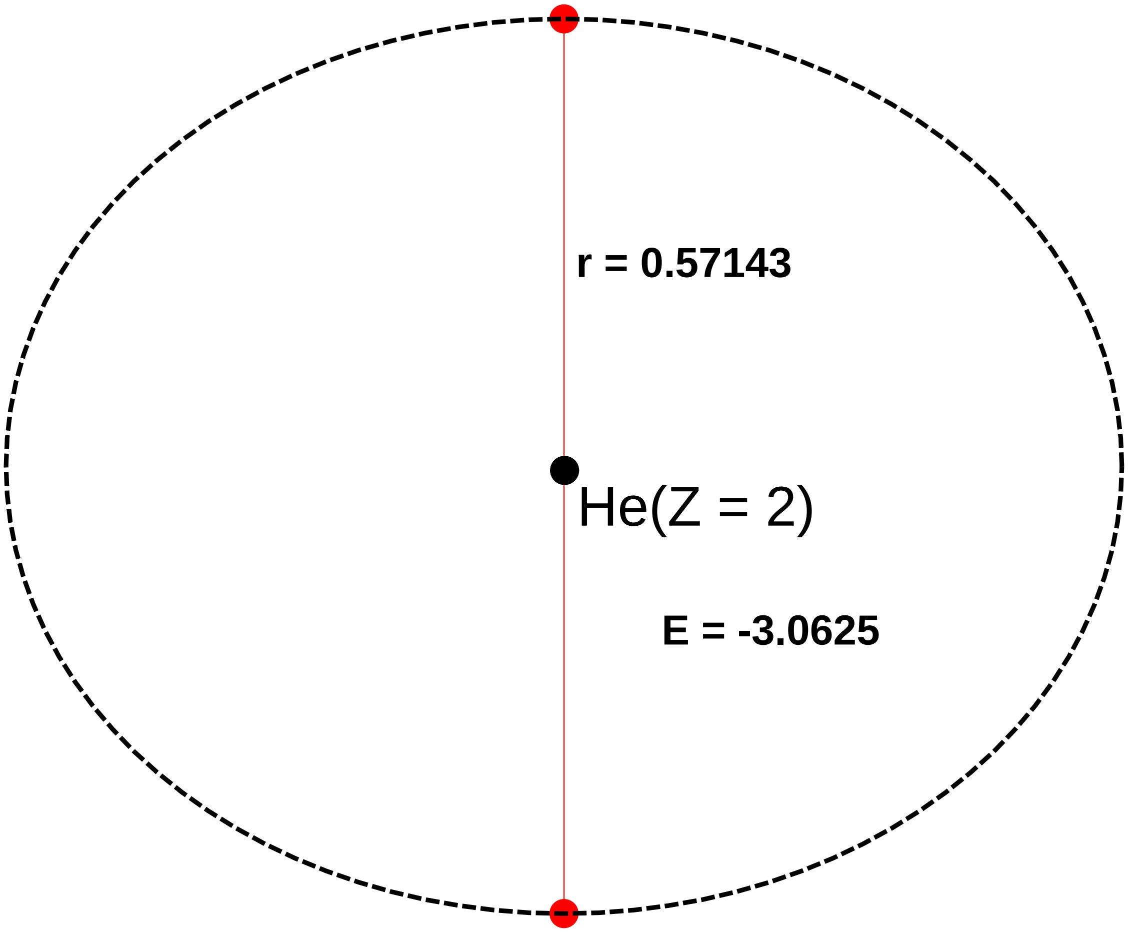

Fig. 3. Diagram for the He atom in Bohr model. Two electrons have same distance from the nucleus and are located at the opposite ends of the diameter, which has the maximum distance from each electron.

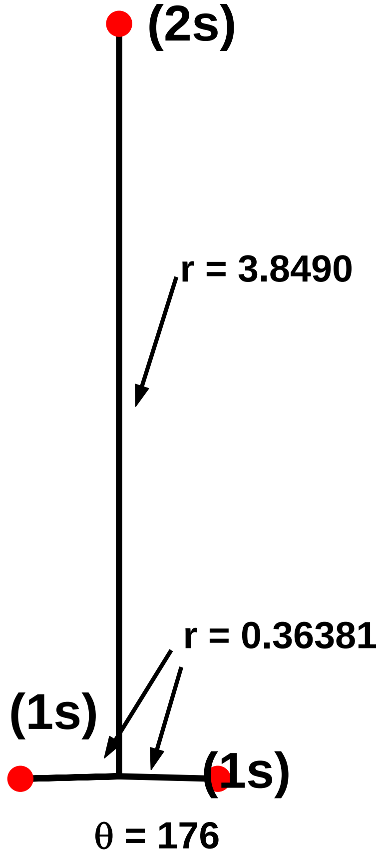

Fig. 4. Diagram for the Li atom in Bohr model. The other electrons in 1s are located slightly off from the straight line adjoining the nucleus and the electron. All three electrons are on the same plain.

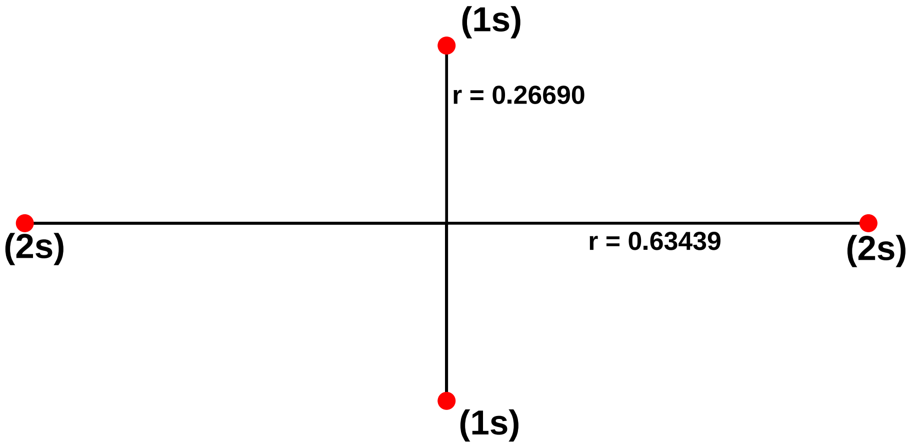

Fig. 5. Diagram for the Be atom in Bohr model. All four electrons are on the same plain.

