this becomes

$$d\Delta(x,t)/dt+T_1^{-1}\Delta(x,t)=\kappa d^2\Delta(x,t)/dx^2. \quad (17)$$

Equation (17) is very similar to the diffusion equation and has the solution

$$\Delta(x,t)=\frac{e^{-t/T_1}}{(4\pi\kappa t)^{\frac{1}{2}}}\int\Delta(y,0)\exp[-(x-y)^2/4\kappa t]dy. \quad (18)$$

Note the concentration dependence enters only through the parameter κ. The spin diffusion time τ is roughly given by

$$\tau=(4\kappa)^{-1}(x-x_0)^2_{\max}\simeq[4\kappa(T_2^*)^2]^{-1}.$$

For a Gaussian C-R linewidth,

$$\tau=2\pi[W'\langle\Delta\nu_c^2\rangle(T_2^*)^3]^{-1}. \quad (19)$$

Equation (19) is easily shown to be precisely equal to Eq. (4). [W' is defined in (8).] Equation (18), however, also describes the spin-lattice relaxation. The properties of (18) are too well known to dwell on the properties of this equation further.

This is the expression which describes the decay of the susceptibility in pulse saturation experiments when spin diffusion occurs.

The general solution of Eq. (16) is naturally very difficult but satisfactory solutions for cases of interest should present no great obstacle.

When $W(0)t<1$, Eq. (15) may be applied except that in the definition of the function $D(x)$, $W(0)$ must be replaced by $(T_2^*/2)\int W(x)dx$.

In a later publication, the application of these results will be discussed in relation to relaxation effects in $K_3(Co,Fe)(CN)_6$.

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Fermion Ensembles of Maximum Entropy

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Ensembles of particles obeying Fermi-Dirac statistics are considered from a point of view which is analogous to some recent work of Mayer on classical particle statistics. The density functions ρ_n are defined for n much smaller than the average number of particles in the ensemble. Since the knowledge of only a few ρ_n is sufficient for the computation of most averages of physical interest, it is important to compare different ensembles with the same density functions, say ρ_1 and ρ_2. The ensemble with the largest entropy is constructed as being the most significant. A number of simple examples are briefly considered.

INTRODUCTION

THE purpose of the present article is to give a quantum-mechanical analog for a theorem which was recently stated and proved by Mayer[1] for classical statistical mechanics. The theorem for Fermi statistics has the same intuitive content, but its statement and proof is more involved. As for the general idea behind the problem, the following may be said: Instead of starting from an assumed kinetic energy, external field, and interaction energy for the particles in order to find their correlation, it is shown how their assumed probabilities of occurrence in certain states and their correlations can be used to find, at least in principle, the simplest Hamiltonian responsible for these probabilities and correlations.

STATEMENT OF THE PROBLEM

An ensemble of Fermi-Dirac particles is more conveniently described if the total number of particles is not assumed to be exactly known. The state vectors Φ of the dynamical system will therefore not necessarily belong to an exact total number of particles. It is then also appropriate to use the formalism of second quantization, in particular the operators $\Psi(x)$ and $\Psi^*(x)$ of particle annihilation and creation, where the coordinate x refers to the position and spin of one particle. The Hilbert space H in which $\Psi(x)$ and $\Psi^*(x)$ operate can be described using an orthonormalized set of one-particle wave functions $\varphi_\kappa(x)$ whose label κ refers, e.g., to wave vector and spin direction, or to a lattice site and rotational state, and so forth. Every state vector of the whole system can be written as a linear combination of Slater determinants which are constructed from an arbitrary subset of the set $\{\varphi_\kappa(x)\}$. The creation and annihilation operators, $\Psi^*(x)$ and $\Psi(x)$, are then defined in terms of the creation and annihilation operators a_κ^* and a_κ in the customary manner

$$\Psi(x)=\sum_\kappa a_\kappa\varphi_\kappa(x), \quad \Psi^*(x)=\sum_\kappa a_\kappa^*\varphi_\kappa^*(x). \quad (1)$$

The operators a_κ^* and a_κ satisfy the anticommutation relations

$$\begin{aligned} &a_\kappa^*a_\lambda+a_\lambda a_\kappa^*=\delta_{\kappa\lambda}, \\ &a_\kappa a_\lambda+a_\lambda a_\kappa=a_\kappa^*a_\lambda^*+a_\lambda^*a_\kappa^*=0. \end{aligned} \quad (2)$$

[1] Joseph E. Mayer, J. Chem. Phys. **33**, 1484 (1960).

