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Review

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Variational principle of Bogoliubov and generalized mean fields in many-particle interacting systems

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The approach to the theory of many-particle interacting systems from a unified standpoint, based on the variational principle for free energy is reviewed. A systematic discussion is given of the approximate free energies of complex statistical systems. The analysis is centered around the variational principle of Bogoliubov for free energy in the context of its applications to various problems of statistical mechanics. The review presents a terse discussion of selected works carried out over the past few decades on the theory of many-particle interacting systems in terms of the variational inequalities. It is the purpose of this paper to discuss some of the general principles which form the mathematical background to this approach and to establish a connection of the variational technique with other methods, such as the method of the mean (or self-consistent) field in the many-body problem. The method is illustrated by applying it to various systems of many-particle interacting systems, such as Ising, Heisenberg and Hubbard models, superconducting (SC) and superfluid systems, etc. This work proposes a new, general and pedagogical presentation, intended both for those who are interested in basic aspects and for those who are interested in concrete applications.

Keywords: Mathematical physics; statistical mechanics; variational methods; many-particle interacting systems; the variational principle of Bogoliubov; Bogoliubov inequality; generalized mean fields; model Hamiltonians of many-particle interacting systems.

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1. Introduction

The fundamental works of Bogoliubov on many-body theory and quantum field theory,[1–4] on the theory of phase transitions and on the general theory of interacting systems provided a new perspective in various fields of mathematics and physics. The variational principle of Bogoliubov[1–5] is a useful working tool and has

been widely applied to many problems of physical interest. It has a well-established place in the many-body theory and condensed matter physics.[6–14] The variational principle of Bogoliubov has led to a better understanding of various physical phenomena such as superfluidity,[1–4] superconductivity,[1–4,15] phase transitions[1–4,15,16] and other cooperative phenomena,[5,15,17,18] etc.

Variational methods in physics and applied mathematics were formulated long ago.[19–28] It was Maupertuis,[25] who wrote in 1774 the celebrated statement:

> "*Nature, in the production of its effects, does so always by simplest means.*"

Since that time variational methods have become an increasingly popular tool in mechanics, hydrodynamics, theory of elasticity, etc. Moreover, the variational methods are useful and workable tools for many areas of the quantum theory of atoms and molecules,[21,29–32] statistical many-particle physics and condensed matter physics. The variational methods have been applied widely in quantum mechanical calculations,[21,29–32] in theory of many-particle interacting systems[6–14] and in theory of transport processes.[33,34] As a result of these efforts, many important and effective methods were elaborated by various researchers.

On the other hand, the study of the quasiparticle excitations in many-particle systems has been one of the most fascinating subjects for many years.[5,15,17,18] The quantum field theoretical techniques have been widely applied to the statistical treatment of a large number of interacting particles. Many-body calculations are often done for model systems of statistical mechanics using the perturbation expansion. The basic procedure in many-body theory is to find the relevant unperturbed Hamiltonian and then take into account the small perturbation operator. This procedure, which works well for the weakly interacting systems, needs a suitable reformulation for the many-body systems with complicated spectra and strong interaction.

The considerable progress in studying the spectra of elementary excitations and thermodynamic properties of many-body systems has been for the most part due to the development of the temperature-dependent Green's functions methods.[5,15,17,18] The very important concept of the whole method is the concept of the generalized mean field.[17,35–37] These generalized mean fields have a complicated structure for the strongly correlated case and are not reduced to the functional of the mean densities of the electrons. The concept of the generalized mean fields and the relevant algebra of operators from which the corresponding Green's functions are constructed are the central ones to our treatment of the strongly interacting many-body systems.

It is the purpose of this paper to discuss some of the general principles which form the physical and mathematical background to the variational approach and to establish the connection of the variational technique with other methods in the theory of many-body problem.

2. The Variational Principles of Quantum Theory

It is well known that in quantum mechanics the eigenfunction ψ_i of the lowest state of any system has the property of making the integral

$$\int \psi_i^* H \psi_i d^3 r \tag{1}$$

a minimum. The value of integral is the corresponding eigenvalue E_i of the Hamiltonian H of a system. These circumstances lead to a specific approximate method (the variational method) of finding ψ_i and E_i by minimizing integral (1) among a restricted class of functions.

The variational method[21,29–32] enables one to make estimates of energy levels by using trial wavefunctions ψ_T

$$E_T = \frac{\int \psi_T^* H \psi_T d^3 r}{\int \psi_T^* \psi_T d^3 r} \,. \tag{2}$$

The ground state E_0 gives the lowest possible energy the system can have. Hence, for the approximation of the ground state energy one would like to minimize the expectation value of the energy with respect to a trial wavefunction.

In other words, the variational principle states that the ground state energy of a quantum mechanical system is less than or equal to the expectation value of the Hamiltonian with an arbitrary wavefunction. Given a trial wavefunction with adjustable parameters, the best values of the parameters are those which minimize the expectation value of the Hamiltonian. The variational principle consists in adjusting the available parameters, so as to maximize this lower bound.

An important method of finding approximate ground state energies and wavefunctions is called as the Rayleigh–Ritz variational principle.[21,29–31] The Rayleigh–Ritz variational principle for the ground state energy is the starting point of many computations and approximations in quantum mechanics and quantum chemistry of atoms and molecules. This principle states that the expectation value of H in any state $|\psi\rangle$ is always greater than or equal to the ground state energy, E_0:

$$\frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle} \geq E_0 \tag{3}$$

or

$$\langle H\rangle \geq \langle\psi|H|\psi\rangle \geq E_0 \,. \tag{4}$$

Here $|\psi\rangle \in \mathcal{G}$ is arbitrary pure quantum state and H is a Hamiltonian acting on a Hilbert space $\mathcal{G}$. This relation becomes equality only when $\psi = \psi_0$. Thus, this principle gives the upper bound to the ground state energy.

It will be instructive also to remind how the variational principle of quantum mechanics complements the perturbation theory.[38,39] For this aim let us consider

the Rayleigh–Schrödinger perturbation expansion. The second-order level-shift E_2^0 of the ground state of a system has the form:

$$E_2^0 = \sum_{j\neq 0} \frac{\langle\psi^0|V|\psi_j\rangle\langle\psi_j|V|\psi^0\rangle}{(E^0 - E_j)} = \sum_{j\neq 0} \frac{|V_{0j}|^2}{(E^0 - E_j)}\,, \tag{5}$$

where $V_{0j} = \langle\psi^0|V_{0j}|\psi_j\rangle$ and $|\psi^0\rangle$ is the unperturbed ground state. It is clear then that E_2^0 is always negative.

The variational principle of quantum mechanics states that the ground state energy E^0 for the total Hamiltonian H is the minimum of the energy functional

$$E\{\Psi\} = \langle\Psi|H|\Psi\rangle\,, \tag{6}$$

where Ψ is a trial wavefunction. It should be noted that it is possible to establish that the sum of all the higher-order level shifts E_n^0, starting with $n = 2$, will be negative, provided the relevant perturbation series will converge to E^0.

To confirm this statement let us consider again the Hamiltonian

$$H = H_0 + \lambda V\,. \tag{7}$$

It is reasonable to suppose that the ground state energy $E^0 = E^0(\lambda)$ and the ground state $\Psi = \Psi(\lambda)$ of the Hamiltonian H are analytic functions (at least for small λ). Note that when one considers the many-body problem, the concept of relative boundedness is of use, where a perturbation λV is small compared to H_0 in a sense that

$$(H_0)^2 \geq (\lambda^2 V^2)\,.$$

This means simply that the eigenvalues of the operator $((H_0)^2 - (\lambda^2 V^2))$ are non-negative. Then the corresponding perturbation expansion may be written in the form:

$$E_0 = E_0^{(0)} + \lambda E_0^{(1)} + \lambda^2 E_0^{(2)} + \lambda^3 E_0^{(3)} + \cdots\,, \tag{8}$$

where $E_0^0 = \langle\psi^0|H|\psi^0\rangle$ and $E_0^1 = \langle\psi^0|V|\psi^0\rangle$. The variational approach states that

$$E_0 = \min(\langle\Psi|H_0 + \lambda V|\Psi\rangle)\,. \tag{9}$$

Thus, we obtain

$$\begin{aligned}\lambda^2 E_0^{(2)} + \lambda^3 E_0^{(3)} + \cdots &= E_0 - (E_0^{(0)} + \lambda E_0^{(1)}) \\ &= (\min\{\langle\Psi|H_0 + \lambda V|\Psi\rangle\} - \langle\psi^0|H_0 + \lambda V|\psi^0\rangle)\,. \end{aligned} \tag{10}$$

In this expression, the second part must satisfy the condition

$$(\min\{\langle\Psi|H_0 + \lambda V|\Psi\rangle\} - \langle\psi^0|H_0 + \lambda V|\psi^0\rangle) \leq 0\,. \tag{11}$$

In addition, in general case the relevant ground state Ψ which yields a minimum will not coincide with ψ^0. Thus, we obtain

$$\lambda^2 E_0^{(2)} + \lambda^3 E_0^{(3)} + \cdots < 0\,. \tag{12}$$

The last inequality can be rewritten as

$$E_0^{(2)} < (\lambda E_0^{(3)} + \lambda^2 E_0^{(4)} + \cdots)\,. \tag{13}$$

In the limit $\lambda \to 0$, we have that $E_0^{(2)} < 0$. Thus, the variational principle of quantum mechanics confirms the results of the perturbation theory.[40]

It is worth mentioning that the Rayleigh–Ritz variational method has a long and interesting history.[41–43] Rayleigh's classical book *Theory of Sound* was first published in 1877. In it are many examples of calculating fundamental natural frequencies of free vibration of continuum systems (strings, bars, beams, membranes, plates) by assuming the mode shape and setting the maximum values of potential and kinetic energy in a cycle of motion equal to each other. This procedure is the well-known *Rayleigh's Method*. In 1908, Ritz laid out his famous method for determining frequencies and mode shapes, choosing multiple admissible displacement functions and minimizing a functional involving both potential and kinetic energies. He then demonstrated it in detail in 1909 for the completely free square plate. In 1911, Rayleigh wrote a paper congratulating Ritz on his work, but stating that he himself had used Ritz's method in many places in his book and in another publication.

Subsequently, hundreds of research articles and many books have appeared which use the above method, some calling it the "Ritz method" and others as the "Rayleigh–Ritz method." The article[41] examined the method in detail, as Ritz presented it, and as Rayleigh claimed to have used it. Leissa[41] concluded that, although Rayleigh did solve a few problems which involved minimization of a frequency, these solutions were not by the straightforward, direct method presented by Ritz and used subsequently by others. Therefore, Rayleigh's name should not be attached to the method. Additional informative comments were carried out in Refs. 42 and 43.

3. The Helmholtz Free Energy and Statistical Thermodynamics

Variational methods in thermodynamics and statistical mechanics have been used widely since the groundbreaking works of Gibbs.[26–28] According to Gibbs' approach, a workable procedure for the development of the statistical mechanical ensemble theory is to introduce the Gibbs entropy postulate. Hence, as a result of the Gibbs ensemble method, the entropy S can be expressed in the form of an average for all the ensembles, namely,

$$S(N,V,E) = -k_B \sum_i p_i \ln p_i = -k_B \Omega \left(\frac{1}{\Omega} \ln \frac{1}{\Omega}\right) = k_B \ln \Omega(N,V,E)\,, \tag{14}$$

where the summation over i denotes a general summation over all states of the system and p_i is the probability of observing state i in the given ensemble and k_B is the Boltzmann constant. This relation links entropy S and probability p_i.

It can be said that in this context the entropy is a state function, which according to the second law[27,44] is defined by the relation

$$dS = \beta(dE - dF)\,. \tag{15}$$

The energy E and the Helmholtz free energy F are the state functions.[27,44] The proportionality coefficient β was termed as the *thermodynamic temperature* ($\beta = 1/k_BT$) of the surrounding with which the system exchanges by heat Q and work W.

Thus, the postulate of equal probabilities in the microcanonical ensemble[45] and the Gibbs entropy postulate can be considered as a convenient starting points for the development of the statistical mechanical ensemble theory in a standard approach.[27] After postulating the entropy by means of Eq. (14), the thermodynamic equilibrium ensembles are determined by the following criterion for equilibrium:

$$(\delta S)_{E,V,N} = 0\,. \tag{16}$$

This variational scheme is used for each ensemble (microcanonical, canonical and grand canonical) with different constraints for each ensemble. In addition, this procedure introduces Lagrange multipliers which, in turn, must be identified with thermodynamic intensive variables (T, P). On the other hand, the procedure of introducing Lagrange multipliers and the task of identifying them with the thermodynamic intensive properties can be clarified by invoking a more general criterion for thermodynamic equilibrium.

From the Gibbs entropy postulate, Eq. (14), and the definitions of average and the normalization constraint $\sum_i p_i = 1$, one obtains

$$\delta S = -k_B \sum_i (1 + \ln p_i)\delta p_i\,, \tag{17}$$

$$\delta E = \sum_i E_i \delta p_i\,, \tag{18}$$

$$\delta V = \sum_i V_i \delta p_i\,, \tag{19}$$

$$\sum_i \delta p_i = 0\,. \tag{20}$$

Using a Lagrange multiplier λ together with the variational condition, we obtain

$$\sum_i (E_i + PV_i + \lambda + k_BT + k_BT \ln p_i)\delta p_i \geq 0\,. \tag{21}$$

Here, all δp_i are considered as the independent variables. Thus, we deduce that

$$p_i = \exp(-\beta\lambda - 1 - \beta(PV_i + E_i)), \quad \beta = (k_BT)^{-1}\,. \tag{22}$$

The Lagrange multiplier λ can be determined directly from the definition of entropy (14).

$$S = -k_B \sum_i p_i \left(\frac{E_i + PV_i + \lambda + k_BT}{k_BT}\right) = \frac{(E + PV + \lambda + k_BT)}{T}\,. \tag{23}$$

Thus, we arrive at

$$\lambda + k_B T = TS - E - PV = -G\,, \tag{24}$$

$$p_i = \exp \beta(G - PV_i - E_i)\,. \tag{25}$$

Here, G is the Gibbs energy (or Gibbs free energy). It may also be defined with the aid of the Helmholtz free energy $G = H - TS$. Here, $H(S, P, N)$ is the enthalpy.[44] The usefulness of the thermodynamic potentials G and F may be clarified within the statistical thermodynamics.[27] For the *microcanonical* ensemble one should substitute $E_i = E$ and $V_i = V$, which are fixed for every system, and since $G - PV - E = S$ Eq. (25) becomes

$$p_i = e^{-S/k_B}\,. \tag{26}$$

For the canonical ensemble one should substitute $V_i = V$, which is given for each system, and in this case Eq. (25) can be written as

$$p_i = e^{\beta(F - E_i)}\,. \tag{27}$$

Here, $F = G - PV$ denotes the *Helmholtz free energy*. Thus, the free energy F is defined by

$$F = E - TS\,. \tag{28}$$

The Helmholtz free energy describes an energy which is available in the form of useful work.

The second law of thermodynamics asserts that in every neighborhood of any state $\mathcal{A}$ in an adiabatically isolated system there exist other states that are inaccessible from $\mathcal{A}$. This statement in terms of the *entropy* S and *heat* Q can be formulated as

$$dS = dQ/T + d\sigma\,. \tag{29}$$

Thus, the only states available in an adiabatic process ($dQ = 0$ or $dS = d\sigma$) are those which lead to an increase of the entropy S. Here, $d\sigma \geq 0$ defines the entropy production σ due to the irreversibility of the transformation.

It is of use to analyze the expression

$$dF = dE - TdS - SdT = -SdT - Td\sigma - PdV + \sum \mu_i N_i\,. \tag{30}$$

Free energy change ΔF of the system during the transformation of the system describes the balance of the work exchanged with the surroundings. If $\Delta F > 0$, ΔF represents the minimum work that must be incurred for the system to carry out the transformation. In case $\Delta F < 0$, $|\Delta F|$ represents the maximum work that can be obtained from a system during the transformation. It is obvious that

$$dF = dE - Td\sigma - SdT\,. \tag{31}$$

In a closed system without chemical reaction and in the absence of any other energy exchange, the variation $\Delta F = -SdT - TdS - PdV + \sum \mu_i N_i$ can be rewritten in the form:

$$dF = -Td\sigma \leq 0. \tag{32}$$

It means that function F decreases and tends towards a minimum corresponding to equilibrium. Thus, the Helmholtz free energy is the thermodynamic potential of a system subjected to the constant constraints T, V, N_i.

The *Gibbs free energy* (free enthalpy) is defined by

$$G = H - TS = F + PV\,. \tag{33}$$

The physical meaning of the Gibbs free energy is clarified when considering the evolution of a system from a certain initial state to a final state. The Gibbs free energy change ΔG then represents the work exchanged by the system with its environment and the work of the pressure forces, during a reversible transformation of the system. Here, $H = E + VP = TS + VP + \sum \mu_i N_i$ is the thermodynamic potential of a system termed by *enthalpy*.[44] The Gibbs' free energy is the thermodynamic potential of a system subjected to the constant constraints T, P, N_i. In this case,

$$dG = -Td\sigma \leq 0\,. \tag{34}$$

Thus, in a closed system without chemical reaction and in the absence of any other energy exchange at constant temperature, pressure and amount of substance, the function G can only decrease and reach a minimum at equilibrium.

It will be of use to mention another class of thermodynamic potentials, termed by the Massieu–Planck functions. These objects may be deduced from the fundamental relations in the entropy representations, $S = S(E, V, N)$. The corresponding differential form may be written as

$$dS = \frac{1}{T}dE + \frac{P}{T}dV - \frac{\mu}{T}dN\,. \tag{35}$$

Thus, the suitable variables for a Legendre transform will be $1/T$, P/T and μ/T. In some cases working with these variables is more convenient.

It is worth noting that in terms of the Gibbs ensemble method the free energy is the thermodynamic potential of a system subjected to the constant constraints T, V, N_i. Moreover, the thermodynamic potentials should be defined properly in the thermodynamic limit. The problem of the thermodynamic limit in statistical physics was discussed in detail by Kuzemsky.[45] To clarify this notion, let us consider the logarithm of the partition function $Q(\theta, V, N)$:

$$F(\theta, V, N) = -\theta \ln Q(\theta, V, N)\,. \tag{36}$$

This expression determines the free energy F of the system on the basis of canonical distribution. The standard way of reasoning in the equilibrium statistical mechanics

does not require the knowledge of the exact value of the function $F(\theta, V, N)$. For real system it is sufficient to know the thermodynamic (infinite volume) limit[15,27,45,46]:

$$\lim_{N\to\infty} \frac{F(\theta, V, N)}{N}|_{V/N=\text{const.}} = f(\theta, V/N)\,. \tag{37}$$

Here, $f(\theta, V/N)$ is the free energy per particle. It is clear that this function determines all the thermodynamic properties of the system.

