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Quantum Statistics of Fields

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Gibbs' theory of ensembles of classical mechanical systems has been modified for the application to quantum-mechanical systems by Klein. In this paper, the formalism of the latter author is applied to hamiltonians of different types of field theories and thus a consistent theory of field thermodynamics is obtained without explicitly referring to the statistical behavior of particles that are "contained" in the fields. Speaking in terms of particles, the thermodynamics obtained in this way is the same as for a mechanical system where only the temperature is known, but no other conditions such as the number of particles, the total charge, etc.

Specifically, the thermodynamic functions of the nonrelativistic and relativistic Schrödinger fields, Dirac's electron field, and the electromagnetic field are deduced. The statistics of the nonrelativistic fields correspond to ordinary Bose and Fermi statistics of an ensemble of identical particles; the relativistic cases, however, yield new expressions. The thermal equilibrium at low temperatures of the Dirac electron field turns out to be the "vacuum" state as described in the hole theory. Finally, it is also shown that the application of the present formalism to the electromagnetic field leads back to Planck's radiation theory.

I. INTRODUCTION

IN connection with the present difficulties in quantum theory of fields it occurred to us that one source of trouble may be that no distinction is made between the positive and negative directions of the time axis. To any nonphysicist it would hardly seem justified to assume equivalence of past and future. Somehow the arrow of the time axis should be inferred into our physical laws. In ordinary mechanics this inference of the time-arrow is obtained by the passage to thermodynamics by means of statistics. Thus it seems to us that statistical methods might shed some light onto the significance of some of the difficulties encountered in present field theories.

The application of statistical mechanics to field theories has been tried before. Thus it is known that Planck applied statistics to the electromagnetic field which led him to the discovery of quantum mechanics in 1900. It is also known that Debye[1] found another deduction of Planck's radiation theory which does not use the equilibrium of the field with other systems.

However, it appears to us that all these previous investigations are somehow inconsistent in their methods. Planck used "resonators" which are supposed to be in thermal equilibrium with the radiation field, and then applied statistical mechanics to an ensemble of such resonators. Debye[1] applied a phenomenological method of counting nodes of waves in a given volume. Similarly, in all more modern treatments of the quantum statistics of "fields," one first quantizes the field and then applies statistics to the particles, the prescriptions for the statistical "weight" of the configurations of the particles being deduced from the degeneracy of the state of the corresponding field. In such a way it is possible to explain the behavior of certain types of particles at certain temperatures (see e.g., Schrödinger's[2] monograph). The thermodynamics of the particles, then, is thought to be identical with the thermodynamics of the corresponding field. This is, however, somewhat questionable, since the interpretation of a field theory as a particle theory can be obtained only by renormalizing infinite terms in the expressions for the energy, etc., and it is by no means evident *a priori* that these renormalizations are the same in a quantum statistics of fields.

On the other hand, it is well known that one has definite prescriptions for dealing with the statistics of ensembles of systems. In classical mechanics one can define a canonical ensemble of systems; then the thermodynamic functions are found by a method devised by Gibbs (see reference 2). The modifications of Gibbs' scheme which are necessary in quantum mechanics have been found by Klein.[3] These remarks show that one actually has all the means for a straightforward application of statistics to any field theory; but, as far as we know, the problem has never been treated in this direct way. An attempt has been made recently by Kaempffer,[4] who tried to deduce the behavior of an ensemble of identical particles from a wave theory. However, his results were not obtained by a consistent application of quantum statistics to the wave field, but rather by phenomenological methods of counting nodes of waves or the like, analogous to the procedures of Debye.[1]

Thus it seems desirable to attempt a consistent quantum statistical treatment of various wave fields,[5] such as the nonrelativistic and relativistic Schrödinger fields, Dirac's electron field, and the electromagnetic field. In the present paper we shall confine ourselves to vacuum fields. Speaking in terms of particles, this means that we shall consider systems where only the temperature is known, but no other additional conditions such as the total number of particles, the total charge, etc.

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[1] See, for instance, *Handbuch d. Physik* (Geiger-Scheel), vol. 24, 1, p. 9.

[2] E. Schrödinger, *Statistical Thermodynamics* (Cambridge University Press, London, 1946).

[3] O. Klein, Z. Physik 72, 767 (1931).

[4] F. Kaempffer, Z. Physik 125, 487 (1949).

[5] G. Wentzel, *Einführung in die Quantentheorie der Wellenfelder* (Deuticke, Wien, 1943).

The question to which physical situations these premises and thus the results are applicable is here of minor importance. Our principal aim is to follow all the statistical consequences of those theories which are commonly used to describe some of the elementary fields; up to the bitter contradiction with physical possibilities, if necessary.

The structure of the present field theories is such that there is a hamiltonian for each of the vacuum fields known. Then, different vacuum fields are linked together in a rather arbitrary and tentative way by assuming interaction terms. Thus it seems to us that the first obvious thing to do is to consider the vacuum fields alone, especially since the general theory permits the existence of such vacuum fields. The extension of the present formalism to the interaction of different fields is the object of further investigations which we hope to present in a future publication.