The effect of the operators a_κ and a_κ^* can be easily visualized if they operate on functions Φ which correspond to Slater determinants constructed from the single-particle wave functions $\varphi_\kappa(x)$. But it cannot be expected, nor will it be assumed, that the state vectors of greatest physical interest correspond to Slater determinants.

An ensemble of Fermi-Dirac particles is mechanically defined in all detail by giving a complete (with respect to the Hilbert space H) orthonormalized set of functions Φ_P and the probabilities W_P associated with Φ_P. It is crucial for the difference between classical and quantum theory that the wave functions Φ_P as well as the probabilities be stated for the definition of the quantum statistical ensemble.

The expectation value $\langle A\rangle$ of an operator A in the ensemble is defined by

$$\langle A\rangle=\sum_P W_P(\Phi_P,A\Phi_P), \tag{3}$$

where (Φ'',Φ') is the scalar product of the state vectors Φ'' and Φ'. A certain average in quantum statistics, such as the mean free energy of the ensemble, is stationary only if its first variation vanishes both with respect to small changes of the values of W_P and with respect to small changes in the wave functions Φ_P. Similarly the same quantity reaches a local minimum only if, in addition to having a vanishing first variation, its second variation is positive again with respect to small changes of both W_P and Φ_P.

Usually the operators A of physical interest are relatively simple in structure, since they consist of sums of operators each of which acts on only a very small number of particles, say one or two. The evaluation of the expectation value for such simple operators A can always be reduced to the evaluation of the one-particle density function

$$\rho_1(y,x)=\langle\Psi^*(y)\Psi(x)\rangle, \tag{4}$$

and the two-particle density function

$$\rho_2(\eta,y;\,\xi,x)=\tfrac{1}{2}\langle\Psi^*(y)\Psi^*(\eta)\Psi(\xi)\Psi(x)\rangle. \tag{5}$$

The generalization of these last definitions to n-particle density functions is obvious:

$$\rho_n(y_1,\cdots,y_n;\,x_1,\cdots,x_n)=(1/n!)\langle\Psi^*(y_n)\cdots\Psi^*(y_1)\Psi(x_1)\cdots\Psi(x_n)\rangle, \tag{6}$$

but the important features are already present in the case $n=2$, so that later examples will be discussed only for $n=1$ and $n=2$.

If the Hilbert space H of the dynamical system is defined by the set of single-particle wave functions $\varphi_\kappa(x)$, as suggested above, then it is natural to consider the n-particle density function ρ_n as an operator in the Hilbert space H_n of the n-particle Slater determinants,

$$\chi_K=\frac{1}{(n!)^{\frac{1}{2}}}\begin{vmatrix}\varphi_{\kappa_1}(x_1)&\cdots&\varphi_{\kappa_n}(x_1)\\ \vdots&&\vdots\\ \varphi_{\kappa_1}(x_n)&\cdots&\varphi_{\kappa_n}(x_n)\end{vmatrix}, \tag{7}$$

where K is an abbreviation for the set of indices $(\kappa_1,\cdots,\kappa_n)$. In this space the operation of the density function on an arbitrary antisymmetric n-particle wave function χ' is described by the formula

$$\chi''(x_1,\cdots,x_n)=\int dy_1\cdots\int dy_n\times\rho_n(y_1,\cdots,y_n;\,x_1,\cdots,x_n)\chi'(y_1,\cdots,y_n). \tag{8}$$

Since the wave functions χ_K are by definition a complete orthnormalized set in the space H_n, the density function ρ_n can be written as

$$\rho_n=\sum_{KL}\sigma_{KL}\chi_L^*(y_1,\cdots,y_n)\chi_K(x_1,\cdots,x_n). \tag{9}$$

It will be proved in the Appendix that

$$0\leqslant w_n(\kappa_1,\cdots,\kappa_n)=\sigma_{KK}\leqslant 1. \tag{10}$$

The quantity $w_n(K)$ can, therefore, be called "the probability of finding simultaneously one particle in a state κ_1, another in the state κ_2 etc." The knowledge of $w_n(K)$ is in general not sufficient to determine ρ_n, because ρ_n is usually not diagonal with respect to the wave functions χ_K. However, those ensembles for which ρ_n is indeed diagonal with respect to the χ_K, i.e., the ensembles with $\sigma_{KL}=0$ for $K\neq L$, will receive special attention later on.