Let us summarize the criteria for equilibrium briefly. In a system of constant V and S, the internal energy has its *minimum* value, whereas in a system of constant E and V, the entropy has its *maximum* value.

It should be noted that the pair of independent variables (V, S) is not the suitable one because the entropy is not convenient to measure or control. Hence, it would be of use to have fundamental equations with independent variables that is easier to control. Two convenient choices are possible. First, we take the P and T pair. From the practical point of view, this is a convenient pair of variables which are easy to control (measure). For systems with constant pressure, the best suited state function is the Gibbs free energy (also called free enthalpy),

$$G = H - TS\,. \tag{38}$$

Second, the relevant pair is V and T. For systems with constant volume (and variable pressure), the best suited state function is the Helmholtz free energy,

$$F = E - TS\,. \tag{39}$$

Any state function can be used to describe any system (at equilibrium, of course), but for a given system some are more convenient than the others. The change of the Helmholtz free energy can be written as

$$dF = dE - TdS - SdT\,. \tag{40}$$

Combining this equation with $dU = TdS - PdV$, we obtain the relation of the form:

$$dF = -PdV - SdT\,. \tag{41}$$

In terms of variables (T, V) we find

$$dF = \left(\frac{\partial F}{\partial T}\right)\Big|_V dT + \left(\frac{\partial F}{\partial V}\right)\Big|_T dV\,. \tag{42}$$

Comparing the equations, one can see that

$$S = -\left(\frac{\partial F}{\partial T}\right)\Big|_V, \quad P = \left(\frac{\partial F}{\partial V}\right)\Big|_T. \tag{43}$$

At constant T and V, the equilibrium states correspond to the minimum of Helmholtz free energy ($dF = 0$). From $F = E - TS$, we may suppose that low values of F are obtained with low values of E and high values of S.

In terms of a general statistical mechanical formalism,[3,4,15] a many-particle system with Hamiltonian H in contact with a heat bath at temperature T in a state described by the statistical operator ρ has a free energy

$$F = \mathrm{Tr}(\rho H) + k_B T \,\mathrm{Tr}(\rho \ln \rho)\,. \tag{44}$$

The free energy takes its minimum value

$$F_{\mathrm{eq}} = -k_B T \ln Z \tag{45}$$

in the *equilibrium* state characterized by the canonical distribution

$$\rho_{\mathrm{eq}} = Z^{-1} \exp(-H\beta), \quad Z = \mathrm{Tr} \exp(-H\beta)\,. \tag{46}$$

Before turning to the next topic, an important remark about the free energy will not be out of place here. Novak[47] attempted to give a microscopic description of Le Chatelier's principle[48] in statistical systems. Novak has carried out interesting analysis based on microscopic descriptors (energy levels and their populations) that provides visualization of free energies and conceptual rationalization of Le Chatelier's principle. The misconception "*nature favors equilibrium*" was highlighted. This problem is a delicate one and requires a careful discussion.[49] Dasmeh *et al.* showed[49] that Le Chatelier's principle states that when a system is disturbed, it will shift its equilibrium to counteract the disturbance. However, for a chemical reaction in a small, confined system, the probability of observing it proceed in the opposite direction to that predicted by Le Chatelier's principle, can be significant. Their study provided a molecular level proof of Le Chatelier's principle for the case of a temperature change. Moreover, a new, exact mathematical expression was derived that is valid for arbitrary system sizes and gives the relative probability that a single experiment will proceed in the endothermic or exothermic direction, in terms of a microscopic phase function. They showed that the average of the time integral of this function is the maximum possible value of the purely irreversible entropy production for the thermal relaxation process. The results obtained were tested against computer simulations of the unfolding of a polypeptide. It was proven that any equilibrium reaction mixture on an average responds to a temperature increase by shifting its point of equilibrium in the endothermic direction.

4. Approximate Calculations of Helmholtz Free Energy

Statistical mechanics provides effective and workable tools for describing the behavior of the systems of many interacting particles. One of such approaches for describing systems in equilibrium consists in evaluating the partition function Z and then the free energy.

Now we must take note of the different methods for obtaining the approximate Helmholtz free energy in the theory of many-particle systems. Roughly speaking, there are two approaches, namely the perturbation method and the variational method.

Thermodynamic perturbation theory[50–53] may be applied to systems that undergo a phase transition. It was shown[54] that certain conditions are necessary in order that the application of the perturbation does not change the qualitative features of the phase transition. Usually, the shift in the critical temperature is determined to two orders in the perturbation parameter. Let us consider here the perturbation method[54] very briefly.

In the Ref. 54, authors considered a system with Hamiltonian H_0 that undergoes a phase transition at critical temperature T_C^0. The task was to determine for what class of perturbing potentials V will the system with Hamiltonian $H_0 + V$ have a phase transition with qualitatively the same features as the unperturbed system. In their paper, the authors[54] had studied that question using thermodynamic perturbation theory.[50–52] They found that an expansion for the perturbed thermodynamic functions can be term-by-term divergent at the critical temperature T_C^0 for a class of potentials V. Under certain conditions the series can be resummed, in which case the phase transition remains qualitatively the same as in the unperturbed system but the location of the critical temperature is shifted.

The starting point was the partition function Z_0 for a system whose Hamiltonian is H_0,

$$Z_0 = \mathrm{Tr}\exp(-H_0\beta)\,. \tag{47}$$

For a system with Hamiltonian $H_0 + \lambda V$, the partition function Z is given by

$$Z = \mathrm{Tr}\exp[-(H_0 + \lambda V)\beta]\,. \tag{48}$$

It is possible to obtain formally an expansion for Z in terms of the properties of the unperturbed system by expanding that part of the exponential containing the perturbation in the following way[54] when V and H_0 commute:

$$Z = \mathrm{Tr}\bigg(\exp(-H_0\beta)\sum_n^\infty \frac{1}{n!}[-\lambda\beta]^n V^n\bigg) = Z_0\sum_n^\infty \frac{1}{n!}[-\lambda\beta]^n\langle V^n\rangle_0\,, \tag{49}$$

where

$$Z_0\langle V^n\rangle_0 = \mathrm{Tr}(\exp[-H_0\beta]V^n)\,. \tag{50}$$

Then the expression for Z can be written as

$$\frac{Z}{Z_0} = \exp\left(\ln\left[1 + \sum_n^\infty \frac{1}{n!}(-\lambda\beta)^n\langle V^n\rangle_0\right]\right). \tag{51}$$

The free energy per particle f is given by

$$\beta f_p = \beta f_0 - \frac{1}{N}\ln\left(1 + \sum_n^\infty \frac{1}{n!}(-\lambda\beta)^n\langle V^n\rangle_0\right), \tag{52}$$

where f_p and f_0 are the perturbed and unperturbed free energy per particle, respectively, and N is the number of particles in the system. The standard way to proceed

consists of in expanding the logarithm in powers of λ. As a result one obtains[54]

$$\beta f_p = \beta f_0 + \frac{\lambda\beta}{N}\langle V\rangle_0 - \frac{\lambda^2\beta^2}{2!}\frac{1}{N}(\langle V^2\rangle_0 - \langle V\rangle_0^2) + \frac{\lambda^3\beta^3}{3!}\frac{1}{N}(\langle V^3\rangle_0 - 3\langle V^2\rangle_0\langle V\rangle_0 + \langle V\rangle_0^3) + \cdots . \quad (53)$$

To proceed, it is supposed usually that the thermodynamics of the unperturbed system is known and the perturbation series (if they converge) may provide us with suitable corrections. If the terms in the expansion diverge, they may, in principle, be regularized under some conditions. For example, perturbation expansions for the equation-of-state of a fluid whose intermolecular potential can be regarded as consisting of the sum of a strong and weak parts give reasonable qualitative results.[55,56]

In the paper by Fernandes,[53] he investigated the application of perturbation theory to the canonical partition function of statistical mechanics. The Schwinger and Rayleigh–Schrödinger perturbation theory were outlined and plausible arguments were formulated that both should give the same result. It was shown that by introducing adjustable parameters in the unperturbed or reference Hamiltonian operator, one can improve the rate of convergence of Schwinger perturbation theory. The same parameters are also suitable for Rayleigh–Schrödinger perturbation theory. The author discussed also a possibility of variational improvements of perturbation theory and gave a simpler proof of a previously derived result about the choice of the energy shift parameter. It was also shown that some variational parameters correct the anomalous behavior of the partition function at high temperatures in both Schwinger and Rayleigh–Schrödinger perturbation theories. It should be stressed, however, that the perturbation method is valid for small perturbations only. The variational method is more flexible tool[38,39,57–62] and in many cases is more appropriate in spite of the obvious shortcomings. But both the methods are interrelated deeply[39] and enrich each other.

Peierls[51,52,63] pointed at the circumstance that for a many-particle system in thermal equilibrium there is a minimum property of the free energy which may be considered as a generalization of the variational principle for the lowest eigenvalue in quantum mechanics. Peierls attracted attention to the fact that the free energy has a specific property which can be formulated in the following way. Let us consider an arbitrary set of orthogonal and normalized functions $\{\varphi_1, \varphi_2, \ldots, \varphi_n, \ldots\}$. The expectation value of the Hamiltonian H for nth term of them will be written as

$$H_{nn} = \int \varphi_n^* H \varphi_n dr\,. \quad (54)$$

The statement is that for any temperature T the function

$$\tilde{F} = -k_B T \log \tilde{Z} = -k_B T \log \sum_n \exp[-H_{nn}\beta]\,, \quad (55)$$

which would represent the free energy if H_{nn} were the true eigenvalues, is *higher* than the true free energy

$$F_0 = -k_B T \log Z_0 = -k_B T \log \sum_n \exp[-E_n \beta] \tag{56}$$

or

$$\tilde{F} \geq F_0 \,. \tag{57}$$

This is equivalent to saying that the partition function, as formed by means of the expectation values H_{nn},

$$\tilde{Z} = \sum_n \exp[-H_{nn}\beta] \tag{58}$$

is less than the true partition function

$$Z_0 = \sum_n \exp[-E_n \beta] \tag{59}$$

or

$$Z_0 = \sum_n \exp[-E_n \beta] \geq \tilde{Z} = \sum_n \exp[-H_{nn}\beta] \,. \tag{60}$$

Peierls[63] formulated the more general statement, namely, that if $f(E)$ is a function with the properties

$$\frac{df}{dE} < 0, \quad \frac{d^2 f}{dE^2} > 0 \,, \tag{61}$$

the expression

$$f = \sum_n f(H_{nn}) \tag{62}$$

is less than

$$f_0 = \sum_n f(E_n) \,. \tag{63}$$

To summarize, Peierls has proved a kind of theorem a special case of which gives a lower bound to the partition sum and hence an upper bound to the free energy of a quantum mechanical system

$$\sum_k \exp[-E_k \beta] \geq \sum_n \exp[-H_{nn}\beta] \,. \tag{64}$$

When $\beta \to \infty$ the theorem is obvious, reducing to the fundamental inequality $E_k \leq H_{nn}$ for all n. However, for finite β it is not so obvious since higher eigenvalues of H do not necessarily lie lower than corresponding diagonal matrix elements H_{nn}. Schultz[64] skillfully remarked that, in fact, the Peierls inequality does not depend on the fact that $\exp[-E\beta]$ is a monotonically decreasing function of E, as might be concluded from the original proof. It depends only on the fact that the exponential function is concave upward. Schultz[64] proposed a simple proof of the theorem under this somewhat general condition.

Let φ_n be a complete orthonormal set of state vectors and let $\mathbf{A}$ be an Hermitian operator which for convenience is assumed to have a pure point spectrum with eigenvalues a_k and eigenstates ψ_k. Let $f(x)$ be a real-valued function such that

$$\frac{d^2 f}{dx^2} > 0 \tag{65}$$

in an interval including the whole spectrum of a_k. Then, if $\mathrm{Tr} f(\mathbf{A})$ exists it can be proven that the following statement holds

$$\mathrm{Tr} f(\mathbf{A}) \geq \sum_n f(a_{nn})\,, \tag{66}$$

where $a_{nn} = \langle n|\mathbf{A}|n\rangle$. The equality holds if φ_n are the eigenstates of $\mathbf{A}$.

Since

$$\mathrm{Tr} f(\mathbf{A}) = \sum_n \langle n|f(\mathbf{A})|n\rangle\,, \tag{67}$$

it is sufficient for the proof to point out that the relation (66) follows from

$$\langle n|f(\mathbf{A})|n\rangle \geq f(a_{nn})\,, \tag{68}$$

which is valid for all n. The inequalities (68) were derived from

$$f(a_k) \geq f(a_{nn}) + (a_k - a_{nn}) f'(a_{nn})\,, \tag{69}$$

which is a consequence of Eq. (65), the right-hand side for fixed n being the line tangent to $f(a_k)$ at a_{nn}. Multiplying (69) by $|\langle n|k\rangle|^2$ and summing on k one obtains (68). Schultz[64] observed further that the equality in (68) holds if, $|\langle n|k\rangle|^2 = 0$ unless $a_k = a_{nn}$, i.e., if φ_n is an eigenstate of $\mathbf{A}$.

If $f(\mathbf{A})$ is positive definite, then the set φ_n need not be complete, since the theorem is true even more strongly if positive terms are omitted from the sum $\sum_n f(a_{nn})$. With the choice $f(\mathbf{A}) = \exp(-\mathbf{A})$ and $\mathbf{A} = \mathbf{H}\beta$, the original theorem of Peierls giving an upper bound to the free energy is reproduced. With $\mathbf{A} = (\mathbf{H} - \mu\mathbf{N})\beta$ we have an analogous theorem for the grand potential. The theorem proved by Schultz[64] is a generalization in which it no longer requires $f(x)$ to be monotonic; it requires only that $\mathrm{Tr} f(\mathbf{A})$ be finite which can occur even if $f(x)$ is not monotonic provided $\mathbf{A}$ is bounded.

Peierls variational theorem was discussed and applied in a number of papers (see, for e.g., Refs. 64–67). It has much more generality than, say, the Lidiard[68] consideration on a minimum property of the free energy. Lidiard[68] derived the approximate free energy expression in a way which shows a strong analogy with the approximate Hartree method of quantum mechanics. By his derivation, he refined the earlier calculations made by Koppe and Wohlfarth in the context of description of the influence of the exchange energy on the thermal properties of free electrons in metals.

5. The Mean Field Concept

In general, a many-particle system with interactions is very difficult to solve exactly, except for special simple cases. Theory of molecular (or mean) field permits one to obtain an approximate solution to the problem. In condensed matter physics, mean field theory (or self-consistent field theory) studies the behavior of large many-particle systems by studying the simpler models. The effect of all the other particles on any given particle is approximated by a single averaged effect, thus reducing a many-body problem to a single-body problem.

It is well known that molecular fields in various variants appear in the simplified analysis of many different kinds of many-particle interacting systems. The mean field concept was originally formulated for many-particle systems (in an implicit form) in the Van der Waals[69,70] dissertation "On the Continuity of Gaseous and Liquid States". Van der Waals conjectured that the volume correction to the equation-of-state would lead only to a trivial reduction of the available space for the molecular motion by an amount b equal to the overall volume of the molecules. In reality, the measurements led him to a much more complicated dependence. He found that both the corrections should be taken into account. Those were the volume correction b and the pressure correction a/V^2, which led him to the Van der Waals equation.[70] Thus, Van der Waals came to conclusion that "the range of attractive forces contains many neighboring molecules". The equation derived by Van der Waals was similar to the ideal gas equation except that the pressure is increased and the volume decreased from the ideal gas values. Hence, the many-particle behavior was reduced to *effective* (or renormalized) behavior of a single particle in a medium (or a field). The later development of this line of reasoning led to the fruitful concept, that it may be reasonable to describe approximately the complex many-particle behavior of gases, liquids and solids in terms of a single particle moving in an average (or effective) field created by all the other particles, considered as some homogeneous (or inhomogeneous) environment.

Later, these ideas were extended to the physics of magnetic phenomena,[5,17,71,72] where magnetic substances were considered as some kind of a specific liquid. This approach was elaborated in the physics of magnetism by Curie and Weiss. The mean field (molecular field) replaces the interaction of all the other particles to an arbitrary particle.[73] In the mean field approximation, the energy of a system is replaced by the sum of identical single-particle energies that describe the interactions of each particle with an effective mean field.

Beginning from 1907 the Weiss molecular field approximation became widespread in the theory of magnetic phenomena,[5,17,71,72] and even at the present time it is still being used efficiently. Nevertheless, back in 1965 it was noticed that[74]:

> "*The Weiss molecular field theory plays an enigmatic role in the statistical mechanics of magnetism.*"

In order to explain the concept of the molecular field on the example of the Heisenberg ferromagnet one has to transform the original many-particle Hamiltonian

$$H = -\sum_{ij} J(i-j)\mathbf{S_i}\mathbf{S_j} - g\mu_B H \sum_i S_i^z \,, \tag{70}$$

into the following reduced one-particle Hamiltonian

$$\mathcal{H} = -2\mu_0\mu_B \mathbf{S}\cdot\mathbf{h}^{(\mathrm{mf})} \,.$$

The coupling coefficient $J(i-j)$ is the measure of the exchange interaction between spins at the lattice sites i and j and is defined usually to have the property $J(i-j=0)=0$. This transformation was achieved with the help of the identity[5,17,71,72]

$$\mathbf{S}\cdot\mathbf{S}' = \mathbf{S}\cdot\langle\mathbf{S}'\rangle + \langle\mathbf{S}\rangle\cdot\mathbf{S}' - \langle\mathbf{S}\rangle\cdot\langle\mathbf{S}'\rangle + C \,.$$

Here, the constant $C = (\mathbf{S}-\langle\mathbf{S}\rangle)\cdot(\mathbf{S}'-\langle\mathbf{S}'\rangle)$ describes the spin correlations. The usual molecular field approximation is equivalent to discarding the third term in the right-hand side of the above equation, and using the approximation $C \sim \langle C\rangle = \langle\mathbf{S}\cdot\mathbf{S}'\rangle - \langle\mathbf{S}\rangle\cdot\langle\mathbf{S}'\rangle$ for the constant C.

