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Approximate Variational Principle in Quantum Statistics*

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The density matrix of von Neumann can be used to formulate an exact variational principle for quantum statistics which embodies the principle of maximization of entropy. Using the formalism of second quantization, we can write this variational principle for fermions or bosons and can then derive 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 yield the generalization of the Hartree-Fock equations for nonzero temperature and the corresponding extension to bosons.

I. INTRODUCTION

THE quantum statistics of interacting identical particles was first attacked from the point of view of the density matrix by Dirac[1] who derived the Hartree-Fock equations for fermions at zero temperature in this way. The problem of a system of interacting fermions at nonzero temperatures has been studied by Husimi[2] in his long paper on the density matrix and, more recently, by Husimi and Nishiyama.[3,4] These authors used the principle of maximization of entropy to derive their results, although the minimization of free energy has been suggested by Lidiard,[5] who has used the method to derive the approximate free energy used by Koppe[6] in a calculation of the influence of the exchange energy on the specific heat of free electrons in metals. Kubo[7] has also minimized the free energy in his treatment of antiferromagnetism.

The purpose of this paper is the formulation of a general approximate variational method in the quantum statistics of fermions and bosons using the grand canonical ensemble of Gibbs and the procedures of second quantization. The emphasis in this treatment is no longer on the individual particles but on the states,[8] and we shall speak appropriately of correlations and interactions between these states for example. After first discussing the exact variational principle, which is equivalent to the entropy maximization principle, we derive its formulation for identical particles by the use of second quantization. In treating the variational principle for identical particles, we introduce the approximation that correlations between particle states are to be neglected. By "no correlation" we mean that the number of particles in one state does not depend strongly upon the number of particles occupying other states. More explicitly, we set the density matrix equal to a product of factors each referring to a particular particle state. We then introduce the further approximation that each factor is a function only of the operator for the number of particles in the particle state to which the factor refers. The now approximate variational principle gives the best form for each factor, in the sense of minimizing the quantum mechanical partition function for the grand canonical ensemble.

Even though correlations between particle states are neglected, the interactions between them are present in a manner like that of the familiar "effective field" theories. This fact appears when we vary the functional form of the particle states in our variational expressions; the equations which emerge are a generalization of the Hartree-Fock equations for fermions at nonzero temperature. These equations have already been given by Husimi[2] for fermions in a somewhat similar derivation. From the point of view adopted in this paper we can also justify the application of our procedure to the boson case in which we obtain a similar set of equations. Although the distributions of particles and the particle states are a natural extension of the fermion case, these latter equations have not been given previously.

II. GENERAL FORMULATION

In quantum statistics the grand canonical ensemble of Gibbs is introduced by taking the density matrix of von Neumann[9] in the form

$$\rho=\exp[\beta(\mu N-H)]/\mathrm{Trace}\sum_{N=0}^{\infty}\exp[\beta(\mu N-H)],\quad (1)$$

where $\beta=(kT)^{-1}$, μ is the chemical potential, H (an ordinary Schrödinger operator) is the Hamiltonian for a system of the ensemble, and N (a scalar) is the number of particles in a system. The trace is to be taken over the space spanned by the eigenstates of the system. It is

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[1] P. A. M. Dirac, Proc. Cambridge Phil. Soc. **26**, 376 (1930).

[2] K. Husimi, Proc. Phys.-Math. Soc. Japan **22**, 264 (1940).

[3] T. Nishiyama, Progr. Theoret. Phys. Japan **5**, 135 (1950); **6**, 1 (1950).

[4] K. Husimi and T. Nishiyama, Progr. Theoret. Phys. Japan **5**, 909 (1950).

[5] A. B. Lidiard (private communication).

[6] H. Koppe, Z. Naturforsch. **2a**, 429 (1947).

[7] Ryo Kubo, Revs. Modern Phys. **25**, 344 (1953).

[8] The term "state" here is intended to denote a possible state for a single particle and not a state of the whole system composed of many particles. To avoid confusion we will call the first-mentioned state a particle state.

[9] J. von Neumann, *Die Mathematische Grundlagen der Quantenmechanik* (Dover Publications, New York, 1943).

well known that Eq. (1) can be derived from the variational principle:

$$\Theta=\mathrm{Trace}\rho(\log\rho-\beta\mu N+\beta H),\quad \delta\Theta=0, \tag{2}$$

where we minimize Θ with respect to ρ subject to the constraint

$$\mathrm{Trace}\rho=1. \tag{3}$$

If the system is homogeneous it can be shown that $\Theta_{\mathrm{min}}=-\beta pV$, where p is the pressure and V is the volume of the system. This variational principle is related to the entropy maximization principle which leads to the Gibbs petite canonical ensemble. The use of the n-particle Hamiltonian and wave functions which are the product of single-particle wave functions in Eq. (2) will lead to the proper wave functions and distributions for Maxwell-Boltzmann particles.