The entropy of the ensemble is given by

$$S=-k_0\sum_P W_P\ln W_P, \tag{11}$$

where k_0 is the Boltzmann constant.

In view of many of its mathematical properties, S can be interpreted as a measure for the lack of information which is contained in the ensemble. Equivalently, S is a measure for the lack of correlation between the states in which the particles of the ensemble are found.

On the other hand, it must be realized that, in general, no other information is obtained experimentally from some dynamical system, except the density functions ρ_1 and ρ_2, but the knowledge of ρ_1 and ρ_2 for some ensemble does not determine it completely. There may be many ensembles which lead to the same density functions ρ_1 and ρ_2, but which have different sets of state vectors Φ_P and associated probabilities W_P. There is then no way of deciding which one of these ensembles describes the dynamical system under consideration. Any particular choice would be equivalent to making some additional assumptions about the system which cannot be checked by the available experiments, since the experiments determine only ρ_1 and ρ_2. In order to avoid such additional uncontrolled assumptions, it seems reasonable to consider that particular ensemble which has the largest entropy among all those with the same density functions ρ_1 and ρ_2.

Therefore the following problem arises: Given some function

$$\omega_n(y_1,\cdots,y_n;\,x_1,\cdots,x_n)=\sum_{KL}\omega_{KL}\chi_L^*(y_1,\cdots,y_n)\chi_K(x_1,\cdots,x_n), \tag{12}$$

it is required to find among all ensembles with $\rho_n=\omega_n$, or equivalently $\sigma_{KL}=\omega_{KL}$, the one with largest entropy. It is evident that the given function ω_n must be such that there exists at least one ensemble for which $\rho_n=\omega_n$.

STATEMENT OF THE THEOREM

It will be shown that the solution of this problem can be described in the following manner. There exists a function

$$\alpha_n(y_1,\cdots,y_n;x_1,\cdots,x_n) = \sum_{KL}\alpha_{LK}\chi_L^*(y_1,\cdots,y_n)\chi_K(x_1,\cdots,x_n), \quad (13)$$

which can be obtained, in principle, directly from ω_n. This function can be interpreted as an operator in the space H_n, exactly like ρ_n is such an operator, and acts according to formula (8). With this function α_n, it is possible to construct an operator B_n in the Hilbert space H by the formula

$$B_n=\sum_{KL} a_{\kappa_n}^*\cdots a_{\kappa_1}^* a_{\lambda_1}\cdots a_{\lambda_n}\alpha_{LK}, \quad (14)$$

where K and L are still abbreviations for the sets of indices $(\kappa_1,\cdots,\kappa_n)$ and $(\lambda_1,\cdots,\lambda_n)$. In the usual interpretation, the operator B_n is the sum of operators which act only on n particles simultaneously, so that B_n represents some n-particle potential acting between the particles of the dynamical system. The ensemble of largest entropy is then determined by the eigenfunctions Φ_P of the operator B_n, i.e.,

$$B_n\Phi_P=\beta_P\Phi_P, \quad (15)$$

and the corresponding probability is given by

$$W_P=\exp(\beta_P+\beta_0), \quad (16)$$

where the constant β_0 serves to satisfy the normalization condition

$$\sum W_P=1. \quad (17)$$

In addition, it will be shown: If $\omega_{KL}=0$ for $K\neq L$, then $\alpha_{KL}=0$, for $K\neq L$. The eigenvalue problem (15) is then immediately solved, since the function Φ_P will correspond to Slater determinants and the eigenvalue β_P will be equal to the sum of those coefficients for which the single-particle wave functions with indices $(\kappa_1,\cdots,\kappa_n)$ occur simultaneously in the Slater determinant Φ_P. Thus, if the function ω_n is diagonal with respect to some collection of Slater determinants in H_n, the ensemble with largest entropy among all those ensembles with $\rho_n=\omega_n$ is defined in terms of Slater determinants in H, which are constructed from the same set of single-particle wave functions.