There is large diversity of the mean field theories adapted to various concrete applications.[5,17,71,72]

Mean field theory has been applied to a number of models of physical systems so as to study the phenomena such as phase transitions.[75,76] One of the first applications was Ising model.[5,17,71,72] Consider the Ising model on an N-dimensional cubic lattice. The Hamiltonian is given by

$$H = -J\sum_{\langle i,j\rangle} S_i S_j - h\sum_i S_i \,, \tag{71}$$

where the $\sum_{\langle i,j\rangle}$ indicates summation over the pair of nearest neighbors $\langle i,j\rangle$ and $S_i = \pm 1$ and S_j are neighboring Ising spins. Bunde[77] has shown that in the correctly performed molecular field approximation for ferromagnet and antiferromagnet, the correlation function $\langle S(\mathbf{q})S(-\mathbf{q})\rangle$ should fulfill the sum rule

$$N^{-1}\sum_q \langle S(\mathbf{q})S(-\mathbf{q})\rangle = 1 \,. \tag{72}$$

The Ising model of the ferromagnet was considered[77] and the correlation function $\langle S(\mathbf{q})S(-\mathbf{q})\rangle$ was calculated as

$$\langle S(\mathbf{q})S(-\mathbf{q})\rangle = \left[N^{-1}\sum_q \frac{1}{1-\beta J(\mathbf{q})}\right]^{-1} \frac{1}{1-\beta J(\mathbf{q})} \,, \tag{73}$$

which obviously fulfills the above sum rule. The Ising model and the Heisenberg model were the two most explored models for the applications of the mean field theory.

It is of instruction to mention that the earlier molecular field concepts described the mean field in terms of some functional of the average density of particles $\langle n\rangle$ (or, using the magnetic terminology, the average magnetization $\langle M\rangle$), that is, as

$F[\langle n\rangle, \langle M\rangle]$. Using the modern language, one can say that the interaction between the atomic spins S_i and their neighbors can be equivalently described by effective (or mean) field $h^{(\mathrm{mf})}$. As a result one can write down

$$M_i = \chi_0[h_i^{(\mathrm{ext})} + h_i^{(\mathrm{mf})}]\,. \tag{74}$$

The mean field $h^{(\mathrm{mf})}$ can be represented in the form (in the case $T > T_C$):

$$h^{(\mathrm{mf})} = \sum_i J(R_{ji})\langle S_i\rangle\,. \tag{75}$$

Here, h^{ext} is the external magnetic field, χ_0 is the system's response function and $J(R_{ji})$ is the interaction between the spins. In other words, in the mean field approximation a many-particle system is reduced to the situation, where the magnetic moment at any site aligns either parallel or antiparallel to the overall magnetic field, which is the sum of the applied external field and the molecular field.

Note that only the "*averaged*" interaction with i neighboring sites was taken into account, while the fluctuation effects were ignored. We see that the mean field approximation provides only a rough description of the real situation and overestimates the interaction between particles. Attempts to improve the homogeneous mean field approximation were undertaken along different directions.[5,17,35–37,71,72]

An extremely successful and quite nontrivial approach was developed by Neel,[5,17,71,72] who essentially formulated the concept of **local mean fields** (1932). Neel assumed that the sign of the mean field could be both positive and negative. Moreover, he showed that below some critical temperature (the Neel temperature) the energetically most favorable arrangement of atomic magnetic moments is such that there is an equal number of magnetic moments aligned against each other. This novel magnetic structure became known as the **antiferromagnetism**.[5,17]

It was established that the antiferromagnetic (AFM) interaction tends to align neighboring spins against each other. In the one-dimensional case this corresponds to an alternating structure, where an "**up**" spin is followed by a "**down**" spin and vice versa. Later, it was conjectured that the state made up from two sublattices inserted into each other is the ground state of the system (in the classical sense of this term). Moreover, there the mean field sign alternates in the "chessboard" (staggered) order.

The question of the true AFM ground state is not completely clarified up to the present time.[5,17,35–37,71,72] This is related to the fact that in contrast to ferromagnets, which have a unique ground state, antiferromagnets can have several different optimal states with the lowest energy. The Neel ground state is understood as a possible form of the system's wavefunction, describing the AFM ordering of all spins. Strictly speaking, the ground state is the thermodynamically equilibrium state of the system at zero temperature. Whether the Neel state is the ground state in this strict sense or not, is still unknown. It is clear though, that in the general case, the Neel state is not an eigenstate of the Heisenberg antiferromagnet's Hamiltonian. On the contrary, similar to any other possible quantum state, it is only some linear

combination of the Hamiltonian eigenstates. Therefore, the main problem requiring a rigorous investigation is the question of Neel state stability.[17] In some sense, only for infinitely large lattices, the Neel state becomes the eigenstate of the Hamiltonian and the ground state of the system. Nevertheless, the sublattice structure is observed in experiments on neutron scattering[17] and, despite certain worries, the actual existence of sublattices is beyond doubt.

Once Neel's investigations were published, the effective mean field concept began to develop at a much faster pace. An important generalization and development of this concept was proposed in 1936 by Onsager[78] in the context of the polar liquid theory. This approach is now called the *Onsager reaction field* approximation. It became widely known, in particular, in the physics of magnetic phenomena.[79–81] In 1954, Kinoshita and Nambu[82] developed a systematic method for description of many-particle systems in the framework of an approach which corresponds to the **generalized mean field** concept. Mermin[83] has analyzed the thermal Hartree–Fock approximation[84] of Green's function theory giving the free energy of a system not at zero temperature.

Kubo and Suzuki[85] studied the applicability of the mean field approximation and showed that the ordinary mean field theory is restricted only to the region $k_BT \geq zJ$, where J denotes the strength of typical interactions of the relevant system and z the number of nearest neighbors. Suzuki[86] has proposed a new type of fluctuating mean field theory. In that approach the true critical point $\tilde{T}_C$ differs from the mean field value and the singularities of response functions are, in general, different from those of the Weiss mean field theory.[17,71]

Zhou and Tao[87] developed a complete Hartree–Fock mean field method to study ferromagnetic (FM) systems at finite temperatures. With the help of the complete Bose transformation, they renormalized all the high-order interactions including both the dynamic and the kinetic ones based on an independent Bose representation, and obtained a set of compact self-consistent equations. Using their method, the spontaneous magnetization of an Ising model on a square lattice was investigated. The result is reasonably close to the exact one. Finally, they discussed the temperature dependences of the coercivities for magnetic systems and showed the hysteresis loops at different temperatures.

Later, various schemes of "effective mean field theory taking into account correlations" were proposed (see Refs. 17 and 37). We will see below that various mean field approximations can be in principle described in the framework of the variation principle in terms of the Bogoliubov inequality[1,3,5,10,15]:

$$\begin{aligned} F &= -\beta^{-1}\ln(\mathrm{Tr}\, e^{-\beta H}) \\ &\leq -\beta^{-1}\ln(\mathrm{Tr}\, e^{-\beta H_{\mathrm{mod}}}) + \frac{\mathrm{Tr} e^{-\beta H_{\mathrm{mod}}}(H - H_{\mathrm{mod}})}{\mathrm{Tr}\, e^{-\beta H_{\mathrm{mod}}}}\,. \end{aligned} \tag{76}$$

Here, F is the free energy of the system under consideration, whose calculation is extremely involved in the general case. The quantity H_{mod} is some trial Hamiltonian describing the effective field approximation. The inequality (76) yields an upper bound for the free energy of a many-particle system.

Variational principle of Bogoliubov

It is well known that the study of Hamiltonians describing strongly correlated systems is an exceptionally difficult many-particle problem, which requires applications of various mathematical methods.[17,88–91] In fact, with the exception of a few particular cases, even the ground state of the Hubbard model is still unknown. Calculation of the corresponding quasiparticle spectra in the case of strong interelectron correlations and correct definition of the mean fields also turned out to be quite a complicated problem.

The Hamiltonian of the Hubbard model[17] is given by

$$H = \sum_{ij\sigma} t_{ij} a^{\dagger}_{i\sigma} a_{j\sigma} + U/2 \sum_{i\sigma} n_{i\sigma} n_{i-\sigma}\,. \tag{77}$$

The above Hamiltonian includes the repulsion of the single-site intra-atomic Coulomb U, and t_{ij}, the one-electron hopping energy describing jumps from a j site to an i site. As a consequence of correlations, electrons tend to "avoid one another". Their states are best modeled by atom-like Wannier wavefunctions $[\phi(\mathbf{r}-\mathbf{R}_j)]$. The Hubbard model's Hamiltonian can be characterized by two main parameters: U and the effective bandwidth of tightly bound electrons

$$\Delta = \left(N^{-1} \sum_{ij} |t_{ij}|^2 \right)^{1/2}.$$

The band energy of Bloch electrons $\epsilon(\mathbf{k})$ is given by

$$\epsilon(\mathbf{k}) = N^{-1} \sum_{\mathbf{k}} t_{ij} \exp[-i\mathbf{k}(\mathbf{R}_i - \mathbf{R}_j]\,,$$

where N is the total number of lattice sites. Variations of the parameter $\gamma = \Delta/U$ allow one to study two interesting limiting cases, the band regime ($\gamma \gg 1$) and the atomic regime ($\gamma \to 0$).

There are many different approaches to construction of generalized mean field approximations; however, all of them have a special case character. The method of irreducible Green's functions[17,35–37] allows one to tackle this problem in a more systematic fashion.

The efficiency of the method of the irreducible Green's functions for description of normal and superconducting (SC) properties of systems with a strong interaction and complicated character of the electron spectrum was demonstrated in the literatures.[17,35–37] Let us consider the Hubbard model (77). The properties of this Hamiltonian are determined by the relationship between the two parameters: The effective bandwidth Δ and the electron's repulsion energy U. Drastic transformations of the metal–dielectric phase transition's type take place in the system as the ratio of these parameters changes. Note that, simultaneously, the character of the system description must change as well, that is, we always have to describe our system by the set of relevant variables. In the case of weak correlation,[17,35–37] the corresponding set of relevant variables contains the ordinary second-quantized Fermi operators and $a^{\dagger}_{i\sigma}$ $a_{i\sigma}$, as well as the number of particles operator $n_{i\sigma} = a^{\dagger}_{i\sigma} a_{i\sigma}$. In the case of strong correlation[17,35–37] the problem is highly complicated.

The Green's function in the generalized mean field approximation has the following very complicated functional structure[17,35–37]:

$$G^{\rm MF}_{k\sigma}(\omega) = \frac{\omega - (n^+_{-\sigma}E_- + n^-_{-\sigma}E_+) - \lambda(k)}{(\omega - E_+ - n^-_{-\sigma}\lambda_1(k))(\omega - E_- - n^+_{-\sigma}\lambda_2(k)) - n^-_{-\sigma}n^+_{-\sigma}\lambda_3(k)\lambda_4(k)}\,. \tag{78}$$

Here, the quantities $\lambda_i(k)$ are the components of the generalized mean field, which cannot be reduced to the functional of the mean particle's densities. The expression for Green's function (78) can be written down in the form of the following **generalized two-pole solution**:

$$\begin{aligned} G^{\rm MF}_{k\sigma}(\omega) &= \frac{n^+_{-\sigma}(1+cb^{-1})}{a - db^{-1}c} + \frac{n^-_{-\sigma}(1+da^{-1})}{b - ca^{-1}d} \\ &\approx \frac{n^-_{-\sigma}}{\omega - E_- - n^+_{-\sigma}W^-_{k-\sigma}} + \frac{n^+_{-\sigma}}{\omega - E_+ - n^-_{-\sigma}W^\dagger_{k-\sigma}}\,, \end{aligned} \tag{79}$$

where

$$\begin{aligned} n^+_{-\sigma}n^-_{-\sigma}W^\pm_{k-\sigma} &= N^{-1}\sum_{ij} t_{ij}\exp[-ik(R_i - R_j)] \\ &\times ((\langle a^\dagger_{i-\sigma}n^\pm_{i\sigma}a_{j-\sigma}\rangle + \langle a_{i-\sigma}n^\mp_{i\sigma}a^\dagger_{j-\sigma}\rangle) \\ &+ (\langle n^\pm_{j-\sigma}n^\pm_{i-\sigma}\rangle + \langle a_{i\sigma}a^\dagger_{i-\sigma}a_{j-\sigma}a^\dagger_{j\sigma}\rangle - \langle a_{i\sigma}a_{i-\sigma}a^\dagger_{j-\sigma}a^\dagger_{j\sigma}\rangle))\,. \end{aligned} \tag{80}$$

Green's function (79) is the *most general solution* of the Hubbard model within the generalized mean field approximation. Equation (80) is nothing else but the explicit expression for the generalized mean field. As we see, this mean field is not a functional of the mean particle's densities. The solution (79) is more general than the solution "*Hubbard III*"[17] and other two-pole solutions. Hence, it was shown in the papers[17,35–37] that the solution "*Hubbard I*"[17] is a particular case of the solution (79), which corresponds to the additional approximation

$$n^+_{-\sigma}n^-_{-\sigma}W^\pm(k) \approx N^{-1}\sum_{ij} t_{ij}\exp[-ik(R_i - R_j)]\langle n^\pm_{j-\sigma}n^\pm_{i-\sigma}\rangle. \tag{81}$$

Assuming $\langle n_{j-\sigma}n_{i-\sigma}\rangle \approx n^2_{-\sigma}$, we obtain the approximation "*Hubbard I*"[17,35–37]. Thus, we have shown that in the cases of systems of strongly correlated particles with a complicated character of quasiparticle spectrums the generalized mean fields can have quite a nontrivial structure, which is difficult to establish by using any kind of independent considerations. The method of irreducible Green's functions allows one to obtain this structure in the most general form.

One should note that the Bardeen–Cooper–Sehrieffer (BCS)–Bogoliubov superconductivity theory[1,3,5,10,15] is formulated in terms of a trial (approximating) Hamiltonian $H_{\rm mod}$, which is a quadratic form with respect to the second-quantized

creation and annihilation operators, including the terms responsible for anomalous (or nondiagonal) averages. For the single-band Hubbard model, the BCS–Bogoliubov functional of generalized mean fields can be written in the following form[92–95]:

$$\Sigma_\sigma^c = U \begin{pmatrix} \langle a_{i-\sigma}^\dagger a_{i-\sigma} \rangle & -\langle a_{i\sigma} a_{i-\sigma} \rangle \\ -\langle a_{i-\sigma}^\dagger a_{i\sigma}^\dagger \rangle & -\langle a_{i\sigma}^\dagger a_{i\sigma} \rangle \end{pmatrix} . \tag{82}$$

The *anomalous* (or nondiagonal) mean values in this expression fix the vacuum state of the system exactly in the BCS–Bogoliubov form.

It is worth mentioning that the modern microscopic theory of superconductivity was given a rigorous mathematical formulation in the classic works of Bogoliubov and co-workers[1,3,5,10,15] simultaneously with the BCS theory. It was shown that the equations of superconductivity can be derived from the fundamental electron–ion and electron–electron interactions. The set of equations obtained is known as the Eliashberg equations. They enable us to investigate the electronic and lattice properties of a metal in both the normal and SC states. Moreover, the Eliashberg equations are appropriate to the description of strong coupling superconductors, in contrast to the equations which are valid in the weak coupling regime, and describe the electron subsystem in the SC state only.

In Ref. 92, on the basis of the BCS–Bogoliubov functional of generalized mean fields a system of equations of superconductivity for the tight-binding electrons in the transition metal described by the Hubbard Hamiltonian was derived. The electron–phonon interaction was written down for the "rigid ion model". Neglecting the vertex corrections in the self-energy operator the closed system of equations was obtained.

In Ref. 93, this approach was extended for the Barisic–Labbe–Friedel model of a transition metal. The renormalized electron and phonon spectra of the model were derived using the method of irreducible Green's functions[17,35–37] in a self-consistent way. For the band and atomic limits of the Hubbard model the explicit solutions for the electron and phonon energies were obtained. The energy gap, appearing between electron bands in the strong correlation limit, persists in that calculations. The Eliashberg-type equations of superconductivity were also obtained.

The equations of strong coupling superconductivity in disordered transition metal alloys have been derived in paper[94] by means of irreducible Green's functions method and on the basis of the alloy version of the Barisic–Labbe–Friedel model for electron–ion interaction. The configurational averaging has been performed by means of the coherent potential approximation. Making some approximations, the formulas for the SC transition temperature T_C and the electron–phonon coupling constant have been obtained. These depend on the alloy component and total densities of states, the phonon Green's function and the parameters of the model.

To summarize, various schemes of "effective mean field theory" taking into account the correlations were proposed.[35–37,96–106] The main efforts were directed to the aim to describe suitably the collective behavior of particles in terms of effective

field distribution which satisfies a self-consistent condition. However, although the self-consistent field approximation often is a reasonable approximation away from the critical point, it usually breaks down in its immediate neighborhood.

It is of importance to stress again that from our point of view, in real mean field theory, the mean field appearing in the single-site problem should be a scalar or vectorial **time-independent** quantity.

6. Symmetry Broken Solutions

The formalism of the previous sections may be extended to incorporate the broken symmetry solutions[17,18,107] of the interacting many-particle systems, e.g., the pairing effects present in superconductors,[3,4,15] etc. Our purpose in this section is to attract the attention to subtle points which are essential for establishing a connection of the generalized mean field approximation and the broken symmetry solutions.[17,18,107]

It is well known that a symmetry can be exact or approximate. Symmetries inherent in the physical laws may be dynamically and spontaneously broken, i.e., they may not manifest themselves in the actual phenomena. It can be as well broken by certain reasons.[108,109]

Within the literature, the term *broken symmetry* is used both very often and with different meanings. There are two terms, the spontaneous breakdown of symmetries and dynamical symmetry breaking, which sometimes have been used as opposed but such a distinction is irrelevant. However, the two terms may be used interchangeably. It should be stressed that a symmetry implies degeneracy. In general, there are a multiplets of equivalent states related to each other by congruence operations. They can be distinguished only relative to a weakly coupled external environment which breaks the symmetry. Local gauged symmetries, however, cannot be broken this way because such an extended environment is not allowed (a superselection rule), so all states are singlets, i.e., the multiplicities are not observable except possibly for their global part.

It is known that when the Hamiltonian of a system is invariant under a symmetry operation, but the ground state is not, the symmetry of the system can be spontaneously broken. Symmetry breaking is termed *spontaneous* when there is no explicit term in a Lagrangian which manifestly breaks the symmetry.