For a system of n identical particles the wave functions for the system must be symmetric or antisymmetric combinations of some single particle states $\psi_k(s)$, where s denotes space and spin coordinates. This restriction is easily incorporated by the use of the second quantization procedure developed by Jordan and Wigner[10] and discussed more fully by Fock.[11] In second quantization we first introduce the ordered orthonormal set of single-particle wave functions $\psi_k(s)$. The symmetric or antisymmetric combinations of the $\psi_k(s)$ which form the permissible states of the n-particle system can then be characterized by the number of particles N_k occupying each state $\psi_k(s)$ and therefore denoted by $\Psi(N_1,\cdots,N_r)$. In so designating the wave functions of this so-called Fock space, we have shifted our emphasis from the particles to the particle states $\psi_k(s)$. Two operators a_m and a_m^* logically appear in the theory as generators of these states:

$$\begin{aligned} a_m^*\Psi(\cdots,N_m,\cdots) &= \epsilon_m(N_m+1)^{\frac12}\Psi(\cdots,N_m+1,\cdots),\\ a_m\Psi(\cdots,N_m,\cdots) &= \epsilon_m(N_m)^{\frac12}\Psi(\cdots,N_m-1,\cdots). \end{aligned} \tag{4}$$

The factor ϵ_m depends on the statistics of the particles; for bosons $\epsilon_m=1$, whereas for fermions

$$\epsilon_m=(-1)^\eta,\quad \eta=\sum_{r=0}^{m-1}N_r.$$

The operators a_m and a_m^* (annihilation and creation operators) satisfy the commutation $[\ \ ]$ and anticommutation relations $[\ \ ]_+$:

$$\begin{aligned} &(\text{bosons}):\quad [a_m,a_n]=[a_m^*,a_n^*]=0, \\ &\qquad\qquad\qquad [a_m,a_n^*]=\delta_{mn}; \\ &(\text{fermions}):\ [a_m,a_n]_+=[a_m^*,a_n^*]_+=0, \\ &\qquad\qquad\qquad [a_m,a_n^*]_+=\delta_{mn}. \end{aligned} \tag{5}$$

The operator whose eigenvalue is the number of particles in the particle-state $\psi_k(s)$ is

$$N_k=a_k^*a_k, \tag{6}$$

and the operator for the total number of particles is then

$$N=\sum N_k=\sum a_k^*a_k. \tag{7}$$

It follows from the commutation relations of Eq. (5) that the eigenvalues of N_k are 0, 1 for fermions whereas for bosons they are the entire set of non-negative integers.

Let the Hamiltonian for interacting particles be expressed in the particle formalism as

$$H=\sum H_1(s)+\tfrac12\sum_{s\neq s'}H_2(s,s'), \tag{8}$$

where $H_1(s)$ is an operator depending only on the coordinates of s, whereas $H_2(s,s')$ is a two-particle interaction term depending on the coordinates of s and s'. The Hamiltonian for interacting identical particles can be shown to be

$$H=\sum\nolimits_{m,n}a_m^*(m|H_1|n)a_n +\tfrac12\sum\nolimits_{mnpq}a_m^*a_n^*(mn|H_2|pq)a_qa_p, \tag{9}$$

where

$$\begin{aligned} (m|H_1|n)&=\int d(1)\psi_m^*(1)H_1(1)\psi_n(1),\\ (mn|H_2|pq)&=\int d(1)d(2)\psi_m^*(1)\psi_n^*(2)\\ &\qquad\times H_2(1,2)\psi_p(1)\psi_q(2). \end{aligned} \tag{10}$$

We can now substitute the expressions for N and H given by (7) and (9) into Eq. (2) and can proceed to minimize Θ with respect to ρ.

We now make the assumption

$$\rho=\prod_m \rho_m(N_m). \tag{11}$$

This equation can be regarded as containing two approximations: (1) ρ is the product of operators each referring to a particle state $\psi_m(s)$, and (2) each of these factors is a function only of N_m. The first approximation is of the same type as that made by Hartree for the wave functions of atomic electrons. This factorization implies the neglect of correlations between particle states. We emphasize that this does not imply a neglect of correlations between two bosons in the same particle state. For the case of fermions, the neglect of correlation between particle states is obviously equivalent to the neglect of correlations between particles since there can be, at most, one particle in a state. For the sake of uniqueness we shall take each factor as individually normalized so that

$$\begin{aligned} &(\text{bosons}):\quad \mathrm{Trace}\ \rho_m(N_m)=\sum_{N_m=0}^{\infty}\rho_m(N_m)=1;\\ &(\text{fermions}):\ \mathrm{Trace}\ \rho_m(N_m)=\rho_m(0)+\rho_m(1)=1. \end{aligned} \tag{12}$$

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[10] P. Jordan and E. Wigner, Z. Physik **47**, 631 (1928).