DETERMINATION OF THE PROBABILITIES W_P

With the coefficients $M_{KL,PQ}$ quite generally defined by

$$M_{KL,PQ}=(a_{\lambda_1}\cdots a_{\lambda_n}\Phi_Q, a_{\kappa_1}\cdots a_{\kappa_n}\Phi_P), \quad (18)$$

the expansion (9) can be written as

$$\sigma_{KL}=\sum_P W_P M_{KL,PP}, \quad (19)$$

so that the condition $\rho_n=\omega_n$ becomes according to (12)

$$\sum_P W_P M_{KL,PP}=\omega_{KL}. \quad (20)$$

The first variation of S vanishes with respect to small changes of W_P, subject to the subsidiary conditions (17) and (20), if W_P is given by the formula

$$W_P=\exp(\sum_{KL}\alpha_{KL}M_{KL,PP}+\alpha_0). \quad (21)$$

The Lagrange multipliers α_0 and α_{KL} have to be determined from the equations, which are obtained from inserting (21) into (17) and (20), namely,

$$\sum_P \exp(\sum_{KL}\alpha_{KL}M_{KL,PP}+\alpha_0)=1, \quad (22)$$

$$\sum_P M_{KL,PP}\exp(\sum_{K'L'}\alpha_{K'L'}M_{K'L',PP}+\alpha_0)=\omega_{KL}. \quad (23)$$

The entropy is then given by

$$S=-k_0(\sum_{KL}\omega_{KL}\alpha_{KL}+\alpha_0). \quad (24)$$

If W_P is considered as a function of some parameter ζ, such that condition (20) is always satisfied, it follows that

$$\sum_P \frac{\partial W_P}{\partial\zeta}M_{KL,PP}=\sum_P \frac{\partial^2 W_P}{\partial\zeta^2}M_{KL,PP}=0. \quad (25)$$

It is also found, in view of $\sum_P \partial W_P/\partial\zeta=0$, that

$$\frac{\partial^2 S}{\partial\zeta^2}=-k_0\sum_P W_P^{-1}\left(\frac{\partial W_P}{\partial\zeta}\right)^2-k_0\sum_P \ln W_P\frac{\partial^2 W_P}{\partial\zeta^2}. \quad (26)$$

Therefore, if W_P is given for $\zeta=0$ by the formula (21), it follows that

$$\frac{\partial^2 S}{\partial\zeta^2}=-k_0\sum_P W_P^{-1}\left(\frac{\partial W_P}{\partial\zeta}\right)^2<0 \quad \text{for} \quad \zeta=0. \quad (27)$$

S reaches a maximum with respect to variations of W_P under the subsidiary conditions (20).

VARIATION OF THE WAVE FUNCTIONS

If the wave functions Φ_P change slightly, the coefficients $M_{KL,PQ}$ change in general too, so that the α_0 and α_{KL} have to be redetermined according to (22) and (23). Therefore, the entropy S of (24) becomes dependent on the variations of Φ_P.

First of all, it is then necessary to compute the variation of $M_{KL,PQ}$. A variation of the wave functions Φ_P is most easily represented by a unitary transformation,

$$\Phi_P'=(e^{i\xi F}\Phi)_P, \quad (28)$$

where F is an arbitrary Hermitian matrix $F_{PQ}=F_{QP}^*$. If the wave functions Φ_P' are inserted into (18) instead of the Φ_P, and the resulting expression is expanded in

powers of ζ, it follows that

$$M_{KL}{}^{(\zeta)}=M_{KL}{}^{(0)}+i\zeta[F,M_{KL}{}^{(0)}] -\zeta^2[F,[F,M_{KL}{}^{(0)}]]+\cdots, \quad (29)$$

where $M_{KL}{}^{(\zeta)}$ is now considered as a matrix with indices P and Q. The following relations are obtained by differentiating the subsidiary conditions (22) and (23) with respect to ζ.

$$\sum_{KL}\omega_{KL}\frac{\partial\alpha_{KL}}{\partial\zeta}+\sum_{KL}\alpha_{KL}\sum_{P}W_P\frac{\partial M_{KL,PP}}{\partial\zeta}+\frac{\partial\alpha_0}{\partial\zeta}=0, \quad (30)$$

$$\sum_P W_P\Big\{\frac{\partial M_{KL,PP}}{\partial\zeta} +M_{KL,PP}\sum_{K'L'}\Big[\frac{\partial\alpha_{K'L'}}{\partial\zeta}M_{K'L',PP}+\alpha_{K'L'}\frac{\partial M_{K'L',PP}}{\partial\zeta}\Big]\Big\} +\omega_{KL}\frac{\partial\alpha_0}{\partial\zeta}=0. \quad (31)$$

With the help of (30) it is found from (24) that

$$\frac{\partial S}{\partial\zeta}=k_0\sum_{KL}\alpha_{KL}\sum_P W_P\frac{\partial M_{KL,PP}}{\partial\zeta}. \quad (32)$$