Peierls[110,111] gave a general definition of the notion of the spontaneous breakdown of symmetries which is suited equally well for the physics of particles and condensed matter physics. According to Peierls,[110,111] the term *broken symmetries* relates to situations in which symmetries which we expect to hold are valid only approximately or fail completely in certain situations.

The intriguing mechanism of spontaneous symmetry breaking is a unifying concept that lie at the basis of most of the recent developments in theoretical physics, from statistical mechanics to many-body theory and to elementary particles theory.[108,109] The existence of degeneracy in the energy states of a quantal system

is related to the invariance or symmetry properties of the system. By applying the symmetry operation to the ground state, one can transform it to a different but equivalent ground state. Thus. the ground state is degenerate, and in the case of a continuous symmetry, infinitely degenerate. The real, or relevant, ground state of the system can only be one of these degenerate states. A system may exhibit the full symmetry of its Lagrangian, but it is characteristic of infinitely large systems that they also may condense into states of lower symmetry.

It should be pointed out that Bogoliubov's method of quasiaverages[3,4,15] gives the deep foundation and clarification of the concept of broken symmetry. It makes the emphasis on the notion of degeneracy and plays an important role in equilibrium statistical mechanics of many-particle systems. According to that concept, infinitely small perturbations can trigger macroscopic responses in the system if they break some symmetry and remove the related degeneracy (or quasidegeneracy) of the equilibrium state. As a result, they can produce macroscopic effects even when the perturbation magnitude tends to zero, provided that happens after passing to the thermodynamic limit.[45] This approach has penetrated, directly or indirectly, many areas of the contemporary physics.

The article[18] examines the Bogoliubov's notion of quasiaverages, from the original papers,[4] through to modern theoretical concepts and ideas of how to describe both the degeneracy, broken symmetry and the diversity of the energy scales in the many-particle interacting systems. Current trends for extending and using Bogoliubov's ideas to quantum field theory and condensed matter physics problems were discussed, including microscopic theory of superfluidity and superconductivity, quantum theory of magnetism of complex materials, Bose–Einstein condensation, chirality of molecules, etc. Practical techniques covered include quasiaverages, Bogoliubov theorem on the singularity of $1/q^2$, Bogoliubov's inequality and its applications to condensed matter physics.

It was demonstrated there that the profound and innovative idea of quasiaverages formulated by Bogoliubov, gives the so-called macro-objectivation of the degeneracy in the domain of quantum statistical mechanics, quantum field theory and in the quantum physics in general.

The quasiaverages may be obtained from the ordinary averages by using the cluster property which was formulated by Bogoliubov.[3,4,15] This was first done when deriving the Boltzmann equations from the chain of equations for distribution functions and in the investigation of the model Hamiltonian in the theory of superconductivity.[3,4,15] To demonstrate this let us consider averages (quasiaverages) of the form:

$$F(t_1, x_1, \ldots t_n, x_n) = \langle \ldots \Psi^\dagger(t_1, x_1) \ldots \Psi(t_j, x_j) \ldots \rangle \,, \tag{83}$$

where the number of creation operators $\Psi^\dagger$ may be not equal to the number of annihilation operators Ψ. We fix times and split the arguments $(t_1, x_1, \ldots, t_n, x_n)$ into several clusters $(\ldots, t_\alpha, x_\alpha, \ldots), \ldots, (\ldots, t_\beta, x_\beta, \ldots)$. Then, it is reasonable to assume that the distances between all clusters $|x_\alpha - x_\beta|$ tend to infinity. Then,

according to the cluster property, the average value (83) tends to the product of averages of collections of operators with the arguments $(\ldots, t_\alpha, x_\alpha, \ldots), \ldots,$ $(\ldots, t_\beta, x_\beta, \ldots)$

$$\lim_{|x_\alpha - x_\beta| \to \infty} F(t_1, x_1, \ldots, t_n, x_n) = F(\ldots, t_\alpha, x_\alpha, \ldots) \ldots F(\ldots, t_\beta, x_\beta, \ldots)\,. \quad (84)$$

For equilibrium states with small densities and short-range potential, the validity of this property can be proved.[3,4,15] For the general case, the validity of the cluster property has not yet been proved. Bogoliubov formulated it not only for ordinary averages but also for quasiaverages, i.e., for anomalous averages, too. It works for many important models, including the models of superfluidity and superconductivity.[3,4,15]

In his work *The Theory of Superfluidity*,[112] Bogoliubov gave a microscopic explanation of the phenomenon of superfluidity.[2,113] Before his works, there were phenomenological theories which were based on an assumption about the form of the spectrum of elementary excitations. Bogoliubov has started from the general Hamiltonian for Bose systems and assumed that a macroscopic number of particles are found in the ground state with zero momentum, and therefore the creation and annihilation operators of particles with zero momentum are c-numbers.[114] As a result a definite *approximating* Hamiltonian was obtained, consisting from a quadratic form of the creation and annihilation operators. The usual perturbation theory proved to be inapplicable to it because of the strong interaction of particles with opposite momenta. Therefore, the Hamiltonian was diagonalized with the help of the canonical transformations (the Bogoliubov $u - v$ transformations). This permitted one to calculate the spectrum of elementary perturbations outside the framework of perturbation theory. Decomposing the field operators into c-numerical and operator parts, Bogoliubov in fact introduced into quantum theory the method of *spontaneous symmetry breakdown* for systems with degenerate ground state. This method was rediscovered in quantum field theory a decade later.[18]

To illustrate these statements consider Bogoliubov's theory of a Bose system with separated condensate, which is given by the Hamiltonian[3,4,15]

$$H_\Lambda = \int_\Lambda \Psi^\dagger(x)\left(-\frac{\Delta}{2m}\right)\Psi(x)dx - \mu\int_\Lambda \Psi^\dagger(x)\Psi(x)dx$$

$$+\frac{1}{2}\int_{\Lambda^2} \Psi^\dagger(x_1)\Psi^\dagger(x_2)\Phi(x_1 - x_2)\Psi(x_2)\Psi(x_1)dx_1dx_2\,. \quad (85)$$

This Hamiltonian can be also written in the following form:

$$H_\Lambda = H_0 + H_1 = \int_\Lambda \Psi^\dagger(q)\left(-\frac{\Delta}{2m}\right)\Psi(q)dq$$

$$+\frac{1}{2}\int_{\Lambda^2} \Psi^\dagger(q)\Psi^\dagger(q')\Phi(q - q')\Psi(q')\Psi(q)dqdq'. \quad (86)$$

Here, $\Psi(q)$ and $\Psi^\dagger(q)$ are the operators of annihilation and creation of bosons. They satisfy the canonical commutation relations:

$$[\Psi(q), \Psi^\dagger(q')] = \delta(q - q'), \quad [\Psi(q), \Psi(q')] = [\Psi^\dagger(q), \Psi^\dagger(q')] = 0\,. \tag{87}$$

The system of bosons is contained in the cube A with the edge L and volume V. It was assumed that it satisfies the periodic boundary conditions and the potential $\Phi(q)$ is spherically symmetric and proportional to the small parameter. It was also assumed that, at temperature zero, a certain macroscopic number of particles having a nonzero density is situated in the state with momentum zero.

The operators $\Psi(q)$ and $\Psi^\dagger(q)$ are represented in the form:

$$\Psi(q) = a_0/\sqrt{V}; \quad \Psi^\dagger(q) = a_0^\dagger/\sqrt{V}\,, \tag{88}$$

where a_0 and $a_0^\dagger$ are the operators of annihilation and creation of particles with momentum zero.

To explain the phenomenon of superfluidity,[4,112] one should calculate the spectrum of the Hamiltonian, which is quite a difficult problem. Bogoliubov suggested the idea of approximate calculation of the spectrum of the ground state and its elementary excitations based on the physical nature of superfluidity. His idea consists of a few assumptions. The main assumption is that at temperature zero the macroscopic number of particles (with nonzero density) has the momentum zero. Therefore, in the thermodynamic limit,[45] the operators $a_0/\sqrt{V}$ and $a_0^\dagger/\sqrt{V}$ commute,

$$\lim_{V\to\infty} [a_0/\sqrt{V}, a_0^\dagger/\sqrt{V}] = \frac{1}{V} \to 0\,, \tag{89}$$

and are c-numbers. Hence, the operator of the number of particles $N_0 = a_0^\dagger a_0$ is a c-number too.

Petrina[115] shed an additional light on the problem of an approximation of general Hamiltonians by Hamiltonians of the theories of superconductivity and superfluidity. In his highly interesting paper,[115] Petrina pointed out that the model Hamiltonian of the theory of superconductivity[3,15] can be obtained from the general Hamiltonian for Fermi systems if the Kronecker symbol, which expresses the law of conservation of momentum in the interaction Hamiltonian, is replaced by two Kronecker symbols so that only particles with opposite momenta interact. The model Hamiltonian of the theory of superfluidity can be obtained from the general Hamiltonian for Bose systems if we replace the Kronecker symbol, which expresses the law of conservation of momentum, by several Kronecker symbols, preserving only the terms that contain at least two operators with momenta zero in the interaction Hamiltonian. This list of model systems can be continued.[116]

The concept of quasiaverages was introduced by Bogoliubov on the basis of an analysis of many-particle systems with a degenerate statistical equilibrium state. Such states are inherent to various physical many-particle systems. Those are

liquid helium in the superfluid phase, metals in the SC state, magnets in the ferromagnetically ordered state, liquid crystal states, the states of superfluid nuclear matter, etc.

In many-body interacting systems, the symmetry is important in classifying different phases and in understanding the phase transitions between them. According to Bogoliubov's ideas[3,4,15,107,112] in each condensed phase, in addition to the normal process, there is an anomalous process (or processes) which can take place because of the long-range internal field, with a corresponding propagator. Additionally, the Goldstone theorem[18] states that, in a system in which a continuous symmetry is broken (i.e., a system such that the ground state is not invariant under the operations of a continuous unitary group whose generators commute with the Hamiltonian), there exists a collective mode with frequency vanishing, as the momentum goes to zero. For many-particle systems on a lattice, this statement needs a proper adaptation. In the above form, the Goldstone theorem is true only if the condensed and normal phases have the same translational properties. When translational symmetry is also broken, the Goldstone mode appears at a zero frequency but at nonzero momentum, e.g., a crystal and a helical spin-density-wave ordering (see for discussion Refs. 17 and 117).

The AFM state is characterized by a spatially changing component of magnetization which varies in such a way that the net magnetization of the system is zero. The concept of antiferromagnetism of localized spins which is based on the Heisenberg model and the two-sublattice Neel ground state is relatively well-founded contrary to the antiferromagnetism of delocalized or itinerant electrons. The itinerant-electron picture is the alternative conceptual picture for magnetism.[118] In the AFM many-body problem, there is an additional "symmetry broken" aspect.[17,117] For an antiferromagnet, contrary to ferromagnet, the one-electron Hartree–Fock potential can violate the translational crystal symmetry. The period of the AFM spin structure L is greater than the lattice constant a. The Hartree–Fock is the simplest approximation but neglects the important dynamical part. To include the dynamics one should take into consideration the correlation effects.

The anomalous propagators for an interacting many-fermion system corresponding to FM, AFM and SC long-range ordering are given by

$$\begin{aligned} &\text{FM}\colon G_{\text{fm}} \sim \langle\langle a_{k\sigma}; a^{\dagger}_{k-\sigma}\rangle\rangle\,, \\ &\text{AFM}\colon G_{\text{afm}} \sim \langle\langle a_{k+Q\sigma}; a^{\dagger}_{k+Q'\sigma'}\rangle\rangle\,, \\ &\text{SC}\colon G_{\text{sc}} \sim \langle\langle a_{k\sigma}; a_{-k-\sigma}\rangle\rangle\,. \end{aligned} \tag{90}$$

In the spin-density-wave case, a particle picks up a momentum $Q-Q'$ from scattering against the periodic structure of the spiral (nonuniform) internal field, and has its spin changed from σ to σ' by the spin-aligning character of the internal field.

The long-range-order (LRO) parameters are

$$\begin{aligned} &\text{FM}\colon m = 1/N \sum_{k\sigma} \langle a^\dagger_{k\sigma} a_{k-\sigma} \rangle \,, \\ &\text{AFM}\colon M_Q = \sum_{k\sigma} \langle a^\dagger_{k\sigma} a_{k+Q-\sigma} \rangle \,, \\ &\text{SC}\colon \Delta = \sum_{k} \langle a^\dagger_{-k\downarrow} a^\dagger_{k\uparrow} \rangle \,. \end{aligned} \tag{91}$$

It is of importance to note that the LRO parameters are functions of the internal field, which is itself a function of the order parameter. There is a more mathematical way of formulating this assertion. As it was stressed earlier,[18] the notion *symmetry breaking* means that the state fails to have the symmetry that the Hamiltonian has.

In terms of the theory of quasiaverages, a true breaking of symmetry can arise only if there are infinitesimal "source fields". Indeed, for the rotationally and translationally invariant Hamiltonian, suitable source terms should be added:

$$\begin{aligned} &\text{FM}\colon \varepsilon\mu_B H_x \sum_{k\sigma} a^\dagger_{k\sigma} a_{k-\sigma} \,, \\ &\text{AFM}\colon \varepsilon\mu_B H \sum_{kQ} a^\dagger_{k\sigma} a_{k+Q-\sigma} \,, \\ &\text{SC}\colon \varepsilon v \sum_{k} (a^\dagger_{-k\downarrow} a^\dagger_{k\uparrow} + a_{k\uparrow} a_{-k\downarrow}) \,, \end{aligned} \tag{92}$$

where $\varepsilon \to 0$ is to be taken at the end of calculations.

For example, broken symmetry solutions of the spin-density-wave type imply that the vector Q is a measure of the inhomogeneity or breaking of translational symmetry.

In this context, the Hubbard model is a very interesting tool for analyzing the broken symmetry concept.[35–37] It is possible to show that AFM state and more complicated states (e.g., ferrimagnetic) can be made eigenfunctions of the self-consistent field equations within an "extended" (or generalized) mean field approach, assuming that the *anomalous* averages $\langle a^\dagger_{i\sigma} a_{i-\sigma} \rangle$ determine the behavior of the system on the same footing as the "normal" density of quasiparticles $\langle a^\dagger_{i\sigma} a_{i\sigma} \rangle$. It is clear, however, that these "spin-flip" terms break the rotational symmetry of the Hubbard Hamiltonian. For the single-band Hubbard Hamiltonian, the averages $\langle a^\dagger_{i-\sigma} a_{i,\sigma} \rangle = 0$ because of the rotational symmetry of the Hubbard model. The inclusion of *anomalous* averages leads to the following approximation:

$$n_{i-\sigma} a_{i\sigma} \approx \langle n_{i-\sigma} \rangle a_{i\sigma} - \langle a^\dagger_{i-\sigma} a_{i\sigma} \rangle a_{i-\sigma} \,. \tag{93}$$

Thus, in addition to the standard Hartree–Fock term, the new so-called "*spin-flip*" terms are retained.[117] This example clearly shows that the structure of mean field follows from the specificity of the problem and should be defined in a proper way.

So, one needs a properly defined effective Hamiltonian $H_{\rm eff}$. In Ref. 117, we thoroughly analyzed the proper definition of the irreducible Green's functions which includes the "spin-flip" terms for the case of itinerant antiferromagnetism of correlated lattice fermions. For the single-orbital Hubbard model,[35–37,117] the definition of the "irreducible" part should be modified in the following way:

$$^{(\rm ir)}\langle\langle a_{k+p\sigma}a^{\dagger}_{p+q-\sigma}a_{q-\sigma}|a^{\dagger}_{k\sigma}\rangle\rangle_{\omega} = \langle\langle a_{k+p\sigma}a^{\dagger}_{p+q-\sigma}a_{q-\sigma}|a^{\dagger}_{k\sigma}\rangle\rangle_{\omega} - \delta_{p,0}\langle n_{q-\sigma}\rangle G_{k\sigma} - \langle a_{k+p\sigma}a^{\dagger}_{p+q-\sigma}\rangle\langle\langle a_{q-\sigma}|a^{\dagger}_{k\sigma}\rangle\rangle_{\omega}\,. \tag{94}$$

From this definition it follows that this way of introduction of the irreducible Green's functions broadens the initial algebra of operators and the initial set of the Green's functions. This means that the "actual" algebra of operators must include the spin-flip terms from the beginning, namely: ($a_{i\sigma}$, $a^{\dagger}_{i\sigma}$, $n_{i\sigma}$, $a^{\dagger}_{i\sigma}a_{i-\sigma}$). The corresponding initial Green's function will be of the form:

$$\begin{pmatrix} \langle\langle a_{i\sigma}|a^{\dagger}_{j\sigma}\rangle\rangle & \langle\langle a_{i\sigma}|a^{\dagger}_{j-\sigma}\rangle\rangle \\ \langle\langle a_{i-\sigma}|a^{\dagger}_{j\sigma}\rangle\rangle & \langle\langle a_{i-\sigma}|a^{\dagger}_{j-\sigma}\rangle\rangle \end{pmatrix}. \tag{95}$$

With this definition, one introduces the so-called anomalous (off-diagonal) Green's functions which fix the relevant vacuum and select the proper symmetry broken solutions. In fact, this approximation was investigated earlier by Kishore and Joshi.[119] They clearly pointed out that they assumed a system to be magnetized in the x-direction instead of the conventional z-axis.

The problem of finding the SC, FM and AFM "symmetry broken" solutions of the correlated lattice fermion models within irreducible Green's functions method was investigated in Refs. 17, 35–37 and 117. A unified scheme for the construction of **generalized mean fields** (elastic scattering corrections) and self-energy (inelastic scattering) in terms of the Dyson equation was generalized in order to include the "source fields". The "symmetry broken" dynamic solutions of the Hubbard model which correspond to various types of itinerant antiferromagnetism were discussed as well.[17,35–37,117] This approach complements the previous studies of microscopic theory of the Heisenberg antiferromagnet[120] and clarifies the concepts of Neel sublattices for localized and itinerant antiferromagnetism and "spin-aligning fields" of correlated lattice fermions.

We shall see shortly that in order to discuss the mean field theory (and generalized mean fields) on the firm ground the Bogoliubov inequality provides the formal basis and effective general approach.

7. The Mathematical Tools

Before entering fully into our subject, we must recall some basic statements. This will be necessary for the following discussion.

The number of inequalities in mathematical physics is extraordinarily plentiful and the literature on inequalities is vast.[121–133] The physicists are interested mostly

in intuitive, physical forms of inequalities rather than in their most general versions. Often it is easier to catch the beauty and importance of original versions rather than decoding their later, abstract forms.