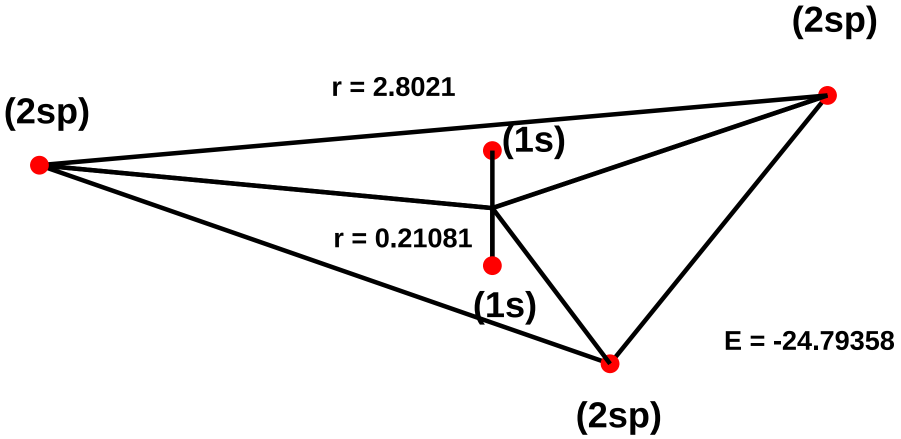

Fig. 6. Diagram for the B atom in Bohr model. (sp)-hybridization. All three electrons in (2sp) are on the same plain and the joining line between two (1s) electrons is prependicular.

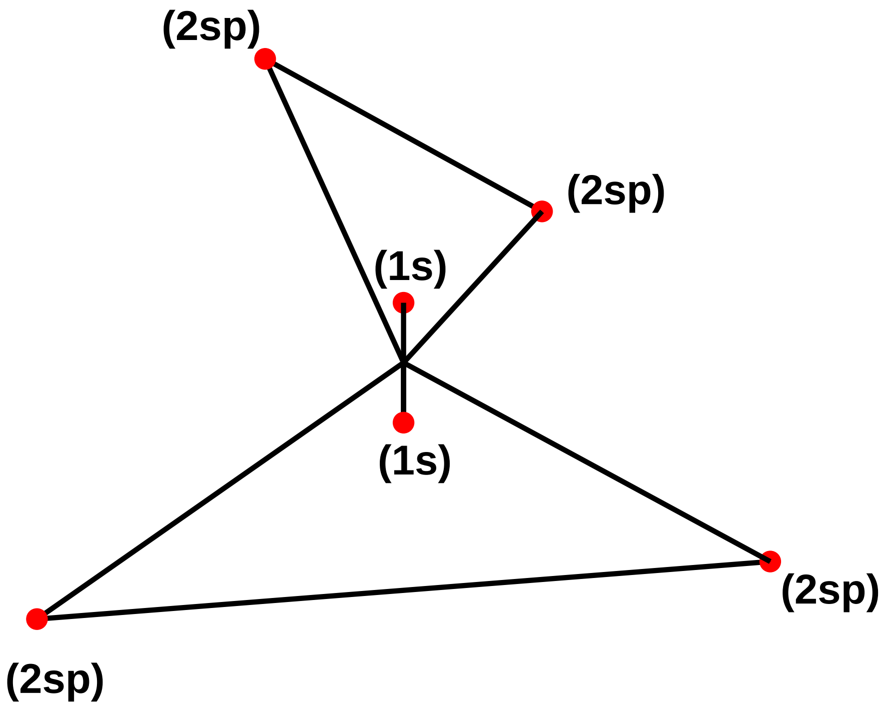

Fig. 7. Diagram for the C atom in Bohr model. Four outer-electrons make (sp^2)-hybridization and tetrahedral structure.

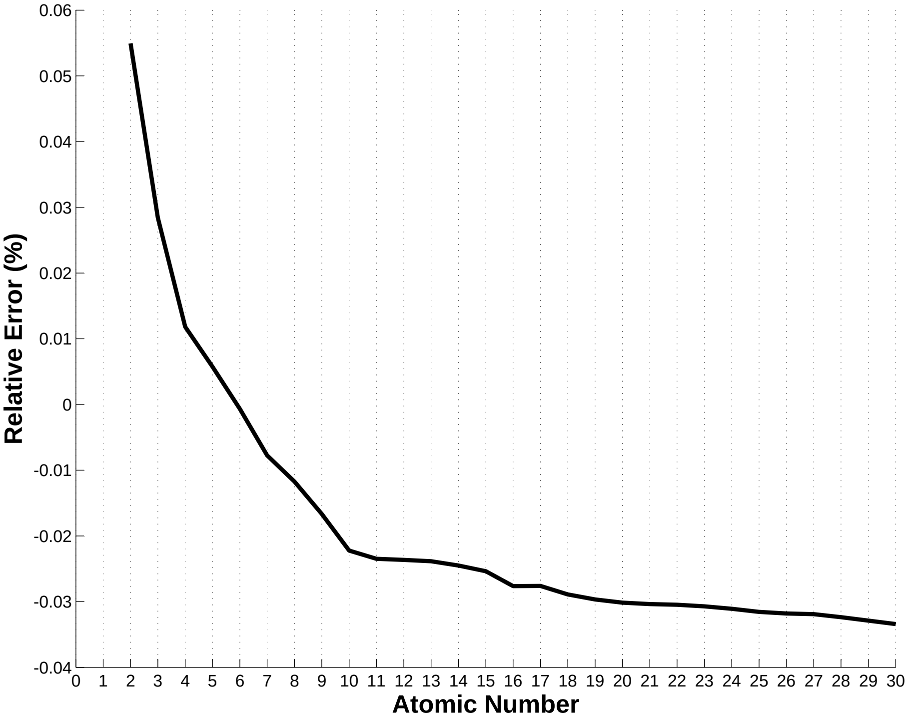

Fig. 8. Relative error of the ground-state energy of the multi-electron atoms compared to the experiments until $Z = 30$. Notice that the carbon atom ($Z = 6$) has the smallest relative error in absolute value.