Now it is easily seen that

$$\alpha_{KL}=\alpha_{LK}{}^* \quad\text{and}\quad M_{KL,PQ}=M_{LK,QP}{}^*. \quad (33)$$

Therefore, the right-hand side of (32) can be written with the help of (29) as

$$\frac{\partial S}{\partial\zeta}=-k_0\,\mathrm{Im}\sum_{PQ}(W_P-W_Q)F_{PQ}\sum_{KL}\alpha_{KL}M_{KL,QP}=0, \quad \text{for}\quad \zeta=0, \quad (34)$$

where Im before the summation indicates the imaginary part of the sum. Since the elements of F_{PQ} are essentially arbitrary, it follows that

$$\sum_{KL}\alpha_{KL}M_{KL,QP}=0, \quad \text{for}\quad Q\neq P, \quad (35)$$

(i.e., for $W_P\neq W_Q$ to be exact) as necessary and sufficient for the vanishing of the first variation of S.

Let us suppose that the coefficients α_{KL} have been determined. By combining the definitions (14) of B_n and the definition (18) of $M_{KL,PQ}$ with the formula (35), it follows that

$$(\Phi_Q,B_n\Phi_P)=0 \quad \text{for}\quad Q\neq P. \quad (36)$$

[Condition (35) holds only for $W_P\neq W_Q$ according to its derivation. But if there are many independent state vectors Φ belonging to the same probability W, then linear combinations can be chosen in such a way that (35) holds every time $Q\neq P$]. Equation (21) also shows that W_P can be written as in (16) with

$$\beta_P=(\Phi_P,B_n\Phi_P). \quad (37)$$

The operator B_n as defined in (14) is Hermitian, so that the equations (36) and (37) together are equivalent to the eigenvalue problem (15). Therefore the ensemble of stationary entropy with a given density function $\rho_n=\omega_n$, is the same as the Boltzmann ensemble with a Hamiltonian operator B_n and $k_0T=1$.

It is worth looking immediately at the special case where ω_n is diagonal with respect to the Slater determinants χ_K, i.e., $\omega_{KL}=0$ for $K\neq L$. The state vectors Φ_P are then the Slater determinants out of which the Hilbert space H was constructed. Indeed, if the Φ_P are chosen in this way it follows at once that

$$M_{KL,PP}=0 \quad \text{for}\quad K\neq L, \qquad M_{KK,PQ}=0 \quad \text{for}\quad P\neq Q. \quad (38)$$

Also one can set $\alpha_{KL}=0$ for $K\neq L$, and Eqs. (35) are satisfied. The operator B_n is now simply

$$B_n=\sum_K\alpha_{KK}N_{\kappa_1}\cdots N_{\kappa_n}, \quad (39)$$

with the occupation number N_κ defined by $N_\kappa=a_\kappa{}^*a_\kappa$.

The eigenvalues of B_n are given by sums of α_{KK} over all the n-tuple $K=(\kappa_1,\cdots,\kappa_n)$ of indices which occur simultaneously in a particular Slater determinant Φ_P.

The second derivative of $R=-S/k_0$ with respect to ζ can be written with the help of (30) and (31) as

$$\Big(\frac{\partial R}{\partial\zeta}\Big)^2+\sum_{KLK'L'}\frac{\partial\alpha_{KL}}{\partial\zeta}\frac{\partial\alpha_{K'L'}}{\partial\zeta} \times\Big(\sum_P W_PM_{KL,PP}M_{K'L',PP}-\omega_{KL}\omega_{K'L'}\Big) -\sum_{KLK'L'}\alpha_{KL}\alpha_{K'L'}\sum_P W_P\frac{\partial M_{KL,PP}}{\partial\zeta}\frac{\partial M_{K'L',PP}}{\partial\zeta} -\sum_{KL}\alpha_{KL}\sum_P W_P\frac{\partial^2M_{KL,PP}}{\partial\zeta^2}. \quad (40)$$

The first term vanishes for the stationary ensemble. The second term is positive definite, because it can be written as

$$\tfrac{1}{2}\sum_{PQ}W_PW_Q(\delta_P{}^2+\delta_Q{}^2-2\delta_P\delta_Q) \quad \text{with}\quad \delta_P=\sum_{KL}\frac{\partial\alpha_{KL}}{\partial\zeta}M_{KL,PP}. \quad (41)$$