Many inequalities are of a great use and directly related with the notion of entropy, especially with quantum entropy.[124,134] The von Neumann entropy of $\rho \in \mathbf{S_n}$, $S(\rho)$, is defined by

$$S(\rho) = -\mathrm{Tr}(\rho \log \rho)\,. \tag{96}$$

The operator $\rho \log \rho$ is defined using the spectral theorem.[124] Here, $\mathbf{S_n}$ denotes the set of density matrices ρ on $\mathbb{C}^n$. In fact, $S(\rho)$ depends on ρ only through its eigenvalues.

$$S(\rho) = -\sum_{j=1}^{n} \lambda_j \log \lambda_j\,. \tag{97}$$

Otherwise put, the von Neumann entropy is unitarily invariant; that is

$$S(U\rho U^*) = S(\rho)\,. \tag{98}$$

The convexity condition leads to[124]

$$-S(\rho) = -\log(n)\,. \tag{99}$$

This equality is valid if each $\lambda_j = 1/n$. Thus, one may arrive at[124]

$$0 \leq S(\rho) \leq \log n \tag{100}$$

for all $\rho \in \mathbf{S_n}$, and there is equality on the left if ρ is a pure state, and there is equality on the right if $\rho = (1/n)I$. Actually, $S(\rho)$ is not only a strictly concave function of the eigenvalues of ρ, it is strictly concave function of ρ itself.

The notions of convexity and concavity of trace functions[124] are of great importance in mathematical physics.[135,136] Inequalities for quantum mechanical entropies and related concave trace functions play a fundamental role in quantum information theory as well.[124,134]

A function f is *convex* in a given interval if its second derivative is always of the same sign in that interval. The sign of the second derivative can be chosen as positive (by multiplying by (-1) if necessary). Indeed, the notion of convexity means that if $d^2f/dx^2 > 0$ in a given interval, x_j are a set of points in that interval, p_j are a set of weights such that $p_j \geq 0$, which have the property $\sum_j p_j = 1$, then

$$\sum_j p_j f(x_j) \geq f\left(\sum_j p_j x_j\right)\,. \tag{101}$$

The equality will be valid only if $x_j = \langle x \rangle = \sum_j p_j x_j$. In other words, a real-valued function $f(x)$ defined on an interval is called convex (or convex downward or concave upward) if the line segment between any two points on the graph of the function lies **above** the graph, in a Euclidean space (or more generally a vector

space) of at least two dimensions. Equivalently, a function is *convex* if its epigraph (the set of points on or above the graph of the function) is a convex set.

A real-valued function f on an interval (or, more generally, a convex set in vector space) is said to be concave if, for any x_1 and x_2 in the interval and for any α in $[0, 1]$,

$$f((1-\alpha)x_1 + (\alpha)x_2) \geq (1-\alpha)f(x_1) + (\alpha)f(x_2)\,. \tag{102}$$

A function $f(x)$ is *concave* over a convex set if the function $-f(x)$ is a convex function over the set.

As an example, we mentioned above briefly a reason why this concavity matters, pointing to the inequality (100) that was deduced from the concavity of the entropy as a function of the eigenvalues of ρ.

It is of importance to stress that in quantum statistical mechanics, equilibrium states are determined by maximum entropy principles,[124] and the fact that

$$\sup S(\rho)\big|_{\rho\in\mathbf{S_n}} = \log n\,, \tag{103}$$

reflects the famous Boltzmann formula

$$S = k_B \log W\,. \tag{104}$$

It follows from Boltzmann definition that the entropy is larger if ρ is smeared out, where ρ is the probability density on phase space. The microscopic definition of entropy given by Boltzmann does not, by itself, explain the second law of thermodynamics, even in classical physics. The task to formulate these questions in a quantum framework was addressed by Klein in his seminal paper[137] of 1931. He found a fundamentally new way for information to be lost hence entropy to increase, special to quantum mechanics. This result was called Klein's lemma.[136–138]

Ruskai[138] has reviewed many fundamental properties of the quantum entropy[134] including one important class of inequalities which relates the entropy of subsystems to that of a composite system. That article presented self-contained proofs of the strong subadditivity inequality for von Neumann quantum entropy, $S(\rho)$, and some related inequalities for the quantum relative entropy, most notably its convexity and its monotonicity under stochastic maps. The approach to subadditivity and relative entropy presented was used to obtain conditions for equality in properties of relative entropy, including its joint convexity and monotonicity. In addition, the Klein inequality was presented there in detail.

Indeed, the fact that the relative entropy is positive,[138] i.e., $H(\rho_1, \rho_2) \geq 0$ when $\mathrm{Tr}\rho_1 = \mathrm{Tr}\rho_2$, is an immediate consequence of the following fundamental convexity result due to Klein.[137,139,140] The corresponding theorem[138] states that for A, $B > 0$

$$\mathrm{Tr}\, A(\log A - \log B) \geq \mathrm{Tr}(A - B)\,, \tag{105}$$

with equality iff $(A = B)$.

In more general form,[124] the Klein inequality may be formulated in the following way. For all $A, B \in \mathbf{H}_n$, and all differentiable convex functions $f\colon \mathbb{R} \to \mathbb{R}$, or for all $A, B \in \mathbf{H}_n^{\dagger}$ and all differentiable convex functions $f\colon (0, \infty) \to \mathbb{R}$,

$$\mathrm{Tr}(f(A) - f(B) - (A - B)f'(B)) \geq 0\,. \tag{106}$$

In either case, if f is strictly convex, there is equality if $A = B$.

A few more words about Oskar Klein and his inequality will not be out of place here. Oskar Klein (1894–1977) was the famous Swedish theoretical physicist who worked on a wide variety of subjects.[141] For example, the Klein–Gordon equation was the first relativistic wave equation. Oskar Klein was also a collaborator of Niels Bohr in Copenhagen. It is interesting to note that Oskar Klein defended his thesis and was awarded his doctoral degree in 1921 for his work in physical chemistry about strong electrolytes. In 1931 Oskar Klein,[137,139–141] using his experience in both quantum and statistical mechanics, succeeded in solving the problem of whether the quantum statistics on molecular level can explain how the entropy increases with time in accordance with the second law of thermodynamics. The problem in classical statistical mechanics had been already noticed by Gibbs earlier. Klein's proof,[137,139,140] which used the statement that only the diagonal elements in the density matrix for the phase space of the particles are relevant for the entropy, has led him to the Klein's lemma. With Klein's lemma, the entropy can increase according to the formula of Boltzmann's microscopic definition, where it is described with the number of states in the phase space. A useful and informative discussion of the Klein's paper and Klein's lemma was carried out in the book of Jancel.[142]

According to Ruskai,[138] the closely related Peierls–Bogoliubov inequality is sometimes used instead of Klein's inequality. Golden–Thompson and Peierls–Bogoliubov inequalities were extended to von Neumann algebras, which have traces, by Ruskai[128] (see also Ref. 143). Araki[129] extended them to a general von Neumann algebra. This kind of investigations is particularly valuable since the Bogoliubov inequality is remarkable because of its significant applications in statistical quantum mechanics.[3,10–12,144,145] It provides insight into a number of other interesting questions as well.

It will be of use to write down the mathematical formulation of Peierls–Bogoliubov inequalities which was provided by Carlen.[124] Let us consider $A \in \mathbf{H_n}$, and let f be any convex function on $\mathbb{R}$. Let $\{u_1, \ldots, u_n\}$ be any orthonormal base of $\mathbb{C}^n$. Then

$$\sum_{j=1}^{n} (\langle u_j, Au_j \rangle) \leq \mathrm{Tr}[f(A)]\,. \tag{107}$$

There is equality if each u_j is an eigenvector of A, and if f is strictly convex, only in this case.

Now consider the formulation of the generalized Peierls–Bogoliubov inequality.[124] For every natural number n, the map $A \mapsto \log(\mathrm{Tr}[\exp(A)])$ is convex on $\mathbf{H_n}$.

As a consequence one may deduce[124] that

$$\log\left(\frac{\mathrm{Tr}[\exp(A+B)]}{\mathrm{Tr}[\exp(A)]}\right) \geq \frac{\mathrm{Tr}[B\exp(A)]}{\mathrm{Tr}[\exp(A)]}\,. \tag{108}$$

Frequently this relation, which has many uses, is referred to as the Peierls–Bogoliubov inequality.

It is worth noting that according to tradition the term *Gibbs–Bogoliubov inequality*[8] is used for a classical statistical mechanical systems and term *Peierls–Bogoliubov inequality*[124] for quantum statistical mechanical systems. At the very least, it must have been meant to indicate that Peierls inequality does not have a classical analog, whereas Bogoliubov inequality has.

8. Variational Principle of Bogoliubov

It is known that there are several variational principles which provide upper bounds for the Helmholtz free energy function. With these instruments, it is possible to construct various approximations to the statistical thermodynamic behavior of systems. For any variational formulation, its effectiveness as a minimal principle will be enhanced considerably if there is a workable tool for determining lower bounds to the Helmholtz free energy function. Bogoliubov inequality for the free energy functional is an inequality that gives rise to a variational principle of statistical mechanics. It is used[1–5] to obtain the exact thermodynamic limit[18] solutions of model problems in statistical physics, in studies using the method of molecular fields, in proving the existence of the thermodynamic limit,[45] and also in order to obtain physically important estimates for the free energies of various many-particle interacting systems. A clear formulation of the variational principle of Bogoliubov and Bogoliubov inequality for the free energy functional was carried out by Tyablikov.[5] We shall follow close to that formulation. Tyablikov[5] used the theorems relating to the minimum values of the free energy. As a result, it was possible to formulate a principle which then was used to deduce the molecular field equations.

Principle of the free energy minimum is based on the following arguments. Let us consider an arbitrary complete system of orthonormalized functions $\{\varphi_n\}$, which are not the eigenfunctions of the Hamiltonian $\mathcal{H}$ of a system. Then it is possible to write down the inequality

$$F(\mathcal{H}) \leq F_{\mathrm{mod}}(\mathcal{H})\,. \tag{109}$$

Here, $F(\mathcal{H})$ is the intrinsic free energy of the system:

$$F(\mathcal{H}) = -\theta \ln Z, \quad Z = \sum_{\nu} \exp(-E_\nu/\theta)\,, \tag{110}$$

$\theta = k_B T$, E_ν are the eigenfunctions of the Hamiltonian $\mathcal{H}$, $F_{\mathrm{mod}}(\mathcal{H})$ is the *model* free energy, which gives approximately the upper limit of the intrinsic free energy:

$$F_{\mathrm{mod}}(\mathcal{H}) = -\theta \ln Z_{\mathrm{mod}}, \quad Z_{\mathrm{mod}} = \sum_{n} \exp(-\mathcal{H}_{nn}/\theta), \quad \mathcal{H}_{nn} = (\varphi_n^*, \mathcal{H}\varphi_n)\,. \tag{111}$$

The inequality (109) may be also written in the following way:

$$Z \geq Z_{\rm mod}\,. \tag{112}$$

The relationships represented by the equality sign in Eqs. (109) and (112) applies if φ_n are eigenfunctions of the Hamiltonian of the system. It should be noted that for finite values of the number of partial sums $Z^{(N)}$, the quantity $F^{(N)}_{\rm mod}$ does not reach its maximum for any system of functions $\varphi_1, \ldots, \varphi_N$. In fact, the inequality will be satisfied really[5,45] in the limit $N \to \infty$.

Using these results, it is possible to formulate a variational principle for the approximate determination of the free energy of a system.[5] To proceed, let us suppose that the functions $\{\varphi_n\}$ depend on some arbitrary parameter λ. It was established above that

$$F(\mathcal{H}) \leq F_{\rm mod}(\mathcal{H}) = -\theta \ln \sum_n \exp(-\mathcal{H}_{nn}(\lambda)/\theta)\,. \tag{113}$$

It is clear that the best approximation for the upper limit of the free energy F is obtained by selecting the values of the parameter λ in accordance with the condition for the minimum of the model free energy $F_{\rm mod}$. Indeed, let the Hamiltonian of the system, $\mathcal{H}$, be written in the form:

$$\mathcal{H} = \mathcal{H}_0(\lambda) + \Delta\mathcal{H}(\lambda) \equiv \mathcal{H}_0(\lambda) + (\mathcal{H} - \mathcal{H}_0(\lambda))\,, \tag{114}$$

where $\mathcal{H}_0(\lambda)$ is some operator depending on the parameter λ. The concrete form of the operator $\mathcal{H}_0(\lambda)$ should be selected on the basis of convenience in calculations. We shall use notation E^0_n and φ_n for the eigenvalues and the eigenfunctions of the operator $\mathcal{H}_0$. To denote the diagonal matrix elements of the operator $\Delta\mathcal{H}$ in terms of the functions φ_n we shall use the notation $\Delta\mathcal{H}_{nn}$.

For a generality, we shall assume that φ_n are not the eigenfunctions of the total Hamiltonian $\mathcal{H}$. Clearly, E^0_n and $\Delta\mathcal{H}_{nn}$ are also some functions of the parameter λ. In this sense, the system of functions $\{\varphi_n\}$ plays a role of a *trial* system of functions. Then, we may write that

$$\mathcal{H}_{nn} = E^0_n + \Delta\mathcal{H}_{nn} \equiv E^0_n + (\mathcal{H}_{nn} - E^0_n)\,. \tag{115}$$

As a consequence, the free energy will satisfy the inequality

$$F(\mathcal{H}) \leq -\theta \ln \sum_n \exp -(E^0_n + \Delta\mathcal{H}_{nn})\frac{1}{\theta}\,. \tag{116}$$

Now let us suppose that the operator $\Delta\mathcal{H}$ can be considered as a *small perturbation* compared with the operator $\mathcal{H}$. We obtain then,[5] to within quantities of the first-order of smallness with respect to $\Delta\mathcal{H}$,

$$F(\mathcal{H}) \leq F(\mathcal{H}_0) + \frac{{\rm Tr}(\Delta\mathcal{H}\exp(-\mathcal{H}_0/\theta))}{{\rm Tr}(\exp(-\mathcal{H}_0/\theta))}\,. \tag{117}$$

Note that in this case, the best approximation to the upper limit of the free energy is obtained by selecting the value of the parameter λ from the condition for the

minimum of the right-hand side of Eq. (117). The formulation of the variational principle of Eq. (117) is more restricted than the initial formulation of Eq. (109).

The variational principle in the form of Eq. (117) can be strengthened, following the Bogoliubov suggestion,[5] by removing the limitation of the smallness of the operator $\Delta\mathcal{H}$. As a result we obtain

$$F(\mathcal{H}) \leq F_{\rm mod}(\mathcal{H})\,. \tag{118}$$

Here,

$$F_{\rm mod}(\mathcal{H}) = F(\mathcal{H}_0) + \frac{{\rm Tr}(\Delta\mathcal{H}\exp(-\mathcal{H}_0/\theta))}{{\rm Tr}(\exp(-\mathcal{H}_0/\theta))}\,, \tag{119}$$

$$F(\mathcal{H}_0) = -\theta \ln {\rm Tr}\exp(-\mathcal{H}_0/\theta)\,. \tag{120}$$

Hence, one may write down also that for a system with the Hamiltonian

$$\mathcal{H} = \mathcal{H}_0 + \Delta\mathcal{H}\,, \tag{121}$$

the free energy has a certain upper bound. Bogoliubov inequality states that:

$$F \leq F_0 + \langle\mathcal{H} - \mathcal{H}_0\rangle_0 \tag{122}$$

or

$$F \leq F_0\langle\mathcal{H}\rangle_0 - TS_0\,, \tag{123}$$

where S_0 is the entropy and the average is taken over the equilibrium ensemble of the reference system with Hamiltonian $\mathcal{H}_0$. Usually $\mathcal{H}_0$ contains one or more variational parameters which are chosen such as to minimize the right-hand side of Eq. (122). In the special case that the reference Hamiltonian is that of a noninteracting system and can thus be written as a sum of single-particle Hamiltonians[5]:

$$\mathcal{H}_0 = \sum_{i=1}^{N} h_i\,. \tag{124}$$

Then it is possible to improve the upper bound by minimizing the right-hand side of the inequality (122). The minimizing reference system is then the trial approximation to the true system using noncorrelated degrees of freedom, and is known as *the mean field approximation*.

Starting with the one-particle model Hamiltonian that can be exactly solved in the Bogoliubov variational method, one may get a self-consistent result such as the molecular field theory in the ferromagnet and the Hartree–Fock approximation in many-particle problems. Since the variational method yields a result which is always greater than the correct answer, the mathematical meaning for improving upon the approximation in the variational method is strictly defined by lowering the upper bound of the free energy. But these variational methods, the molecular field theory and the Hartree–Fock approximation, have such a feature that the correlation effects cannot be taken into account correctly. In general case,[5] the Hamiltonian of a

system contains interparticle interactions. Thus, Bogoliubov variational principle can be considered as the mathematical foundation of the mean field approximation in the theory of many-particle interacting systems.

Using the Klein inequality (106) it is possible to write down a general form of the Bogoliubov inequality for the free energy functional. The following inequality is valid for any Hermitian operators H_1 and H_2:

$$N^{-1}\langle H_1 - H_2\rangle_{H_1} \leq (f(H_1) - f(H_2)) \leq N^{-1}\langle H_1 - H_2\rangle_{H_2}\,, \tag{125}$$

where

$$f(H) = -\theta N^{-1} \ln \mathrm{Tr} \exp(-H/\theta)\,. \tag{126}$$

This expression has the meaning of the free energy density for a system with Hamiltonian H and the extensive parameter N may be treated as the number of particles or the volume, depending on the system.

Derrick[146] established a simple variational bound to the entropy $S(E)$ of a system with energy E,

$$S(E) \geq -k_B \ln(\mathrm{Tr}\, U^2)\,, \tag{127}$$

for all Hermitian matrices U (with no negative eigenvalues) for which $\mathrm{Tr}\, U = 1$ and $\mathrm{Tr}(HU) = E$, where H is the Hamiltonian. This principle has the advantage that U^2 is in general much easier to evaluate than $U \ln U$ which appears in the conventional bound given by von Neumann,

$$S(E) \geq -k_B(\mathrm{Tr}\, U \ln U)\,. \tag{128}$$

There are numerous methods for proving the Bogoliubov inequality.[5,10–12,39,48,147,148] Oguchi[149] proposed an approach for determination of an upper bound and a lower bound of the Helmholtz free energy in the statistical physics. He used the Klein's lemma as a basic tool.[124,137,138] He obtained a new approximate expression of the free energy. This approximate value of the free energy was conjectured to be greater than the lower bound and less than the upper bound. An approach which can be extended to improve the approximation was formulated. The upper bound and the lower bound of the approximate free energy converge to the true free energy as the successive approximation proceeds. The method was first applied to the Ising ferromagnet and then applied to the Heisenberg ferromagnet. In the simplest approximation, the results agree with the Bethe–Peierls approximation for the Ising model and the constant-coupling approximation for the Heisenberg model. In his subsequent paper, Oguchi[150] formulated a new variational method for the free energy in statistical physics. According to his calculations, the value of the free obtained by using this new variational method was lower than that of the Bogoliubov variational method. Author concluded that the new variational free energy satisfies the thermodynamic stability criterion.