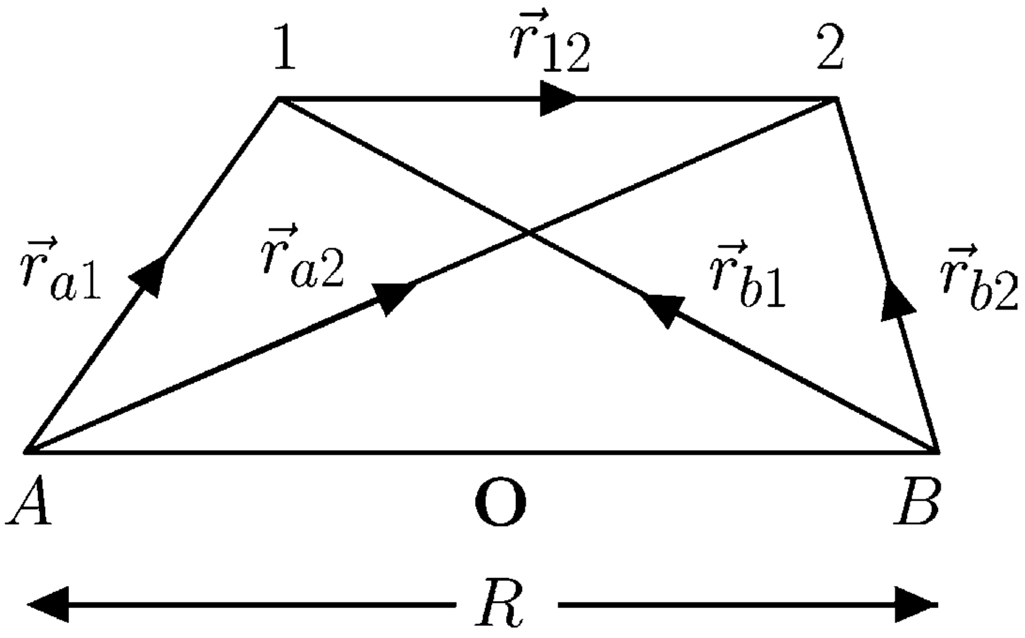

Fig. 9. Electronic distances in diatomic molecule. A and B are the positions of the nuclei with nuclear charges Z_a and Z_b, respectively. The nuclei are fixed and the distance between them is taken to be the equilibrium bond length for the given molecule, $R = R_0$. The positions of the electrons are denoted by 1 and 2.

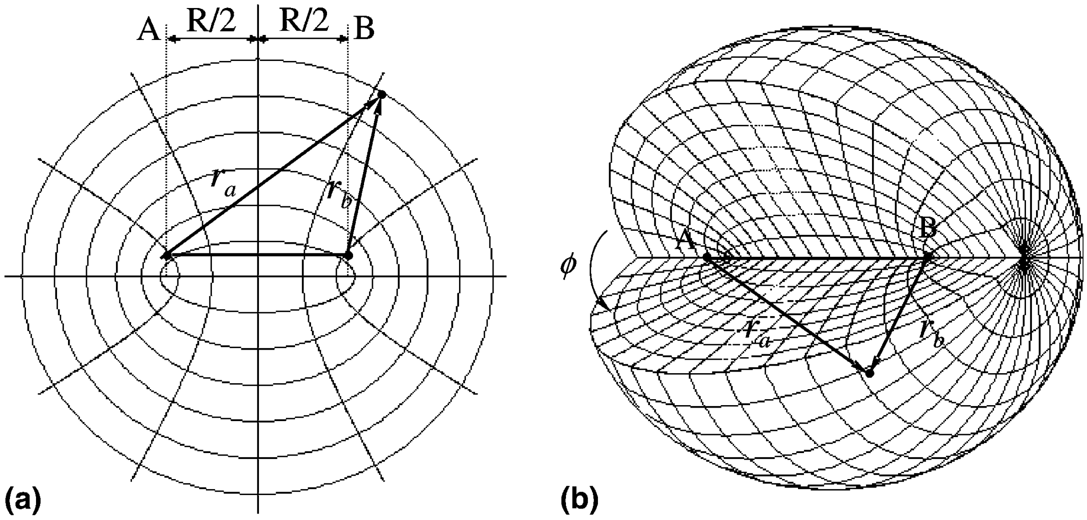

Fig. 10. (a) Elliptical coordinates (λ, μ). (b) Prolate spheroidal coordinates (λ, μ, ϕ) with $\lambda = (r_a + r_b)/R$ and $\mu = (r_a - r_b)/R$. The range of coordinates is $1 \leq \lambda \leq \infty$, $-1 \leq \mu \leq 1$ and $0 \leq \phi \leq 2\pi$.