The third term can be written in terms of the quantity

$$\gamma_P=\sum_{KL}\alpha_{KL}\frac{\partial M_{KL,PP}}{\partial\zeta} =-2\,\mathrm{Im}\{\sum_Q F_{PQ}\sum_{KL}\alpha_{KL}M_{KL,QP}\}, \quad (42)$$

with the help of (29) and (33). Now, if Φ_P are eigenfunctions of the operator B_n the conditions (35) can be made to hold every time $P\neq Q$. Therefore, the summation over Q in (42) contains only the term $Q=P$, and

the quantity in curly brackets is real, so that finally $\gamma_P=0$ as a consequence of (35). For the same reason, only terms $M_{KL,PP}$ have to be considered in the last term of (40), which becomes, therefore, with the help of (29)

$$\begin{aligned}&2\sum_{KL}\alpha_{KL}\sum_P W_P[F,[F,M_{KL}{}^{(0)}]]_{PP}\\&=4\sum_{KL}\alpha_{KL}\sum_P W_P\sum_Q|F_{PQ}|^2(M_{KL,PP}-M_{KL,QQ})\\&=2\sum_{PQ}|F_{PQ}|^2(W_P-W_Q)\\&\quad\times(\sum_{KL}\alpha_{KL}M_{KL,PP}-\sum_{KL}\alpha_{KL}M_{KL,QQ})\\&=2\sum_{PQ}|F_{PQ}|^2(W_P-W_Q)(\ln W_P-\ln W_Q)\geqslant 0,\end{aligned}\quad(43)$$

where the expression (21) for W_P has been used. Therefore, the second variation of R is positive, also with respect to small changes of the wave vectors Φ_P.

EXAMPLES

(*1*) *Semiconductors:* For many problems, only the probability ω_κ for certain single-electron states $\varphi_k(x)$ to be occupied is of interest. Therefore, only the single-particle density function

$$\rho_1(y,x)=\sum_\kappa \omega_\kappa\varphi_\kappa{}^*(y)\varphi_\kappa(x)\quad(44)$$

is determined, and the ensemble of largest entropy is defined in terms of the Slater determinants belonging to the set $\{\varphi_\kappa(x)\}$. The condition (22) becomes

$$\exp(\alpha_0)\prod_\kappa[1+\exp(\alpha_\kappa)]=1.\quad(45)$$

α_κ is, therefore, determined from condition (23) by

$$\exp(\alpha_\kappa)[1+\exp(\alpha_\kappa)]^{-1}=\omega_\kappa.\quad(46)$$

This is, indeed, the Fermi distribution function corresponding to an energy α_κ with $k_0T=1$. The probability W_P for a certain Slater determinant is given by (21), and can then be written as

$$W_P=\prod_\kappa\begin{cases}\omega_\kappa, & \text{if } \varphi_\kappa(x) \text{ is contained in } \Phi_P;\\ (1-\omega_\kappa), & \text{if } \varphi_\kappa(x) \text{ is not contained in } \Phi_P.\end{cases}\quad(47)$$

This is just the ensemble which was indicated by Gutzwiller[2] as typical of all elementary methods in quantum statistics. Its entropy, according to (24), is given by the well-known formula

$$S=-k_0\sum_\kappa[\omega_\kappa\ln\omega_\kappa+(1-\omega_\kappa)\ln(1-\omega_\kappa)].\quad(48)$$

As was pointed out in reference 2, this ensemble can be used also in the case where there is interaction between the electrons, by minimizing the free energy with respect to the occupation numbers ω_κ or with respect to the single-electron wave functions $\varphi_\kappa(x)$. In the latter case, a set of generalized Hartree-Fock equations results, whereas in the former case a generalized Fermi distribution is obtained.

(*2*) *Ising model:* The index κ now refers to a lattice-site and spin direction, for instance, and the interaction energy is such as not to change the spin direction or the lattice-site of any electron in the system. The eigenfunctions of the total Hamiltonian are, therefore, Slater determinants, and the density function ρ_n is diagonal with respect to the Slater determinants of order n. In the case of only two-body interaction, ρ_2 is of interest, and the system is completely described by the probability $w_2(\kappa,\lambda)$ that the single-electron states $\varphi_\kappa(x)$ and $\varphi_\lambda(x)$ are simultaneously occupied. From $w_2(\kappa,\lambda)$ the two-body interaction can be computed in principle by maximizing the entropy among all ensemble compatible with the assumed function $w_2(\kappa,\lambda)$.