However, Stolze[151] by careful examination of the papers,[149,150] has shown that the calculation in Ref. 150 contains a mistake which invalidates the result. He

also pointed out several errors seriously affecting the results of an earlier paper.[149] Oguchi assumed that the Hamiltonian $\mathcal{H}_0$ contains a variational parameter "a" distributed according to a probability density $P(a)$. Stolze derived a corrected inequality which clearly states that the new upper bound on the free energy suggested by Oguchi[149,150] cannot be better (i.e., lower) than the Peierls–Bogoliubov bound, no matter how cleverly $P(a)$ was chosen. This shows clearly that no advantage over the Peierls–Bogoliubov bound was obtained.

The standard proof was given in Callen's second edition book on thermodynamics[48] for the case when the unperturbed Hamiltonian and the perturbation commute. Another proof (for the general case), was carried out in Feynman book on statistical mechanics.[147] Feynman used Baker–Campbell–Hausdorff expansion[123,124] for the exponential of a sum of two noncommuting operators. Prato and Barraco[148] presented a proof of the Bogoliubov inequality that does not require the Baker–Campbell–Hausdorff expansion.

Several variational approaches for the free energy have been proposed[152,153] as attempts to improve the results obtained through the well-established Bogoliubov principle. This principle requires the use of a trial Hamiltonian depending on one or more variational parameters. The only way to improve the Bogoliubov principle by itself is to choose a more complete trial Hamiltonian, closing it to the exact one, but in almost all cases the possibilities are soon exhausted. The usual mean field approximation may be obtained using the above principle utilizing a sum of single spins in an effective field (the variational parameter) as the trial Hamiltonian.

Lowdin[154] and Lowdin and Nagel[155] studied a generalization of the Gibbs–Bogoliubov inequality $F \leq F_0 + \langle \mathcal{H} - \mathcal{H}_0 \rangle_0$ for the free energy F which leads to a variation principle for this quantity that may be of importance in certain computational applications to quantum systems. This approach is coupled with a study of the perturbation expansion of the free energy for a canonical ensemble with $\mathcal{H} = \mathcal{H}_0 + \lambda V$ in the general case when $\mathcal{H}_0$ and V do not commute. A simple proof was given for the thermodynamic inequality $F - F_0 - \langle \mathcal{H} - \mathcal{H}_0 \rangle_0 < 0$ in the case when the two Hamiltonian $\mathcal{H}_0$ and V do not commute. The second- and high-order derivatives of the free energy with respect to the perturbation parameter λ were calculated. From the second-order term a second-order correction to the previous variational minimum was finally obtained for the free energy.

Decoster[39] established a sequence of inequalities which generalize the Gibbs–Bogoliubov inequality in classical statistical mechanics and the Peierls and Bogoliubov inequalities in quantum mechanics; they can be presented as rearrangements of perturbation expansions, which provide exact bounds which are used in variational calculations.

Kramarczyk[156] argued that the Bogoliubov variational principle may be shown to be equivalent to the minimizing of the information gained while replacing the exact state by an approximate one. Consequently, the quasiparticles introduced in the thermal Hartree–Fock approximation may be redefined information theoretically.

9. Applications of the Bogoliubov Variational Principle

Bogoliubov variational principle has been successfully applied to a wide range of problems in the theory of many-particle systems. The first application of Bogoliubov inequality to concrete many-particle problem was carried out in the work by Kvasnikov[157] on the application of a variational principle to the Ising model of ferromagnetism.

Ising model[17,158] is defined by the following Hamiltonian $\mathcal{H}$ (i.e., energy functional of variables; in this case the "spins" $S_i = \pm 1$ on the N sites of a regular lattice in a space of dimension d)

$$\mathcal{H} = -\frac{1}{2}\sum_{i<j=1}^{N} J_{ij} S_i S_j - \mu_B H \sum_{i=1}^{N} S_i \,. \tag{129}$$

Here, J_{ij} play the role of "exchange constants", H is a (normalized) magnetic field, involving an interpretation of the model to describe magnetic ordering in solids ($\mathbf{M} = \sum_{i=1}^{N} S_i$ is "magnetization"; $\mu_B H \mathbf{M}$ is the Zeeman energy, i.e., is the energy gained due to application of the field). The main task is to calculate statistical sum Z as

$$Z = \sum_{S_i} \exp -(\mathcal{H}/\theta) \,. \tag{130}$$

Kvasnikov[157] considered the approximation of nearest neighbors, i.e., $J_{ij} = J$ for nearest neighbors $\langle i, j\rangle$.

According to Bogoliubov variational principle, one can write

$$F \le F_0 + \langle \mathcal{H} - \mathcal{H}_0 \rangle_0 \,. \tag{131}$$

The upper bound for the free energy $F_{\sup}$ is given by

$$F_{\sup} = -\theta \ln Z_{\inf} \,, \tag{132}$$

where

$$Z_{\inf} = Z_0 \exp -(S/\theta), \quad Z_0 = \mathrm{Tr} \exp -(\mathcal{H}_0/\theta) \,; \tag{133}$$

$$S = (Z_0)^{-1} \mathrm{Tr}(\Delta\mathcal{H} \exp -[\mathcal{H}_0/\theta]) \,. \tag{134}$$

The parameters of partition, which were introduced into $\mathcal{H}_0$ and $\Delta\mathcal{H}$, and, hence, into Z_0 and S, should be determined from the condition of the minimum of $F_{\sup}$. Thus, we obtain

$$-\frac{\mathcal{H}_0}{\theta} = \mu_B (B - \chi) \sum_{i=1}^{N} S_i \,, \tag{135}$$

$$-\frac{\Delta\mathcal{H}}{\theta} = \mu_B \chi \sum_{i=1}^{N} S_i + \frac{1}{2}\sum_{i\neq j}^{N} K_{ij} S_i S_j \,, \tag{136}$$

where $B = H/\theta$, $K = J/\theta$, χ is some parameter. Then, according to relation (132), one finds

$$(Z_{\inf}(\chi))^{-1} = 2\coth\mu_B(B-\chi)\exp\left\{\mu_B\chi\tanh\mu_B(B-\chi) + \frac{1}{2N}\sum_{i\neq j}^{N}K_{ij}\tanh^2\mu_B(B-\chi)\right\}. \quad (137)$$

Parameter χ is determined by the equations

$$\tanh\mu_B(\chi - B) = \frac{N}{\sum K_{ij}}\mu_B\chi, \quad 1 - \frac{1}{N}\sum K_{ij} + \frac{N}{\sum K_{ij}}(\mu_B\chi)^2 > 0\,. \quad (138)$$

When the approximation of nearest neighbors is considered in the above equations the following substitution should be done:

$$\sum_{i\neq j}^{N}K_{ij} = zKN\,, \quad (139)$$

where z is the number of nearest neighbors. Hence $F_{\sup}$ is an approximate expression for the free energy and $Z_{\inf}$ is the approximate statistical sum of the model. It will be of instruction to compare these values with those which were calculated by other methods. To proceed, let us consider the regions of low and high temperatures. In the first case, we will have that $\theta \ll zJ$. The low-temperature approximation is expressed as a series expansion in terms of the small parameter $\exp(-K)$. The iterative solution of Eq. (138) will have the form:

$$\mu_B\chi = -zK(1 - 2\exp 2(-Kz - \mu_B B) - 8zK\exp 4(-Kz - \mu_B B) + \cdots)\,. \quad (140)$$

It is sufficient to confine oneself to the values of the order $\exp(-2Kz)$. The result is

$$(Z_{\inf})^{-1} = \exp(Kz/2 + \mu_B B)(1 + \exp 2(-Kz - B) + \cdots)\,. \quad (141)$$

This result is in accordance with the other low-temperature expansions[5,158]

$$Z = \exp 2(Kz/2 + \mu_B B)N \times \left(1 + N\exp 2(-Kz - \mu_B B) + \frac{Nz}{2}\exp 4[-K(z-1) - \mu_B B] + \left\{\frac{N(N-1)}{2} - \frac{Nz}{2}\right\}\exp 4(-Kz - \mu_B B) + \ldots\right). \quad (142)$$

In the case of the high temperature, when $\theta \geq zJ$, the approximate solution of the Eq. (138) will have the form:

$$\mu_B\chi \simeq -zK\frac{\tanh\mu_B B}{1 - [zK/\cosh^2\mu_B B]}\,. \quad (143)$$

Then after some transformations one can arrive to the expression (up to the terms K^3):

$$Z_{\text{inf}} \simeq [2\cosh \mu_B B]^N \left(1 + \frac{1}{2} K z \tanh^2 \mu_B B + \frac{1}{8} K^2 z N [4z \tanh^2 \mu_B B + (Nz + 4z) \tanh^4 \mu_B B]\right) . \quad (144)$$

This expression is also in accordance with the known high-temperature expansions[5,158] for $N \gg z$. Let us consider now the expression for magnetization[159] (the averaged magnetic moment)

$$M = \frac{1}{N} \frac{\partial \ln Z_{\text{inf}}}{\partial B} . \quad (145)$$

Using Eq. (138), we obtain

$$\frac{m}{\mu_B p} = \tanh \mu_B \left(\frac{H}{\theta} + n \frac{m}{\theta}\right) , \quad (146)$$

where p is the number of lattice sites per unit volume, $m = Mp$ is the magnetization per unit volume. This result coincides with the result of the phenomenological theory.[5] The corresponding basic values of the Weiss theory, the Curie point θ_0 and Weiss parameter w have the form:

$$\theta_0 = \frac{1}{N} \sum_{i \neq j}^{N} J_{ij}; \quad w = \frac{N^{-1} \sum J_{ij}}{\mu_B^2 p} = \frac{\theta_0}{\mu_B^2 p} . \quad (147)$$

Hence, with the help of the Bogoliubov variational scheme it was possible to calculate the reasonable approximate expression for the statistical sum of the Ising model and describe the macroscopic properties of FM systems in the wide interval of temperatures. It is thus seen that one may derive directly a consistent mean field-type theory from a variational principle.

Clearly Bogoliubov variational principle had a deep impact on the field of statistical mechanics of classical and quantum many-particle systems by making possible the analysis of complex statistical systems. Many interesting developments can be viewed from the point of a central theme, namely the Bogoliubov inequality, in particular in quantum theory of magnetism[5,159–163] and interacting many-body systems.[91,164–171]

Radcliffe[160] carried out a systematic investigation of the approximate free energies and Curie temperatures that can be obtained by using trial density matrices (which describe various possible decompositions of the ferromagnet into clusters) in a variational calculation of the free energy. Single-spin clusters lead to the molecular field model (as is well known) and two-spin clusters yield the Oguchi pair model.[71] The relation of the *constant-coupling* method to these approximations was clarified. A rigorous calculations using three-spin clusters were carried out.

Rudoi[161] investigated the link between Bogoliubov statistical variational principle for free energy, the method of partial diagram summation of the perturbation theory and the Luttinger–Ward theorem. On the basis of Matsubara's Green's function method he solved the nonlinear integral Dyson equation by approximating the effective potential. As a result, a new implicit equation of magnetic state was obtained for the Ising model.

Soldatov[172] generalized the Peierls–Bogoliubov inequality. A set of inequalities was derived instead, so that every subsequent inequality in this set approximates the quantity in question with better precision than the preceding one. These inequalities lead to a sequence of improving upper bounds to the free energy of a quantum system if this system allows representation in terms of coherent states. It follows from the results obtained that nearly any upper bound to the ground state energy obtained by the conventional variational principle can be improved by means of the proposed method.

Abubrig[173] studied the mixed spin-3/2 and spin-2 Ising ferrimagnetic system with different single-ion anisotropies in the absence of an external magnetic field within the mean field theory based on Bogoliubov inequality for the Gibbs free energy. Second-order critical lines were obtained in the temperature anisotropy plane. Tricritical line separating second-order and first-order lines was found. Finally, the existence and dependence of a compensation points on single-ion anisotropies was also investigated for the system. It was shown that this mixed-spin model exhibits one, two or three compensation temperature depending on the values of the anisotropies.

10. The Variational Schemes and Bounds on Free Energy

During last few decades, numerous variational schemes have become an increasingly popular workable tool in quantum mechanical many-particle theory.[5,10,11,14] Bounds of free energy and canonical ensemble averages were of considerable interest as well. For many complex systems, such as Ising and Heisenberg ferromagnets or composite materials, methods of obtaining bounds are the practical useful tools which are both tractable and informative. A few illustrative topics will be of instruction to discuss in this context.

MacDonald and Richardson[174] used the density matrix of von Neumann to formulate an exact variational principle for quantum statistics which embodies the principle of maximization of entropy. In terms of the formalism of second quantization, the authors wrote this variational principle for fermions or bosons and then derived from it an approximate variational procedure which yields the particle states of a system of interacting bosons or fermions as well as the distribution of particles in these states. These equations, in authors opinion, yield the generalization of the Hartree–Fock equations for nonzero temperature and the corresponding extension to bosons.

Schattke[175] found an upper bound for the free energy for SC system in magnetic field. Starting from the BCS theory, the free energy was obtained by a combination of a variational method and perturbation theory. The variational equations obtained were nonlocal. The parameters of the perturbation calculation were the vector potential and the spatial variations of the order parameter, which have to be small. Boundary conditions were set for the case of diffuse reflection and pair-breaking at the surface. As an example, the SC plate was discussed.

Krinsky *et al.* used[176] the variational principle to derive a new approximation to a ferromagnet in a magnetic field, below its critical temperature. They considered[176] a ferromagnet in an external magnetic field with $T \leq T_C$. Using a variational approximation based on the zero-field solution, the authors obtained an upper bound on the free energy, an approximate equation-of-state and a lower bound on the magnetization, all having the correct critical indices. Explicit numerical calculations have been carried out for the two-dimensional Ising model, and it was found that the results obtained provide a good approximation to the results of series expansions throughout the region $T \leq T_C$.

The Gibbs–Bogoliubov inequality[8] was used[177] to develop a first-order perturbation theory that provides an upper bound on the Helmholtz free energy per unit volume of a classical statistical mechanical system in terms of the free energy and pair distribution function. Charged systems as well as a system of Lennard-Jones particles were discussed and detailed numerical estimates of the bounds were presented.

Okubo and Isihara[178] derived important general inequalities for the derivatives of the partition function of a quantum system with respect to the parameters included in the Hamiltonian. Applications of the inequalities were used to discuss relations for critical initial exponents, kinetic energy, susceptibility, electrical conductivity and so on. Existence of an inconsistency analogous to the Schwinger-term difficulty in the quantum field theory was pointed out.

In their second paper,[179] Okubo and Isihara analyzed from a general point of view an inequality for convex functions in quantum statistical mechanics. From an inequality for a convex function of two Hermitian operators, the Peierls and Gibbs operators, coarse graining and other important inequalities were derived in a unified way. Various different forms of the basic inequality were given. They are found useful in discussing the entropy and other physical problems. Special accounts were given of functions such as $\exp(x)$ and $x \log x$.

A variational method for many-body systems using a separation into a difference of Hamiltonians was presented by Hader and Mertens.[180] A particular ansatz for the wavefunction was considered which leads to an upper bound for the exact ground state energy. This allowed a variation with respect to a separation parameter. The method was tested for a one-dimensional lattice with Morse interactions where the Toda subsystems can be solved by the Bethe ansatz. In two limiting cases the results obtained were exact, otherwise they were in agreement with the quantum transfer integral method.

Yeh[181–183] proposed a derivation of a lower bound on the free energy; in addition he analyzed the bounds of the average value of a function.[183] He also established[181] a weaker form of Griffiths theorem for the FM Heisenberg model. It was described as follows[182]: Free energy in the canonical ensemble was taken as

$$F = -\beta^{-1} \ln \sum_n \langle n| \exp(-H\beta)|n\rangle \,, \tag{148}$$

where $|n\rangle$ is any complete set of orthonormal states. Bounds of F can be obtained from bounds of $\langle n| \exp(-H\beta)|n\rangle$. As we seen, a very simple upper bound of F was given by Peierls[63]; one way to prove his theorem is by showing that

$$\langle \psi| \exp(-H\beta)|\psi\rangle \geq \exp(-\beta\langle\psi|H|\psi\rangle) \,. \tag{149}$$

Yeh[182] derived a rather simple lower bound of F by similar method. He considered a Hamiltonian with a ground state energy $E_0 = 0$. He considered a real function $f(E) = \exp(-E\beta)$, $\beta > 0$. It was shown that for any normalized state $|\psi\rangle$ a weaker but simpler upper bound for f may be written as

$$\exp(-\beta\langle\psi|H|\psi\rangle p) \geq \langle\psi| \exp(-H\beta)|\psi\rangle \geq \exp(-\beta\langle\psi|H|\psi\rangle) \,, \tag{150}$$

where

$$p = \exp\left(\frac{(-\beta\langle\psi|H^2|\psi\rangle)}{\langle\psi|H|\psi\rangle}\right) . \tag{151}$$

Identifying $\beta = (k_B T)^{-1}$ and H as Hamiltonian, a lower bound of free energy was obtained from Eq. (150) as

$$F \geq -\beta^{-1} \ln \sum_\psi \exp\big(-\beta\langle\psi|H|\psi\rangle p\big) \tag{152}$$

where $|\psi\rangle$ is any complete orthonormal set of states. This is a general formula for a lower bound on the free energy.