[11] V. Fock, Z. Physik **75**, 622 (1932); **76**, 852 (1932).

Even though the results of minimizing the exact variational expression are invariant to the choice of particle state, the minimum of the approximate variational expression which incorporates Eq. (12) depends on the choice of the orthonormal set. For this reason we shall minimize Θ not only with respect to the ρ_m but also with respect to the functional form of the set ψ_m, with the orthonormality condition (5) as the only constraint.

III. INTERACTING FERMIONS

For the case of fermions we can take $\rho_m(N_m)$ in the form

$$\rho_m(N_m)=(1-w_m)(1-N_m)+w_m N_m, \qquad (13)$$

in which w_m is clearly the probability for the occupation of the particle state ψ_m. We can combine Eqs. (2), (11), and (12) to obtain

$$\begin{aligned}\Theta=&\textstyle\sum_m (1-w_m)\log(1-w_m)\\&+\textstyle\sum_m w_m[\log w_m-\beta\mu+(m|H_1|n)]\\&+\tfrac{1}{2}\textstyle\sum_{m,n} w_m w_n[(mn|H_2|mn)-(mn|H_2|nm)]. \qquad (14)\end{aligned}$$

Carrying out the variation on w_m we find

$$w_m=\{\exp[\beta(\epsilon_m-\mu)]+1\}^{-1}, \qquad (15)$$

where ϵ_m is an effective energy which includes the direct and exchange interaction energy

$$\begin{aligned}\epsilon_m=&(m|H_1|n)+\textstyle\sum_n w_n\\&\times[(mn|H_2|mn)-(mn|H_2|nm)]. \qquad (16)\end{aligned}$$

Aside from the fact that ϵ_m is an effective energy, Eq. (15) is what one obtains for noninteracting fermions.

The variation of $\psi_m{}^*$ subject to the orthonormality constraint yields

$$H_1(1)\psi_m(1)+\textstyle\sum_n w_n \displaystyle\int d(2)\psi_n{}^*(2)H_2(1,2)\psi_n(2)\psi_m(1)-\textstyle\sum_n w_n\Big[\displaystyle\int d(2)\psi_n{}^*(2)H_2(1,2)\psi_m(2)+\lambda_{mn}\Big]\psi_n(1)=0. \qquad (17)$$

We emphasize that the integral represents summation over spin as well as integration over space. λ_{mn} is a Lagrange multiplier for the orthonormality condition. The variation of ψ_m gives the complex conjugate of Eq. (17). The Hartree-Fock equation is a special case of Eq. (17) obtained by letting the temperature go to zero ($\beta\rightarrow\infty$) so that $w_m=1$ if $\epsilon_m<\mu$ and $w_m=0$ if $\epsilon_m>\mu$.

Husimi has derived Eqs. (15), (16), and (17) from a different point of view. He asserts, therefore, that Eq. (11) implies the neglect of correlations between *particles* and that this approximation makes the treatment of the boson case unreasonable by this approach. We have pointed out that the approximation neglects correlations only between particle states and in the boson case will also provide reasonable results.

IV. INTERACTING BOSONS

In treating interacting bosons we do not have a simple form for $\rho_m(N_m)$ but instead must carry along the normalization of Eq. (12) by Lagrange multipliers. In the representation in which the N_m are diagonal, Eq. (14) reduces to

$$\begin{aligned}\Theta=&\sum_m\sum_{N_m}\rho_m(N_m)\{\log\rho_m(N_m)+\beta[-\mu+(m|H_1|n)]N_m\\&+\tfrac{1}{2}\beta(mm|H_2|mm)N_m(N_m-1)\}\\&+\tfrac{1}{2}\textstyle\sum_{m\neq n}\sum_{N_m,N_n}\rho_m(N_m)\rho_n(N_n)\\&\times[(mn|H_2|mn)+(mn|H_2|nm)]N_mN_n. \qquad (18)\end{aligned}$$

Upon minimizing this with respect to $\rho_m(Nm)$ and $\psi_m{}^*$, we find

$$\rho_m(N_m)=\rho_m(0)\exp[-\beta(N_m\epsilon_m-\mu)], \qquad (19)$$

where, for bosons,

$$\begin{aligned}\epsilon_m=&(m|H_1|n)+(mm|H_2|mm)(N_m-1)\\&+\textstyle\sum_n\rho_n(N_n)[(mn|H_2|mn)+(mn|H_2|nm)], \qquad (20)\end{aligned}$$

$$\begin{aligned}&H_1(1)\psi_m(1)+2N_m\int d(2)\psi_m{}^*(2)H_2(1,2)\psi_m(2)\psi_m(1)\\&+\lambda_m\psi_m(1)+\sum_{n\neq m}\textstyle\sum_{N_n}\rho_n(N_n)N_n\\&\times\Big[\int d(2)\psi_n{}^*(2)H_2(1,2)\psi_n(2)\psi_m(1)\\&+\int d(2)\psi_n{}^*(2)H_2(1,2)\psi_m(2)\psi_n(1)\\&+\lambda_{mn}\psi_n(1)\Big]=0. \qquad (21)\end{aligned}$$