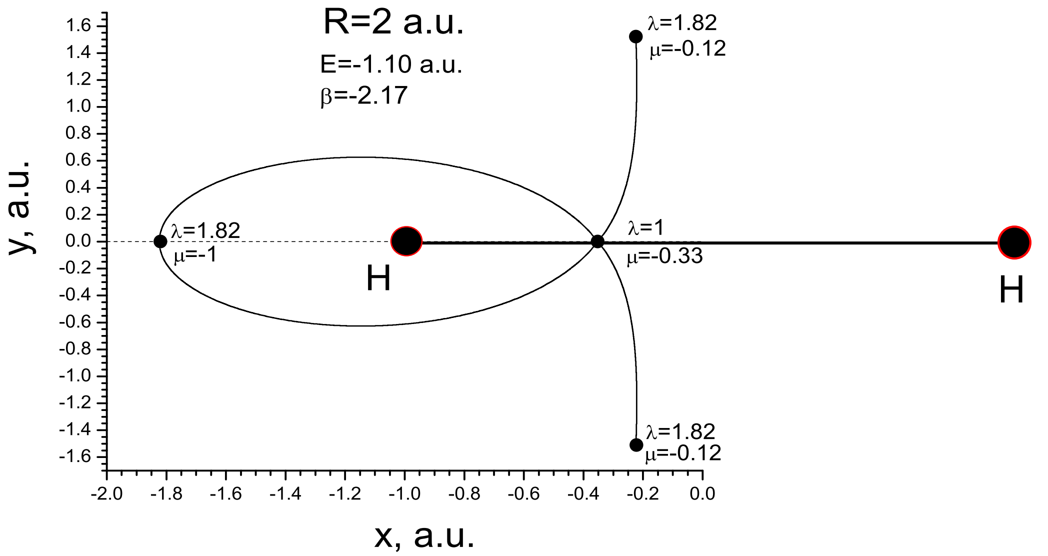

Fig. 11. Trajectory of a periodic electron motion in H_2^+. The electron moves in a plane that passes through the molecular axis.

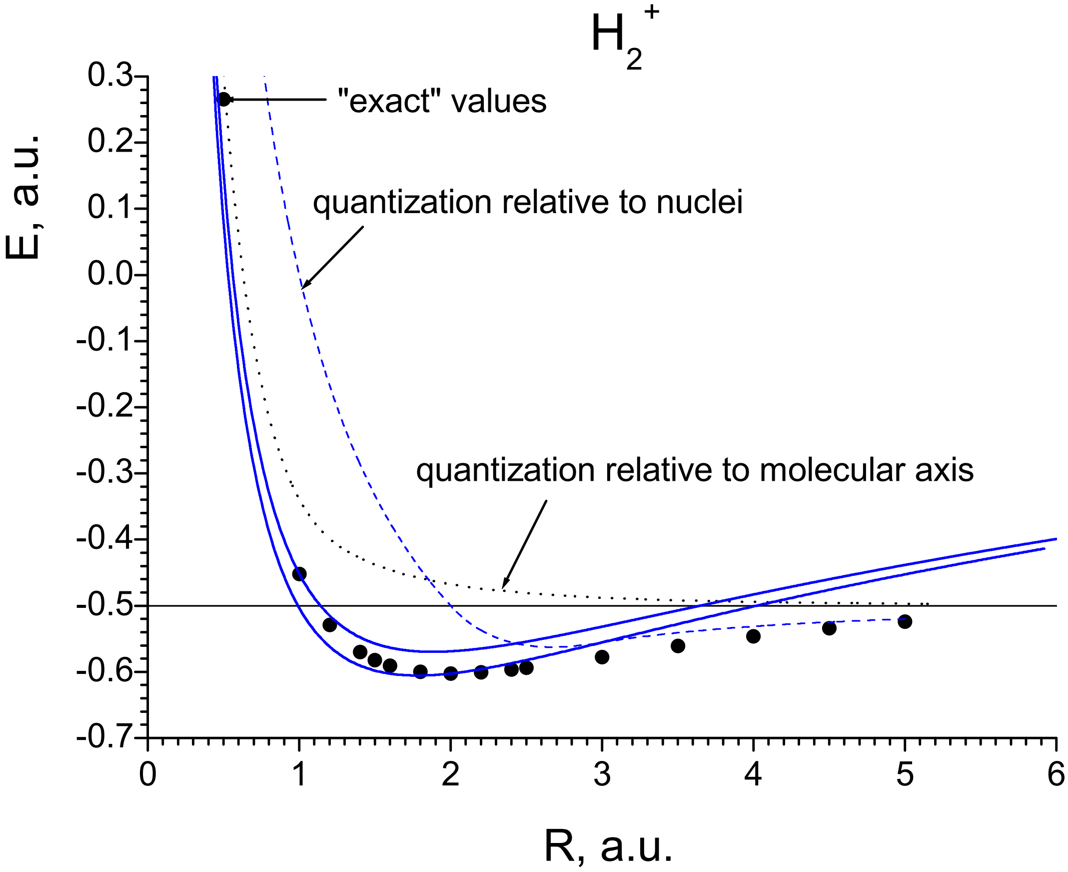

Fig. 12. Ground state potential energy curve of H_2^+ molecule.