Upper and lower bounds of the canonical ensemble average of any operator A can be written down in terms of $\langle\varphi_n|H|\varphi_n\rangle$, where φ_n are the eigenstates of A. Furthermore, bounds of thermodynamic derivatives can be obtained by noting that the bounds of

$$\frac{\partial^i \bar{f}}{\partial\beta^i} \tag{153}$$

can be also derived[182] in similar manner. Here,

$$\bar{f} = \langle\psi| \exp(-H\beta)|\psi\rangle = \sum_n \rho_n \exp(-E_n\beta); \quad \sum_n \rho_n = 1 \,. \tag{154}$$

From Eq. (150), it is clear that all the bounds are more accurate at higher temperatures. These bounds have been useful in determining the properties of Heisenberg ferromagnets.[181]

Symanzik[184] proved, refined and generalized a lower bound given by Feynman for the quantum mechanical free energy of an oscillator. The method, application of

a classical inequality to path integrals, also gives upper bounds for one-temperature Green's functions.

Heise and Jelitto[185] formulated the asymptotically exact variational approach to the strong coupling Hubbard model. They used a generalization of Bogoliubov variational principle, in order to develop a molecular field theory of the Hubbard model, which becomes asymptotically exact in the strong coupling limit. In other words, in their paper the authors have started from a generalized form of Bogoliubov variational theorem in order to set up a theory of the Hubbard model, which yields nontrivial results in the strong coupling regime and becomes asymptotically exact in the strong coupling limit. For this purpose the Hamiltonian was rotated by a unitary two-particle transformation, before the variational principle was applied. However, the real form of the generalized mean fields for the Hubbard model in the strong coupling regime was not determined in complete form. This task was fulfilled by Kuzemsky in a series of papers.[17,35–37]

Zeile[186] proposed a generalization of Feynman variational principle for real path integrals in a systematic way. He obtained an asymptotic series of lower bounds for the partition function. The author claimed that the method was tested on the anharmonic oscillator and showed excellent agreement with exact results. However, Dorre *et al.*[187] using the equivalence between Feynman and Bogoliubov variational principle, discussed[187] in the formalism of Hamiltonian quantum mechanics an improved upper bound for the free energy which has been given by Zeile[186] using path integral methods. It was shown that Zeile's variational principle does not guarantee a thermodynamically consistent description.

Brandt and Stolze formulated[188] a new hierarchy of upper and lower bounds on expectation values. Upper and lower bounds were constructed for expectation values of functions of a real random variable with derivatives up to the order $(N+1)$ which are alternately negative and positive over the whole range of interest. The bounds were given by quadrature formulas with weights and abscissas determined by the first $(N+1)$ moments of the underlying probability distribution. Application to a simple disordered phonon system yielded sharp bounds on the specific heat.

Vlachos[171] proposed a variational method that uses the frequency and the energy shift as variational parameters. The quantum mechanical partition function was approximated by a formally simple expression, for a generalized anharmonic oscillator in one and many dimensions. The numerical calculations for a single quartic and two coupled quartic oscillators have led to nearly exact values for the free energy, the ground state and the difference between the ground state and the first excited state.

Predescu[189] presented a generalization of the Gibbs–Bogoliubov–Feynman inequality for spinless particles and then illustrated it for the simple model of a symmetric double-well quartic potential. The method gives a pointwise lower bound for the finite-temperature density matrix and it can be systematically im-

proved by the Trotter composition rule. It was also shown to produce ground state energies better than the ones given by the Rayleigh–Ritz principle as applied to the ground state eigenfunctions of the reference potentials. Based on this observation, it was conjectured that the *local variational principle* may perform better than the equivalent methods based on the centroid path idea and on the Gibbs–Bogoliubov–Feynman variational principle, especially in the range of low temperatures. However, clear evidence for such a statement was not given.

All these points of view acquire significance of the variational principles as a general method of solution for better insight into the complicated behavior of the many-particle systems.

11. The Hartree–Fock–Bogoliubov Mean Fields

The microscopic theory of superconductivity was created simultaneously by Bardeen *et al.* and Bogoliubov.[192–198] An important contribution to the theory of superconductivity were the works of Fröhlich,[199] who put forward the idea of the importance of the electron–phonon interaction for the phenomenon of superconductivity, and the theory of Schafroth, Butler and Blatt,[200] who conjectured that superconductivity is due to Bose–Einstein condensation of correlated electron pairs. In their paper, Bardeen *et al.*, determined the ground state energy and the spectrum of elementary excitations of their model.[190,191] The BCS theory was constructed on the basis of a model Hamiltonian that takes into account only the interaction of electrons with opposite momenta and spins, whereas Bogoliubov theory was based on the Fröhlich Hamiltonian[199] and used the method of compensation of dangerous diagrams.[194] Bogoliubov *et al.*, have generalized to Fermi systems the Bogoliubov method of canonical transformations proposed earlier in connection with a microscopic theory of superfluidity for Bose systems.[112] This approach has formed the basis of a new method for investigating the problem of superconductivity. Starting from Fröhlich Hamiltonian, the energy of the SC ground state and the one-fermion and collective excitations corresponding to this state were obtained. It turns out that the final formulae for the ground state and one-fermion excitations obtained independently by Bardeen *et al.*[190] were correct in the first approximation. The physical picture appears to be closer to the one proposed by Schafroth, Butler and Blatt. The effect on superconductivity of the Coulomb interaction between the electrons was analyzed in detail. A criterion for the superfluidity of a Fermi system with a four-line vertex Hamiltonian was established.

Roughly speaking, to explain simply the theory of superconductivity it is possible to say that the Fermi sea is unstable against the formation of a bound Cooper pair when the net interaction is attractive; it is reasonable to expect that the pairs will be condensed until an equilibrium point is reached. The corresponding antisymmetric wavefunctions for many electrons was constructed in BCS model.[201,202] They noted also that their solution may be considered as an exact in the thermodynamic limit.

The most clear and rigorous arguments in favor of the statement that the BCS model is an exactly solvable model of statistical physics were advanced in the papers of Bogoliubov *et al.*[192,197,198] They showed that the free energy and the correlation functions of the BCS model and a model with a certain approximating quadratic Hamiltonian are indeed identical in the thermodynamic limit. In his theory,[192–198] Bogoliubov gave a rigorous proof that at vanishing temperature the correlation functions and mean values of the energy of the BCS model and the Bogoliubov–Zubarev–Tserkovnikov model are equal in the thermodynamic limit. Moreover, Bogoliubov constructed a complete theory of superconductivity on the basis of a model of interacting electrons and phonons.[192–198] Generalizing his method of canonical transformations[15,203,204] to Fermi systems and advancing the principle of compensation of dangerous graphs,[194] he determined the ground state consisting of paired electrons with opposite moments and spins, its energy and the energy of elementary excitations. It was shown also that the phenomenon of superconductivity consists in the pairing of electrons and a phase transition from a normal state with free electrons to a SC state with pair condensate.

The pairing Hamiltonian has the form:

$$\mathcal{H} - \mu\mathcal{N} = \sum_{k\sigma} E(k) a^{\dagger}_{k\sigma} a_{k\sigma} + \sum_{kp} V(k,p) a^{\dagger}_{k\uparrow} a^{\dagger}_{-k\downarrow} a_{-p\downarrow} a_{p\uparrow}\,, \tag{155}$$

where μ is the chemical potential and $\mathcal{N}$ is the number of particles.

The essential step which was made by Bogoliubov was connected with introducing the anomalous averages or the generalized mean fields $F_p = \langle a_{-p\downarrow} a_{p\uparrow}\rangle$. It is reasonable to suppose that because of the large number of particles involved, the fluctuations of $a_{-p\downarrow} a_{p\uparrow}$ about these expectations values F_p must be small. Hence, it is possible to express such products of operators in the form:

$$a_{-p\downarrow} a_{p\uparrow} = F_p + (a_{-p\downarrow} a_{p\uparrow} - F_p)\,. \tag{156}$$

It is reasonable to suppose that one may neglect the quantities which are bilinear in the presumably small fluctuation term in brackets. This way leads to the Bogoliubov model Hamiltonian of the form:

$$\mathcal{H}_{\rm mod} - \mu\mathcal{N} = \sum_{k\sigma} E(k) a^{\dagger}_{k\sigma} a_{k\sigma} + \sum_{kp} V(k,p)(a^{\dagger}_{k\uparrow} a^{\dagger}_{-k\downarrow} F_p + F^{*}_k a_{-p\downarrow} a_{p\uparrow} - F^{*}_k F_p)\,. \tag{157}$$

Here the F_k should be determined self-consistently.[192–198]

Thus, Bogoliubov created a rigorous theory of superfluidity[112] and superconductivity[198] within the unified scheme[115] of the nonzero anomalous averages or the generalized mean fields, and showed that at the physical basis of these two fundamental phenomena of nature lies the process of condensation of Bose particles[116] and, respectively, pairs of fermions.

Indeed, Bogoliubov *et al.*,[192,197] have shown on the basis of the model Hamiltonian of BCS–Bogoliubov, that the thermodynamic functions of a superconducting

system, which were obtained by a variation method in BCS, are asymptotically exact for $V \to \infty, N/V = \text{const}$. ($V$ is the volume of the system and N the number of particles). This conclusion was based on the fact that each term of the perturbation theory series, by means of which the correction to that solution was calculated, is asymptotically small for $V \to \infty$. In addition, it was shown that it is possible to satisfy with asymptotic exactness the entire chain of equations for Green's functions constructed on the basis of the model Hamiltonian of BCS–Bogoliubov. Thus, the asymptotic exactness of the known solution for the SC state was proved without the use of perturbation theory. It was shown also that the trivial solution that corresponds to the normal state should be rejected at temperatures below the critical temperature. In other words, starting with the *reduced Hamiltonian of superconductivity theory*, Bogoliubov *et al.*[192,197] proved the possibility of exact calculation of the free energy per unit volume.

Somewhat later, on the basis of the BCS theory, a similar investigation was made by other authors.[205–208] Muhlschlegel[205] studied an asymptotic expansion of the BCS partition function by means of the functional method. The canonical operator $\exp[-\beta(H - \mu N)]$ associated with the BCS model Hamiltonian of superconductivity was represented as a functional integral by the use of Feynman's ordering parameter. General properties of the partition function in this representation were investigated. Taking the inverse volume of the system as an expansion parameter, it was possible to calculate the thermodynamic potential including terms independent of the volume. Muhlschlegel's theory yielded an additional evidence that the BCS variational value is asymptotically exact. The behavior of the canonical operator for large volume was described and related to the state of free quasiparticles. A study of the terms of the thermodynamic potential which were of smaller order in volume in the low-temperature limit, showed that the ground state energy is *nondegenerate* and belongs to a number eigenstate.

Thirring and Wehrl[209] investigated in which sense the Bogoliubov–Haag treatment of the BCS–Bogoliubov model gives the correct solution in the limit of infinite volume. They found that in a certain subspace of the infinite tensor product space the field operators show the correct time behavior in the sense of strong convergence. Thus, a solution of the SC type with a gap in the spectrum of elementary excitations really can exist for the model Hamiltonian of BCS–Bogoliubov.

In general, the problem of explaining the phenomenon of superconductivity required the solution of the very difficult mathematical problems associated with the foundation of applied approximations.[2,15] In connection with this, Bogoliubov investigated[192–198] the reduced Hamiltonian, in which the interaction of single electrons is studied, and carried out for it a complete mathematical investigation for zero temperature. In this connection, he laid the bases of a new powerful method of the *approximating Hamiltonian*, which allows linearization of nonlinear quantum equations of motion, and reduction of all nonlinearity to *self-consistent equations* for the ordinary functions into which the defined operator expressions translate. This method was extended later to nonzero temperatures and a wide class of

systems, and became one of most powerful methods of solving nonlinear equations for quantum fields.[2,15]

Petrina contributed much to the further clarification of many complicated aspects of the BCS–Bogoliubov theory. He performed a close and subtle analysis[15,115,210–213] of the BCS–Bogoliubov model and various related mathematical problems.

In his paper[210] "Hamiltonians of quantum statistics and the model Hamiltonian of the theory of superconductivity", an investigation was made of the general Hamiltonian of quantum statistics and the model Hamiltonian of the theory of superconductivity in an infinite volume. The Hamiltonians were given a rigorous mathematical definition as operators in a Hilbert space of sequences of translation-invariant functions. It was established that the general Hamiltonian is *not symmetric* but possesses a real spectrum; the model Hamiltonian is *symmetric* and its spectrum has a gap between the energy of the ground state and the excited states.

In the following paper,[211] the model Hamiltonian of the theory of superconductivity was investigated for an infinite volume and a complete study was made of its spectrum. The grand partition function was determined and the equation-of-state was found. In addition, the existence of a phase transition from the normal to the SC state was proved. It was shown that in the limit $V \to \infty$ the chain of equations for the Green's functions of the model Hamiltonian has two solutions, namely the free Green's function and the Green's function of the approximating Hamiltonian.

In his paper,[212] Petrina has shown that the Bogoliubov result that the average energies (per unit volume) of the ground states for the BCS–Bogoliubov Hamiltonian and the approximating Hamiltonian asymptotically coincide in the thermodynamic limit is also valid for all excited states. He also established that, in the thermodynamic limit, the BCS–Bogoliubov Hamiltonian and the approximating Hamiltonian asymptotically coincide as quadratic forms.

Petrina[213] considered also the BCS Hamiltonian with sources, as it was proposed by Bogoliubov and Bogoliubov, Jr. It was proved that the eigenvectors and eigenvalues of the BCS–Bogoliubov Hamiltonian with sources can be exactly determined in the thermodynamic limit. Earlier, Bogoliubov proved that the energies per volume of the BCS–Bogoliubov Hamiltonian with sources and the approximating Hamiltonian coincide in the thermodynamic limit. These results clarified substantially the microscopic theory of superconductivity and provided a deeper mathematical foundation to it.

Raggio and Werner[169] have shown the existence of the limiting free energy density of inhomogeneous (site-dependent coupling) mean field models in the thermodynamic limit,[45] and derived a variational formula for this quantity. The formula requires the minimization of an energy term plus an entropy term as a functional depending on a function with values in the one-particle state space. The minimizing functions describe the pure phases of the system, and all cluster points of the sequence of finite volume equilibrium states have unique integral decomposition into

pure phases. Some applications were considered; they include the full BCS model and random mean field models.

A detailed and careful mathematical analysis of certain aspects of the BCS–Bogoliubov theory was carried out by Watanabe,[214–222] mainly in the context of the solutions to the BCS–Bogoliubov gap equation for superconductivity.

BCS–Bogoliubov theory correctly yields an energy gap.[223,224] The determination of this important energy gap is by solving a nonlinear singular integral equation. An investigation of the solutions to the BCS–Bogoliubov gap equation for superconductivity was carried out by Watanabe.[214–222] In his works, the BCS–Bogoliubov equations were studied in full generality. Watanabe investigated the gap equation in the BCS–Bogoliubov theory of superconductivity, where the gap function is a function of the temperature T only. It was shown that the squared gap function is of class C^2 on the closed interval $[0, T_C]$. Here, T_C stands for the transition temperature. Furthermore, it was shown that the gap function is monotonically decreasing on $[0, T_C]$ and the behavior of the gap function at $T = T_C$ was obtained and some more properties of the gap function were pointed out.

On the basis of his study Watanabe then gave, by examining the thermodynamical potential, a mathematical proof that the transition to a SC state is a second-order phase transition. Furthermore, he obtained a new and more precise form of the gap in the specific heat at constant volume from a mathematical point of view. It was shown also that the solution to the BCS–Bogoliubov gap equation for superconductivity is continuous with respect to both the temperature and the energy under the restriction that the temperature is very small. Without this restriction, the solution is continuous with respect to both the temperature and the energy, and, moreover, the solution is Lipschitz continuous and monotonically decreasing with respect to the temperature.

van der Walt *et al.*[225,226] have obtained analytic expressions for the BCS–Bogoliubov gap of a many-electron system within the BCS model interaction in one, two and three dimensions in the weak coupling limit, but for *arbitrary* interaction width $\nu = \hbar D/E_F$, $0 < \nu < \infty$. Here, $\hbar D$ is the maximum energy of a force-mediating boson and E_F is the Fermi energy (which is fixed by the electronic density). The results obtained addressed both phononic ($\nu \ll 1$) as well as nonphononic (e.g., exciton, magnon, plasmon, etc.) pairing mechanisms where the mediating boson energies are *not* small compared with E_F, provided weak electron–boson coupling prevails. The essential singularity in coupling, sometimes erroneously attributed to the two-dimensional character of the BCS model interaction with ($\nu \ll 1$), was shown to appear in one, two and three dimensions *before* the limit $\nu \to 0$ is taken.

McLeod and Yang[227] studied the uniqueness and approximation of a positive solution of the BCS–Bogoliubov gap equation at finite temperatures. When the kernel was positive representing a phonon-dominant phase in a superconductor, the existence and uniqueness of a gap solution was established in a class which contains solutions obtainable from bounded domain approximations. The critical

temperatures that characterize SC–normal phase transitions realized by bounded domain approximations and full space solutions were also investigated. It was shown under some sufficient conditions that these temperatures are identical. In this case, the uniqueness of a full space solution follows directly. The authors[227] also presented some examples for the nonuniqueness of solutions. The case of a kernel function with varying signs was also considered. It was shown that, at low temperatures, there exist *nonzero gap solutions* indicating a SC phase, while at high temperatures, the only solution is the zero solution, representing the dominance of the normal phase, which establishes again the existence of a transition temperature.

In a series of papers,[228–230] Combescot *et al.* studied various aspects of the BCS ansatz for superconductivity[190] in the light of the Bogoliubov approach.

In Ref. 228, they extended the one-pair Cooper configuration towards BCS–Bogoliubov model of superconductivity by adding one-by-one electron pairs to an energy layer, where a small attraction acts. To do it, they solved Richardson's equations analytically in the dilute limit of pairs on the one-Cooper pair scale. It was found, through keeping only the first-order term in this expansion, that the N correlated pair energy reads as the energy of N isolated pairs within a $N(N-1)$ correction induced by the *Pauli exclusion principle* which tends to decrease the average pair binding energy when the pair number increases. Quite remarkably, extension of this first-order result to the dense regime gives the BCS–Bogoliubov condensation energy exactly. These facts may lead one to a different interpretation of the BCS–Bogoliubov condensation energy with a pair number equal to the number of pairs feeling the potential and an average pair binding energy reduced by Pauli blocking to half the single Cooper pair energy — instead of the more standard but far larger SC.