Again the integral represents integration over space and summation over spin. The Lagrange multipliers λ_m and λ_{mn} are again the result of the orthonormality conditions. Equation (21) then constitutes a "consistent field" or Hartree-Fock equation for bosons. We note that the most significant differences between Eqs. (17) and (21) are in the presence of an interaction term between bosons in the same particle state and in the sign of the exchange term. We can easily see that in the case of no interaction Eqs. (19) and (20) lead to the Bose-Einstein distribution, for these equations become

$$\rho_m(N_m)=\rho_m(0)\exp\{-\beta N_m[\mu-(m|H_1|n)]\}. \qquad (22)$$

The average number of particles in the particle state

ψ_m is then

$$\langle N_m\rangle=\sum_{N_m}\rho_m(N_m)N_m$$
$$=\{\exp\beta[(m|H_1|n)-\mu]-1\}^{-1}. \quad (23)$$

SUMMARY

The approximate variational procedure described herein has enabled us to obtain suitable wave functions for the description of the individual particle states of a system of "weakly" interacting bosons or fermions and to give the distribution of particles in these states. The procedure is not limited to these two cases, which are to be considered merely as illustrative of the general procedure. An application to ferromagnetism or antiferromagnetism can be made and a quantum theory of liquids can be derived along the lines of the classical cell theory as developed by Richardson and Brinkley.[12] In a discussion of helium II, however, one should expect the correlation between different particle states to play an important part, and this requires a modification of the simple assumption of Eq. (11).

One of us (WMM) is indebted to Professor J. A. Wheeler and Professor A. S. Wightman and to L. van Hove for several interesting discussions of this paper.

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Mobility of Impurity Ions in Germanium and Silicon*

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Lithium has been shown to migrate as a singly-charged positive ion in single crystals of both Ge and Si in temperature ranges of 150–600°C and 360–860°C, respectively. The mobility of the Li^+ in crystalline Ge and Si has been measured as a function of temperature. Through the use of the Einstein relation between diffusion constant and mobility, values of the diffusion constants in cm^2/sec of Li^+ in Ge and Si are obtained as follows: $D=25\times10^{-4}\exp\{(-11\,800)/RT\}$ for Ge and $D=23\times10^{-4}\exp\{(-15\,200)/RT\}$ for Si, in satisfactory agreement with previously published results on the thermal diffusion of Li^+. A curious reversion of conductivity type of solid solutions of Li in Ge is discussed. Copper has likewise been found to move as a positive ion in germanium in the temperature range 800°–900°C leading to diffusivities in agreement with previously published results.

INTRODUCTION

LITHIUM has already been shown to diffuse rapidly into crystalline germanium and silicon, behaving as a donor element in these semiconductors,[1] and the diffusion constants for these processes have been determined by means of a method involving the measurement of *p-n* junction positions.[2] An alternative method, capable of greater experimental accuracy, and based on fewer assumptions consists of measuring the mobilities of the Li^+ ions under an applied electric field. In theory, the diffusivity D can then be determined from the Einstein relationship between diffusion constant and mobility. The sign of the ionic charge (positive in the case of Li as required by its donor properties) can also be ascertained by noting the direction the impurity ion moves in the electric field. The activation energies for diffusion can be obtained in the usual way from the slopes of plots of the logarithm of the diffusion constant against reciprocal of the absolute temperature. In the present work this method has been applied successfully to Li in solution in Ge and Si.

THEORY

The basic principle of the method (see Fig. 1) is the diffusion of a hemispherical cloud of impurity ions into the semiconductor. We shall refer to such an ion cloud as a "pulse" because of its similarity to the analogous pulses employed in the measurement of electron and hole mobilities by the Haynes-Shockley method.[3] The impurity ion pulse is put in at a temperature chosen so as to obtain a relatively high concentration of Li in solution. The location of the diffusion region in the semiconductor is then determined from the location of the *p-n* junction. Thereupon the sample is subjected at a given temperature to a dc electric field for a fixed time after which the pulse, now less concentrated due to thermal diffusion is again located from the new *p-n* junction position. If the net drift motion of the center of the pulse is x, then the mobility is obtained from the relation $\mu=x/Et$; where t is the drift time in seconds and

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* A brief report of this work first appeared as a Letter to the Editor, Phys. Rev. **92**, 1322 (1953).

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