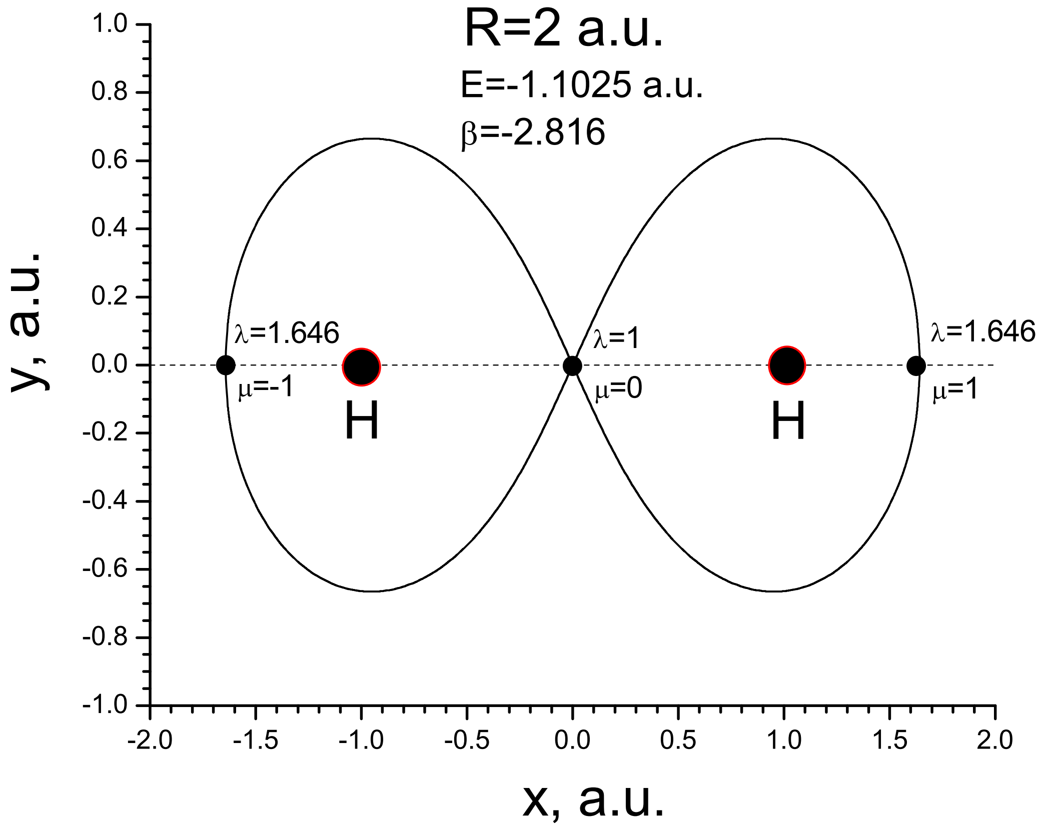

Fig. 13. Trajectory of ∞-like electron motion in H_2^+. The electron moves in a plane that passes through the molecular axis.

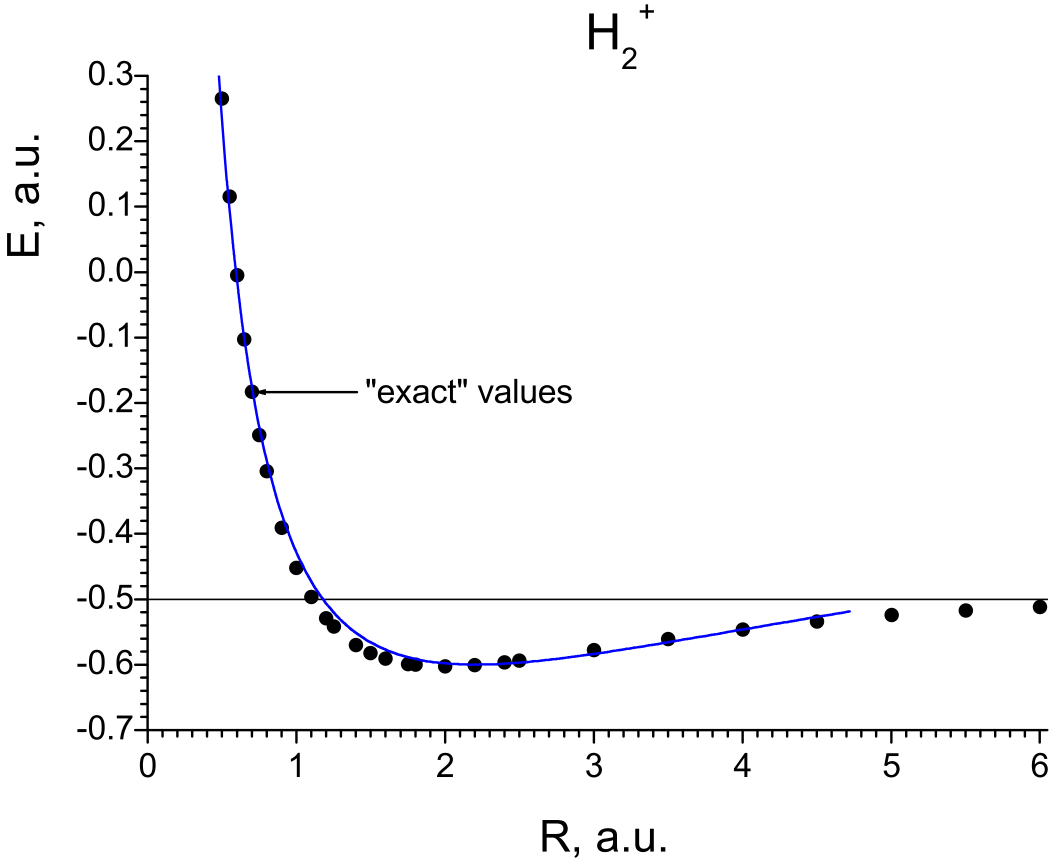

Fig. 14. Ground state potential energy curve of H_2^+ molecule obtained for ∞-like electron trajectory and "exact" quantum mechanical dots from Ref. [36].