In the subsequent paper[229] the usual formulation of the BCS–Bogoliubov ansatz for superconductivity in the grand canonical ensemble makes the handling of the Pauli exclusion principle between paired electrons straightforward. It however masks that the many-body effects between Cooper pairs interacting through the reduced BCS–Bogoliubov potential are entirely controlled by this exclusion. To show it up, one has to work in the canonical ensemble. The proper handling of Pauli blocking between a fixed number of composite bosons is however known to be quite difficult. To do it, the authors have developed a commutator formalism for Cooper pair condensate, along the line that they used for excitons. The authors[229] then rederived, within the N-pair subspace, a few results of BCS–Bogoliubov theory of superconductivity obtained in the grand canonical ensemble, to evidence their Pauli blocking origin. They ended by reconsidering what should be called *Cooper pair wavefunction* and concluded differently from the usual understanding.

In their third paper, Combescot *et al.*[230] showed that the Bogoliubov approach to superconductivity provides a strong mathematical support to the wavefunction ansatz proposed by Bardeen, Cooper and Schrieffer.[190] However, there are some subtle differences in the both the approaches. Indeed, the BCS ansatz — with all pairs condensed into the same state — corresponds to the ground state of the

Bogoliubov Hamiltonian. From the other hand, this Hamiltonian only is part of the BCS Hamiltonian. As a result, the BCS ansatz definitely differs from the BCS Hamiltonian ground state. This can be directly shown either through a perturbative approach starting from the Bogoliubov Hamiltonian or better by analytically solving the BCS Schrödinger equation along Richardson–Gaudin exact procedure. Still, the BCS ansatz leads not only to the correct extensive part of the ground state energy for an arbitrary number of pairs in the energy layer where the potential acts — as recently obtained by solving Richardson–Gaudin equations analytically — but also to a few other physical quantities such as the electron distribution, as it was shown by the authors. The paper[230] also considered arbitrary filling of the potential layer and evidences the existence of a super dilute and a super dense regime of pairs, with a gap different from the usual gap. These regimes constitute the lower and upper limits of density-induced BEC–BCS crossover in Cooper pair systems. It should be noted, however, that this theory needs an additional careful examination.

In 1958, Bogoliubov[231] proposed a new variational principle in the many-particle problem. This variational principle is the generalization of the Hartree–Fock variational principle.[5,10] It is well known[232,233] that the Hartree–Fock approximation is a variational method that provides the wavefunction of a many-body system assumed to be in the form of a Slater determinant for fermions and of a product wavefunction for bosons. It treats correctly the statistics of the many-body system, antisymmetry for fermions and symmetry for bosons under the exchange of particles. The variational parameters of the method are the single-particle wavefunctions composing the many-body wavefunction.

Bogoliubov[231] considered a model dynamical Fermi system describing the Hamiltonian with two-body forces. The Hamiltonian of a nonrelativistic system of identical fermions interacting by two-body interactions was

$$H = \sum_{k\sigma}(E(k) - E_F)a^{\dagger}_{k\sigma}a_{k\sigma} + \frac{1}{2V}\sum_{k,k',\sigma} J(k,k'|\sigma_1\sigma_2\sigma'_2\sigma'_1)a^{\dagger}_{k\sigma}a^{\dagger}_{k\sigma}a_{k\sigma}a_{k\sigma}\,. \quad (158)$$

The $a^{\dagger}_{k\sigma}$ and $a_{k\sigma}$ are single-particle creation and annihilation operators satisfying the usual anticommutation relations, E_F is the Fermi energy level and V is the volume of the system.

The Hamiltonian under consideration is a model Hamiltonian; it takes into account the pair interaction of the particles with opposite momentum only. It can be rewritten in the following form[231]:

$$H = \sum_{qs}(E(k) - E_F)a^{\dagger}_{qs}a_{qs} + \frac{1}{2V}\sum_{q,q',s} I(q,q'|s_1,s_2,s'_2s'_1)a^{\dagger}_{qs_1}a^{\dagger}_{qs_2}a_{q's'_2}a_{q's'_1}\,. \quad (159)$$

Here $\mathbf{q}$ describes the pair of momentum $(\mathbf{k}, -\mathbf{k})$; hence $\mathbf{q}$ and $-\mathbf{q}$ describe the same pair. Index $s = (\sigma, \nu)$, where $\nu = \pm 1$ is an additional index[231] permitting to classify k as (q, ν). Bogoliubov[231] had shown that the ground state of the system can be

found asymptotically exact for the limit $V \to \infty$ by following the approach of the paper.[192]

This approach found numerous applications in the many-body nuclear theory.[232–240] The properties of all existing and theoretically predicted nuclei can be calculated based on various nuclear many-body theoretical frameworks. The classification of nuclear many-body methods can be also done from the point of view of the pair nuclear interaction, from which the many-body Hamiltonian is constructed. An important goal of nuclear structure theory is to develop the computational tools for a systematic description of nuclei across the chart of the nuclides. Nuclei come in a large variety of combinations of protons and neutrons (≤ 300). Understanding the structure of the nucleus is a major challenge. To study some collective phenomena in nuclear physics, we have to understand the pairing correlation due to residual short-range correlations among the nucleons in the nucleus. This has usually been calculated by using the BCS theory or the Hartree–Fock–Bogoliubov theory. The Hartree–Fock–Bogoliubov theory is suited well for describing the level densities in nuclei..[237,239] The theory of level densities reminds in certain sense the ordinary thermodynamics. The simplest level density of nucleons calculations were based usually on a model Hamiltonian which included a simple version of the pairing interaction (between nucleons in states differing only by the sign of the magnetic quantum number).

Sheikh and Ring[236] derived the symmetry-projected Hartree–Fock–Bogoliubov equations using the variational ansatz for the generalized one-body density-matrix in the Valatin form. It was shown that the projected-energy functional can be completely expressed in terms of the Hartree–Fock–Bogoliubov density matrix and the pairing tensor. The variation of this projected-energy was shown to result in Hartree–Fock–Bogoliubov equations with modified expressions for the pairing potential and the Hartree–Fock field. The expressions for these quantities were explicitly derived for the case of particle number projection. The numerical applicability of this projection method was studied in an exactly soluble model of a deformed single-j shell.

Behkami and Kargar[237] have determined the nuclear level densities and thermodynamic functions for light A nuclei, from a microscopic theory, which included nuclear pairing interaction. Nuclear level densities have also been obtained using Bethe formula as well as constant temperature formula. Level densities extracted from the theories were compared with their corresponding experimental values. It was found that the nuclear level densities deduced by considering various statistical theories are comparable; however, the Fermi-gas formula[241] becomes inadequate at higher excitation energies. This conclusion, which has also been arrived at by other investigations, revealed that a realistic treatment of the statistical nuclear properties requires the introduction of residual interaction. The effects of the pairing interaction and deformation on nuclear state densities were illustrated and discussed.

Robledo and Bertsch[238] have presented a computer code for solving the equations of the Hartree–Fock–Bogoliubov theory by the gradient method, motivated by the need for efficient and robust codes to calculate the configurations required by extensions of the Hartree–Fock–Bogoliubov theory, such as the generator coordinate method. The code was organized with a separation between the parts that are specific to the details of the Hamiltonian and the parts that are generic to the gradient method. This permitted total flexibility in choosing the symmetries to be imposed on the Hartree–Fock–Bogoliubov solutions. The code solves for both even and odd particle number ground states, with the choice determined by the input data stream.

Lewin and Paul[240] have shown that the best method for describing attractive quantum systems is the Hartree–Fock–Bogoliubov theory. This approach deals with a nonlinear model which allows for the description of pairing effects, the main explanation for the superconductivity of certain materials at very low temperature. Their paper is a detailed study of Hartree–Fock–Bogoliubov theory from the point of view of numerical analysis. Lewin and Paul started by discussing its proper discretization and then analyzed the convergence of the simple fixed point (Roothaan) algorithm. Following the works for electrons in atoms and molecules, they had shown that this algorithm either converges to a solution of the equation or oscillates between two states, none of them being solution to the Hartree–Fock–Bogoliubov equations. They also adapted the *Optimal Damping Algorithm* to the Hartree–Fock–Bogoliubov setting and also analyzed it. The last part of the paper was devoted to numerical experiments. The authors considered a purely gravitational system and numerically discovered that pairing always occurs. They then examined a simplified model for nucleons, with an effective interaction similar to what is often used in nuclear physics. In both cases, Lewin and Paul[240] discussed the importance of using a damping algorithm.

Many other applications of the Hartree–Fock–Bogoliubov theory to various many-particle systems were discussed in Refs. 242–246. Generalization of Lieb variational principle[166] to Bogoliubov-Hartree–Fock theory was considered recently by Bach *et al.*[167] In its original formulation, Lieb variational principle holds for fermion systems with purely repulsive pair interactions. As a generalization, authors proved for both fermion and boson systems with semibounded Hamiltonian that the *infimum* of the energy over quasifree states coincides with the *infimum* over pure quasifree states. In particular, the Hamiltonian was not assumed to preserve the number of particles.

It is instructive to remind that in mathematics, the *infimum* (abbreviated inf; plural infima) of a subset S of a partially ordered set T is the greatest element of T that is less than or equal to all elements of S. Consequently the term greatest lower bound is also commonly used. *Infima* of real numbers are a common special case that is especially important in analysis. However, the general definition remains valid in the more abstract setting of order theory where arbitrary partially ordered sets are considered.

To shed light on the relation between authors' result and the usual formulation of Lieb variational principle in terms of one-particle density matrices, it was also included a characterization of pure quasifree states by means of their generalized one-particle density matrices.

12. Method of an Approximating Hamiltonian

It is worth noting that a complementary method, which was called the *method of an approximating Hamiltonian*, was formulated[3,4,247–249] for treating model systems of statistical mechanics. The essence of the method consists in replacement of the initial model Hamiltonian H, which is not amenable to exact solution, by a suitable *approximating* (or trial) Hamiltonian $H^{\rm appr}$. The next step consists of proving their thermodynamical equivalence, i.e., proving that the thermodynamic potentials and the mean values calculated on the basis of H and $H^{\rm appr}$ are asymptotically equal in the thermodynamic limit[45] N, $V \to \infty$, $N/V = \text{const}$.

When investigating the phenomenon of superconductivity, Bogoliubov suggested the method of approximating Hamiltonian and justified it for the case of temperatures close to zero. By employing this method, Bogoliubov rigorously solved the BCS model of superconductivity at zero temperature. This model was defined by the Hamiltonian of interacting electrons with opposite momenta and spins.

To explain the superconductivity phenomenon, it was necessary to solve very difficult mathematical problems connected with the justification of approximations employed. In this connection, Bogoliubov considered the reduced Hamiltonian in which only the interaction of electrons was taken into account. He gave a complete mathematical investigation of this Hamiltonian at zero temperature. Moreover, he laid the foundation of a new powerful method of approximating Hamiltonian which allows one to linearize nonlinear quantum equations of motion so that the nonlinearity is preserved only in self-consistent equations for ordinary functions that are obtained from certain operator expressions. This method was then extended to the case of nonzero temperatures and applied to a broad class of systems. Later, this approach became one of the most effective methods for solving nonlinear equations for quantum fields.

The method of approximating Hamiltonian is based on the proof of the thermodynamic equivalence of the model under consideration and *approximating Hamiltonian*. Thermodynamic equivalence means here the coincidence of specific free energies and Green's functions for model and approximating Hamiltonian in the thermodynamic limit[45] when V and N tends to ∞, $N/V = \text{const}$.

It was shown above that in many cases it may be assumed that the effective Hamiltonian H for the system of particles may be written as the sum of the Hamiltonian of the reference system $H^{\rm appr}$, plus the rest of the effective Hamiltonian $H = H^{\rm appr} + \Delta H$. Then the Bogoliubov inequality states that the Helmholtz free energy F of the system is given by

$$F \leq F^{\rm appr} + \langle H - H^{\rm appr} \rangle_{\rm appr} \,, \tag{160}$$

where F^{appr} denotes the free energy of the reference system and the brackets a canonical ensemble average over the reference system.

Bogoliubov Jr. elaborated a new method[247–251] of finding exact solutions for a broad class of model systems in quantum statistical mechanics — the method of approximating Hamiltonian. As it was mentioned above, this method appeared in the theory of superconductivity.[197,198]

Bogoliubov Jr. investigated some dynamical models[247] generalizing those of the BCS type. A complete proof was presented that the well-known approximation procedure leads to an asymptotically exact expression for the free energy, when the usual limiting process of statistical mechanics is performed. Some special examples were considered.

A detailed analysis of Bogoliubov approach to investigations of (Hartree–Fock–Bogoliubov) mean field-type approximations for models with a four-fermion interaction was given in the papers.[250,251] An exactly solvable model with paired four-fermion interaction that is of interest in the theory of superconductivity was considered. Using the method of approximating Hamiltonian, it was shown that it is possible to construct an asymptotically exact solution for this model. In addition, a theorem was proved that allows us to compute, with asymptotic accuracy in the thermodynamic limit, the density of the free energy under sufficiently general conditions imposed on the parameters of the model system. An approximate method for investigating models with four-fermion interaction of general form was presented. The method was based on the idea of constructing an approximating Hamiltonian and it allows one to study the dynamical properties of these models. The method combines the standard approach to the method of the approximating Hamiltonian for the investigation of models with separable interaction and the Hartree–Fock scheme of approximate computations based on the concept of self-consistency. To illustrate the efficiency of the approach presented, the BCS model that plays an important role in the theory of superconductivity was considered in detail. Thus, the effective and workable approach was formulated which allows one to investigate dynamical and thermodynamical properties of models with four-fermion interaction of general type. The approach combines the ideas of the standard Bogoliubov approximating Hamiltonian method for the models with separable interaction with the method of Hartree–Fock approximation based on the ideas of self-consistency.

Bakulev *et al.*[252] discussed thoroughly the principle of thermodynamic equivalence in statistical mechanics in the approach of the method of approximating Hamiltonian. They discussed the main ideas that lie at the foundations of the approximating Hamiltonian method in statistical mechanics. The principal constraints for the model Hamiltonian to be investigated by approximating Hamiltonian method were considered along with the main results obtainable by this method. It was shown how it is possible to enlarge the class of model Hamiltonians solvable by approximating Hamiltonian method with the help of an example of the BCS-type model. Additional rigorous studies of the theory of superconductivity with

Coulomb-like repulsion was carried out by Bakulev.[253] The traditional method of the approximating Hamiltonian was applied for the investigation of a model of a superconductor with interaction of the BCS-type and Coulomb-like repulsion, the latter being described by unbounded operators. It was shown that the traditional method can be generalized in such a way that for the model under consideration one can prove the asymptotic (in the thermodynamic limit $V \to \infty, N \to \infty$, $N/V = \text{const.}$) coincidence not only of the free energies (per unit volume) but also of the correlation functions of the model and approximating Hamiltonian.

13. Conclusion

The aim of the present overview was to justify a statement that in many cases the methods of quantum statistical mechanics, many of which were formulated and developed by Bogoliubov,[1–4] allow one to develop efficient approaches for solution of complicated problems of the many-particle interacting systems.

In the present survey, we discussed tersely the Bogoliubov variational principle. It was shown in the preceding sections that this principle provides an extremely valuable treatment of mean field methods and their application to the problems in statistical mechanics and many-particle physics of interacting systems. With its remarkable workability, the Bogoliubov variational principle has found many applications as an effective method not only in condensed matter physics but also in many other areas of physics (see, e.g., Ref. 254). It is also hoped that this work will lead to greater insight into the application of variational principles to various many-particle problems.

There is another aspect of the problem under consideration. It is of great importance to determine correctly the mean field contribution when one describes the interacting many-particle systems by the equations-of-motion method.[5,17] It was mentioned briefly that the method of two-time temperature Green's functions[5,17] allows one to investigate efficiently the quasiparticle many-body dynamics generated by the main model Hamiltonians from the quantum solid state theory and the quantum theory of magnetism. The method of quasiaverages allows one to take a deeper look at the problems of spontaneous symmetry breaking, as well as at the problems of symmetry and dissymmetry in the physics of condensed matter.[5,17,18] Summarizing the basic results obtained by Bogoliubov by inventing the variational principles, method of quasiaverages and results in the area of creation of asymptotic methods of statistical mechanics, one must especially emphasize that thanks to their deep theoretical content and practical direction, these methods have obtained wide renown everywhere. They have enriched many-particle physics and statistical mechanics with new achievements in the area of mathematical physics as well as in the areas of concrete applications to physics, e.g., theories of superfluidity and superconductivity.

In the papers,[17,35–37] we have formulated the *self-consistent theory* of the correlation effects for many-particle interacting systems using the ideas of quantum

field theory for interacting electron and spin systems on a lattice. The workable and self-consistent irreducible Green's functions approach to the decoupling problem for the equation-of-motion method for double-time temperature Green's functions has been presented. The main achievement of this formulation was the derivation of the Dyson equation for double-time retarded Green's functions instead of causal ones. That formulation permitted to unify convenient analytical properties of retarded and advanced Green's functions and the formal solution of the Dyson equation, that, in spite of the required approximations for the self-energy, provides the correct functional structure of single-particle Green's function. The main advantage of the mathematical formalism was brought out by showing how elastic scattering corrections (generalized mean fields) and inelastic scattering effects (damping and finite lifetimes) could be self-consistently incorporated in a general and compact manner. We have presented there the novel method of calculation of quasiparticle spectra for basic spin lattice models, as the most representative examples. Using the irreducible Green's functions method, we were able to obtain a closed self-consistent set of equations determining the electron Green's function and self-energy. For the Hubbard and Anderson models, these equations gave a general microscopic description of correlation effects both for the weak and strong Coulomb correlation, and, thus, determined the interpolation solutions of the models. Moreover, this approach gave the workable scheme for the definition of relevant *generalized mean fields* written in terms of appropriate correlators.

We hope that these methods of statistical mechanics have been explained with sufficient details to bring out their scope and power, since we believe that those techniques will have application to a variety of many-body systems with complicated spectra and strong interaction.

These applications have illustrated some of subtle details of the irreducible Green's functions approach and exhibited their physical significance in a representative form. As it was seen, these treatments has advantages in comparison with the standard methods of decoupling of higher-order Green's functions within the equation-of-motion approach.

The main advantage of the whole method is the possibility of a *self-consistent* description of quasiparticle spectra and their damping in a unified and coherent fashion.

The most important conclusion to be drawn from the present consideration is that the *generalized mean fields* for the case of strong Coulomb interaction in the Hubbard model has quite a nontrivial structure and cannot be reduced to the *mean density functional*.

Recently the problem of the advanced mean field methods in complex systems[255] has attracted big attention. Our consideration reveals the fundamental importance of the adequate definition of *generalized mean fields* at finite temperatures, that results in a deeper insight into the nature of quasiparticle states of the correlated lattice fermions and spins and other interacting many-particle systems.

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