(*3*) *Bardeen-Cooper-Schrieffer theory of superconductivity:* The single-electron wave functions are assumed to be Bloch waves which are characterized by their wave vector $\mathbf{k}$ and their spin direction $\uparrow$ or $\downarrow$. A complete system of orthonormalized state vectors Φ is constructed by operating on the vacuum for each value of $\mathbf{k}$, with one of the four following operators

$$\begin{aligned}&C_{\mathbf{k}}{}^{(1)}=(1-h_{\mathbf{k}})^{\frac{1}{2}}+(h_{\mathbf{k}})^{\frac{1}{2}}a_{\mathbf{k}\uparrow}{}^*a_{-\mathbf{k}\downarrow}{}^*,\quad p_{\mathbf{k}}{}^{(1)}=(1-f_{\mathbf{k}})^2,\\&C_{\mathbf{k}}{}^{(2)}=-(h_{\mathbf{k}})^{\frac{1}{2}}+(1-h_{\mathbf{k}})^{\frac{1}{2}}a_{\mathbf{k}\uparrow}{}^*a_{-\mathbf{k}\downarrow}{}^*,\quad p_{\mathbf{k}}{}^{(2)}=f_{\mathbf{k}}{}^2,\\&C_{\mathbf{k}}{}^{(3)}=a_{\mathbf{k}\uparrow}{}^*,\qquad\qquad p_{\mathbf{k}}{}^{(3)}=f_{\mathbf{k}}(1-f_{\mathbf{k}}),\\&C_{\mathbf{k}}{}^{(4)}=a_{-\mathbf{k}\downarrow}{}^*,\qquad\qquad p_{\mathbf{k}}{}^{(4)}=f_{\mathbf{k}}(1-f_{\mathbf{k}}).\end{aligned}\quad(49)$$

The numbers $C_{\mathbf{k}}{}^{(i)}$ associated with the operators $p_{\mathbf{k}}{}^{(i)}$ are the probabilities for $C_{\mathbf{k}}{}^{(i)}$ to operate on the vacuum. Thus, each state Φ_P is written as

$$\Phi_P=\prod_{\mathbf{k}}C_{\mathbf{k}}|\text{vac}\rangle,\quad(50)$$

where for each possible value of $\mathbf{k}$ the operator $C_{\mathbf{k}}$ is one of the four operators $C_{\mathbf{k}}{}^{(i)}$. The probabilities W_P are given by an analogous formula

$$W_P=\prod_{\mathbf{k}}p_{\mathbf{k}},\quad(51)$$

where for each possible value of $\mathbf{k}$ the number $p_{\mathbf{k}}$ is one of the four probabilities $p_{\mathbf{k}}{}^{(i)}$. The numerical values of $h_{\mathbf{k}}$ and $f_{\mathbf{k}}$ are restricted to the interval from 0 to 1, and are determined by minimizing the free energy of the ensemble.

The density functions and the entropy can be calculated in a straightforward manner for the Bardeen-Cooper-Schrieffer ensemble. The results are the well-known formulas

$$\begin{aligned}\rho_1(y,x)=&\sum_{\mathbf{k}}n_{\mathbf{k}}\{\varphi_{\mathbf{k}\uparrow}{}^*(y)\varphi_{\mathbf{k}\uparrow}(x)\\&+\varphi_{-\mathbf{k}\downarrow}{}^*(y)\varphi_{-\mathbf{k}\downarrow}(x)\},\end{aligned}\quad(52)$$

$$\begin{aligned}\rho_2(\eta,y;\xi,x)=&\rho_1(\eta,\xi)\rho_1(y,x)-\rho_1(\eta,x)\rho_1(y,\xi)\\&+\chi^*(\eta,y)\chi(\xi,x),\end{aligned}\quad(53)$$

$$\begin{aligned}\chi(\xi,x)=&\sum_{\mathbf{k}}[n_{\mathbf{k}}(1-n_{\mathbf{k}})-f_{\mathbf{k}}(1-f_{\mathbf{k}})]^{\frac{1}{2}}\\&\times\{\varphi_{\mathbf{k}\uparrow}(\xi)\varphi_{-\mathbf{k}\downarrow}(x)-\varphi_{-\mathbf{k}\downarrow}(\xi)\varphi_{\mathbf{k}\uparrow}(x)\},\end{aligned}\quad(54)$$

$$S=-2k_0\sum_{\mathbf{k}}\{(1-f_{\mathbf{k}})\ln(1-f_{\mathbf{k}})+f_{\mathbf{k}}\ln f_{\mathbf{k}}\},\quad(55)$$

$$h_{\mathbf{k}}=(n_{\mathbf{k}}-f_{\mathbf{k}})/(1-2f_{\mathbf{k}}).\quad(56)$$

[2] M. C. Gutzwiller, Helv. Phys. Acta **34**, 514 (1961).