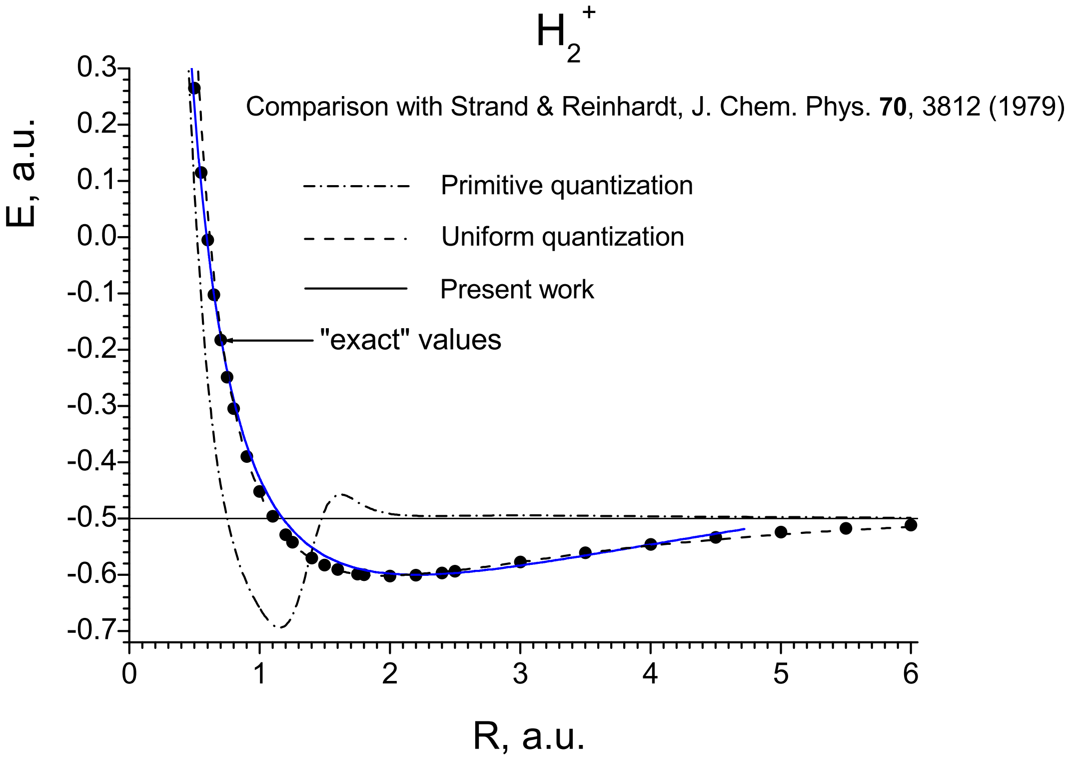

Fig. 15. Ground state potential energy curve of H_2^+ molecule obtained for ∞-like electron trajectory (solid line), "exact" quantum mechanical dots and curves from Ref. [17] obtained using primitive quantization (dash-dot line) and uniform quantization (dashed line).

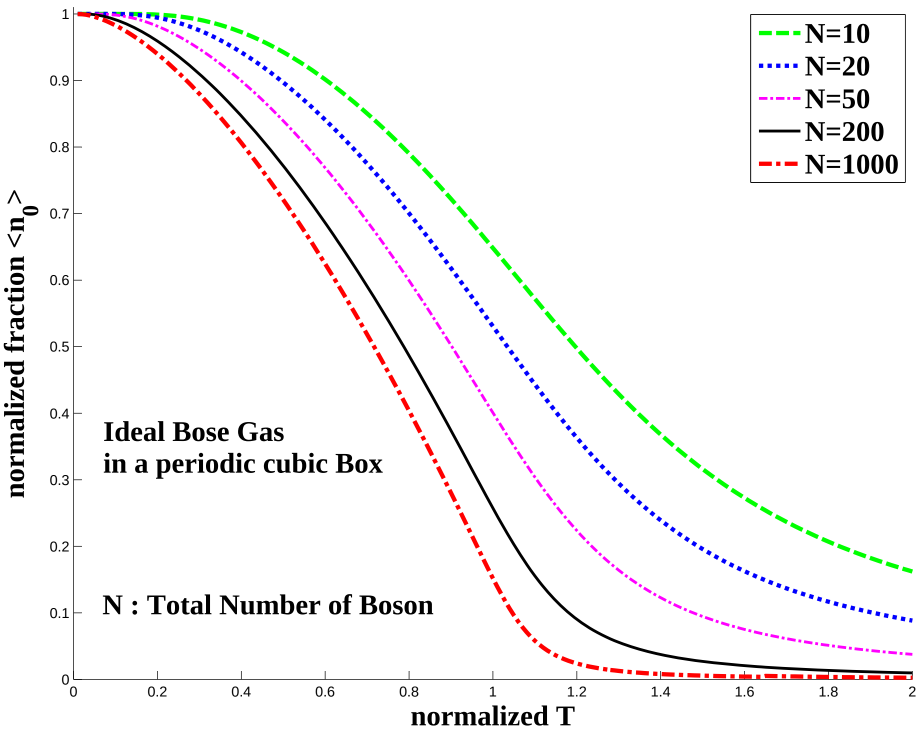

Fig. 16. Average occupation number in condensate state of an ideal Bose gas.

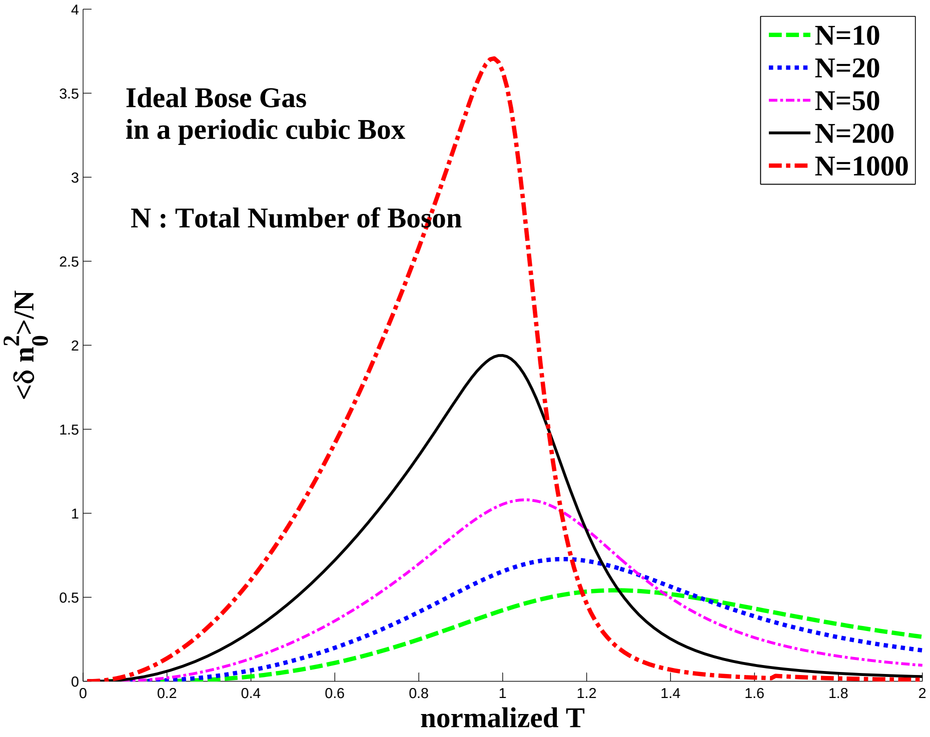

Fig. 17. Variance of the occupation number in condensate state of an ideal Bose gas.

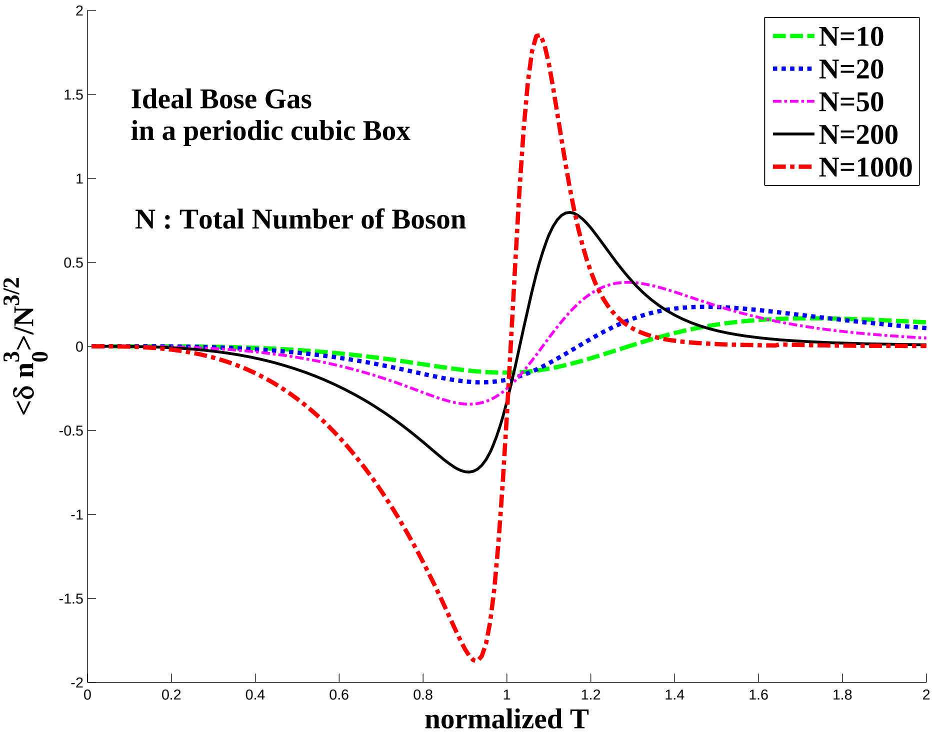

Fig. 18. 3rd moment of the occupation number in condensate state of an ideal Bose gas.

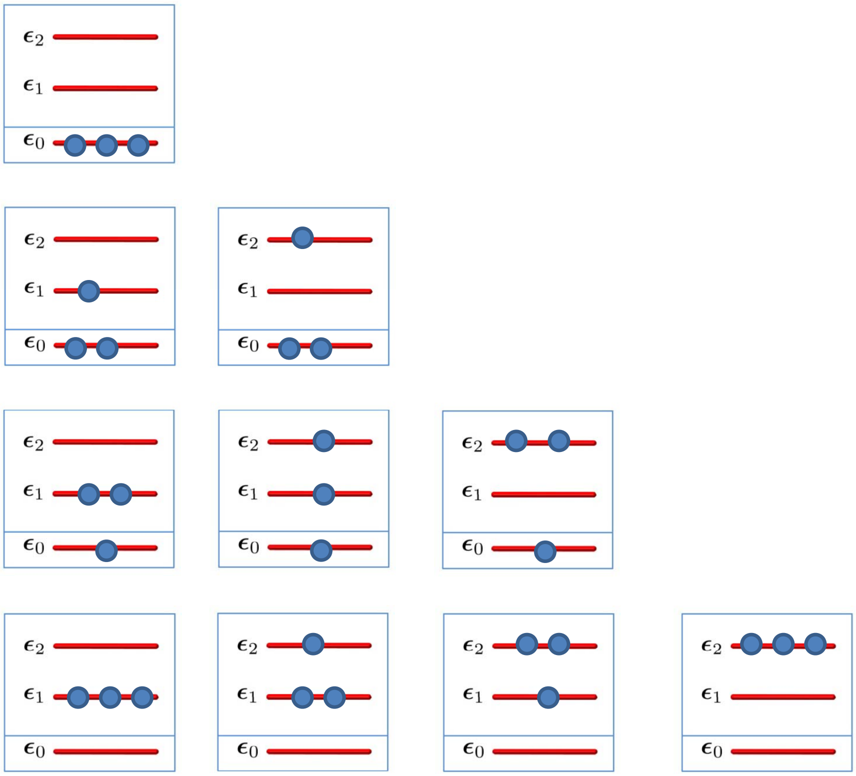

Fig. 19. Distribution of 3 bosonic particles in 3 level system.