The function $\chi(\xi,x)$ defined by (54) is the same as the one used by Valatin,[3] although it results in that article from a different definition.

The assumption (49) for the probabilities $p_k^{(i)}$ seems unduly restrictive. One might at first think of an ensemble where the only relation between the probabilities $p_k^{(i)}$ is

$$p_k^{(1)}+p_k^{(2)}+p_k^{(3)}+p_k^{(4)}=1. \tag{57}$$

Such an ensemble might be further specified by requiring its first-order density function to be given by (52) and its second-order density function by (53) with given values for n_k and f_k, but the parameter h_k and the probabilities $p_k^{(i)}$ to be found by maximizing the entropy. A simple but somewhat tedious calculation shows, however, that under these conditions the entropy is indeed maximized by the values (49) for $p_k^{(i)}$ and the values (56) for h_k. In order to maximize the entropy of an ensemble with the density functions ρ_1 and ρ_2 given by (52) and (53), it is, therefore, necessary to couple the probabilities W_P in a more involved manner than in (51) and to choose state vectors Φ_P of a more complicated type than (50). Such ensembles may be of interest in view of the problem of the specific heat in superconductors.[4]

(4) *Kinetic equation:* For many problems it seems sufficient to consider a description in which only the first-order density function is taken into account, e.g. Landau's[5] theory of the Fermi liquid. At each time t an ensemble has to be found which is compatible with the first-order density function without introducing too many additional hypotheses. It is again at this point that the entropy of the chosen ensemble has to be considered in order to eliminate unwarranted assumptions. This problem will be left to a later paper.

[3] J. G. Valatin, Phys. Rev. **122**, 1012 (1961).
[4] *Cf.* H. A. Boorse, Phys. Rev. Letters **2**, 391 (1959).
[5] L. D. Landau, Soviet Phys.—JETP **3**, 920 (1957).

APPENDIX

Let us consider an arbitrary ensemble which is specified by the complete orthonormalized set of state vectors Φ_P and the associated probabilities W_P. The quantity $w_n(\kappa_1,\cdots,\kappa_n)$ can be written as the expectation value,

$$w_n(\kappa_1,\cdots,\kappa_n)=\langle a_{\kappa_1}^*\cdots a_{\kappa_n}^* a_{\kappa_n}\cdots a_{\kappa_1}\rangle,$$

for that ensemble. The state vectors Φ_P are now expanded in terms of the Slater determinants Φ_Q' which are constructed from the set of orthonormalized single-particle wave functions $\varphi_\kappa(x)$. Let us therefore write

$$\Phi_P=\sum_Q c_{PQ}\Phi_Q'.$$

With the help of formula (3) and introducing the statistical matrix (or density matrix)

$$\tau_{QR}=\sum_P c_{PR}^* W_P c_{PQ},$$

the quantity $w_n(\kappa_1,\cdots,\kappa_n)$ becomes

$$w_n(\kappa_1,\cdots,\kappa_n)=\sum_{QR}\tau_{QR}(\Phi_R',a_{\kappa_1}^*\cdots a_{\kappa_n}^* a_{\kappa_n}\cdots a_{\kappa_1}\Phi_Q').$$

But the operator acting on Φ_Q' is just $N_{\kappa_n}\cdots N_{\kappa_1}$, where $N_\kappa=a_\kappa^* a_\kappa$ is diagonal with respect to the state vectors Φ_Q' and has only the eigenvalues 1 or 0 according to whether or not the single-particle wave function $\varphi_\kappa(x)$ is contained in the Slater determinant Φ_Q'. Therefore one finds

$$w_n(\kappa_1,\cdots,\kappa_n)=\sum_Q{}' \tau_{QQ},$$

where the prime on the summation restricts the values of Q to those for which Φ_Q' contains simultaneously $\varphi_{\kappa_1}(x),\cdots,\varphi_{\kappa_n}(x)$. Now one can write

$$\sum_Q{}'\tau_{QQ}=\sum_P W_P\sum_Q{}'|c_{PQ}|^2,$$

which is obviously greater or equal to zero, but also smaller than one because of (17) and the unitarity of the transformation c_{PQ},

$$\sum_Q{}'|c_{PQ}|^2\leqslant\sum_Q|c_{PQ}|^2=1.$$

This completes the proof of the inequality (10).