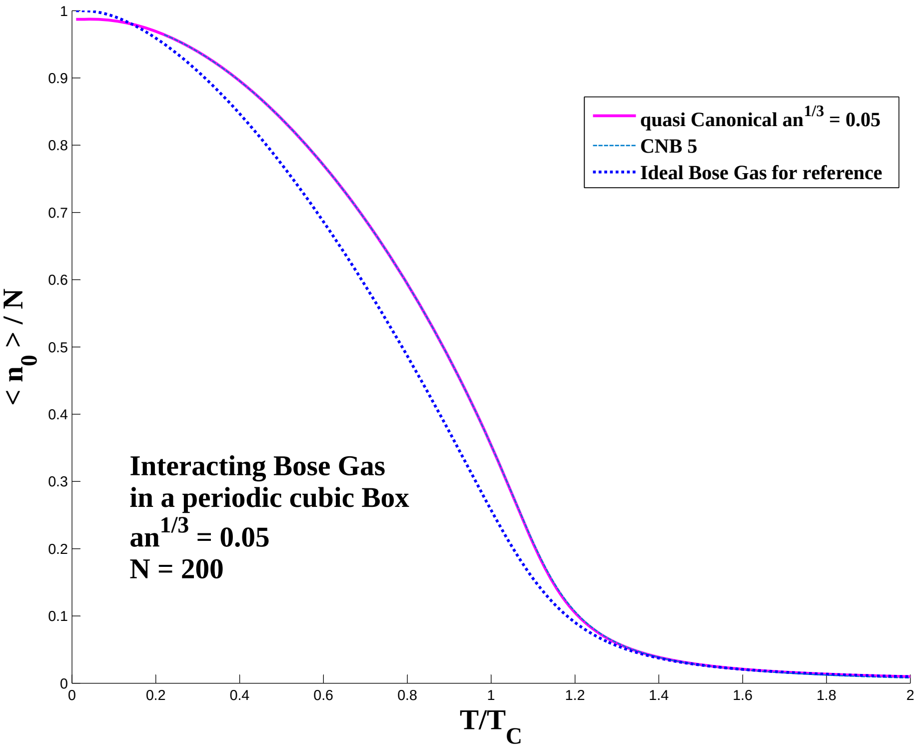

Fig. 20. Average number of particles in condensate state : $N = 200$.

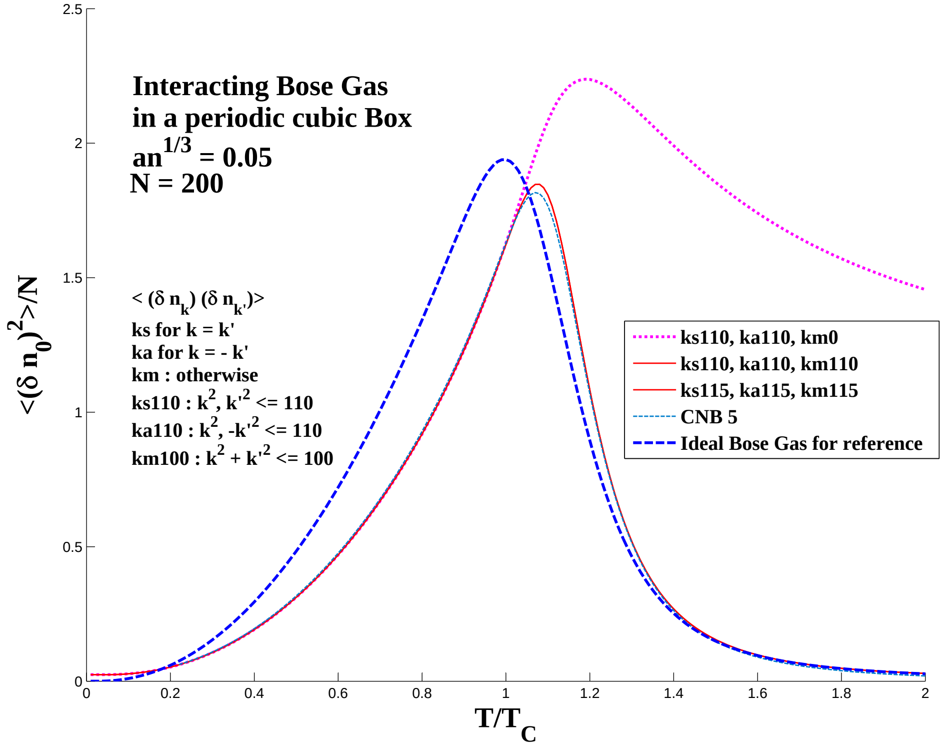

Fig. 21. Fluctuation of the number of particles in condensate state : $N = 200$.

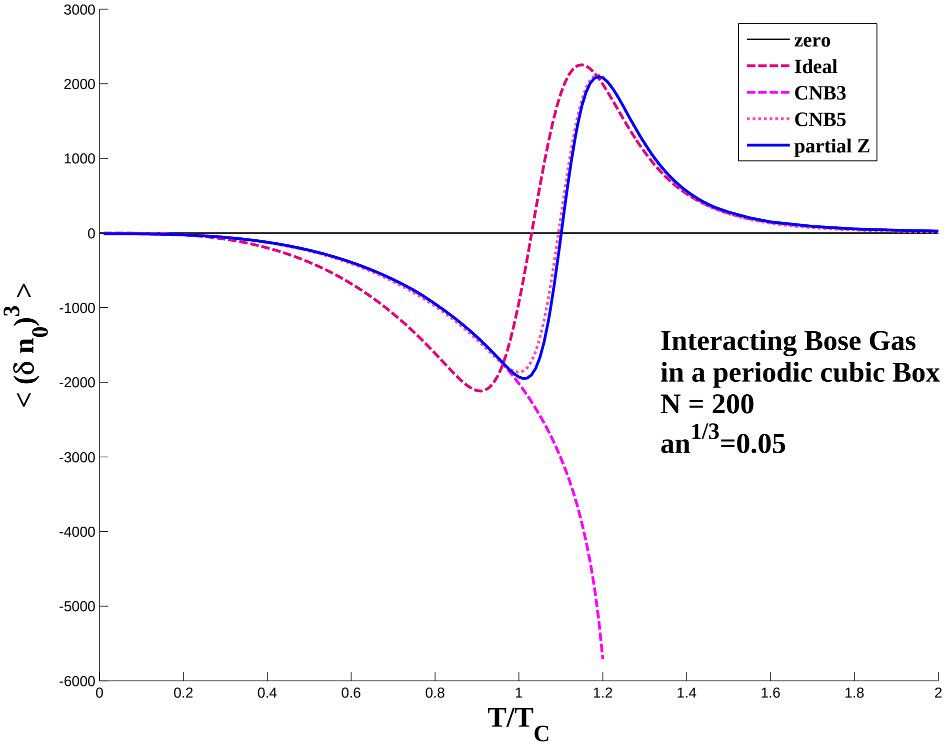

Fig. 22. 3rd centered moment of the number of particles in condensate state : $N = 200$.

VITA

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