II. GENERAL THEORY

We summarize first the principles of Gibbs' statistical mechanics as applied to an ensemble of arbitrary mechanical systems. If $H(p_k, q_k)$ denotes the hamiltonian of the systems concerned, then one can define a canonical ensemble as follows:

$$P=(1/Z)\exp(-\vartheta H). \tag{2.1}$$

Here Pd^fpd^fq is the probability of finding the system with coordinates between q_i and q_i+dq_i and momenta between p_i and p_i+dp_i. The partition function is given by

$$Z=\int\exp(-\vartheta H)d^fqd^fp. \tag{2.2}$$

With the knowledge of Z, one can find all the thermodynamic functions of the ensemble, namely, the Helmholtz free energy F

$$F=-\vartheta^{-1}\log Z=-\vartheta^{-1}\log\int\exp(-\vartheta H)d^fpd^fq \tag{2.3}$$

the temperature T

$$T=1/k\vartheta \tag{2.4}$$

and the entropy

$$S=-\partial F/\partial T=-kT\int P\log Pd^fpd^fq. \tag{2.5}$$

The modifications which have to be made in these formulas if one is dealing with quantum-mechanical systems, have been set up by Klein.[3] It is seen that one has to replace P by Neumann's density matrix $\mathbf{P}$, which is defined as follows:

$$(P)_{nm}=c_nc_m{}^*, \tag{2.6a}$$

if a certain state of the system in an ensemble is given by ψ (ψ is normalized)

$$\psi=\sum c_iv_i, \tag{2.6b}$$

where the v's are the eigenfunctions of the hamiltonian. The formulas (2.1) to (2.5) all remain valid if the integrations are replaced by the traces of the matrices which occur as integrands. Thus we have for a canonical ensemble

$$\mathbf{P}=(1/Z)\exp(-\vartheta\mathbf{H});\quad \bar{A}=\mathrm{trace}\mathbf{PA}, \tag{2.7}$$

where A denotes an arbitrary observable and $\bar{A}$ its expectation value in the ensemble (matrices are denoted by faced types). Furthermore, we have

$$Z=\mathrm{trace}\exp(-\vartheta\mathbf{H}), \tag{2.8}$$

$$F=-\vartheta^{-1}\log Z=-(1/\vartheta)\log\mathrm{trace}\exp(-\vartheta\mathbf{H}), \tag{2.9}$$

$$T=1/k\vartheta, \tag{2.10}$$

$$S=-\partial F/\partial T=-kT\,\mathrm{trace}\mathbf{P}\log\mathbf{P}. \tag{2.11}$$

The next step is to apply our scheme to a field theory. It is known that in all cases of interest one can find a diagonal representation for the hamiltonian, and thus it will be particularly easy to set up the quantum statistics of fields by means of Eqs. (2.8)–(2.11).

III. THE NONRELATIVISTIC SCHRÖDINGER FIELD

As a first example, we treat the nonrelativistic Schrödinger field. The field equation is

$$i\hbar\dot{\psi}=-\frac{\hbar^2}{2m}\Delta\psi. \tag{3.1}$$

It may be represented in the hamiltonian form as follows (see Schiff,[6] Sec. 46):

$$\mathcal{L}=i\hbar\psi^*\dot{\psi}-\frac{\hbar^2}{2m}\,\mathrm{grad}\psi^*\,\mathrm{grad}\psi, \tag{3.2}$$

$$\mathcal{H}=-\frac{i\hbar}{2m}\,\mathrm{grad}\pi\,\mathrm{grad}\psi. \tag{3.3}$$

The total hamiltonian may be written as the following symbolic sum in a diagonal matrix representation:

$$\mathbf{H}=\textstyle\sum_K \mathbf{N}_K E_K, \tag{3.4}$$

E_K being the eigenvalues of the one-particle Schrödinger equation. $\mathbf{N}_K$ has diagonal elements N_K ranging from 0 to infinity in integer steps. For particles in a box (a "periodicity cube" of volume V) one has

$$E_K=p^2/2m=\hbar^2K^2/2m. \tag{3.5}$$

Having the eigenvalues of the hamiltonian, we may now consider an ensemble of such fields and define the Neumann density matrix as

$$\mathbf{P}=(1/Z)\exp(-\vartheta\mathbf{H}). \tag{3.6}$$

The important quantity Z, the partition function, is

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[6] L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1949).

then

$$Z = \text{trace}\exp(-\vartheta \mathbf{H}) = \sum_{N_K} \exp(-\vartheta \sum N_K E_K) \quad (3.7)$$

or

$$\log Z = \sum_K \log \sum_0^\infty \exp(-N_K E_K/kT)$$
$$= -\sum\nolimits_K \log\{1-\exp(-E_K/kT)\}. \quad (3.8)$$

We wish to replace the sum in the above expression by an integral. In the periodicity cube, K is restricted to the values given by

$$K^2 = (2\pi)^2 L^{-2}\{n_x^2+n_y^2+n_z^2\}, \quad (3.9)$$

where n_x, n_y, n_z are all integers or zero, and L^3 the volume of the cube. Thus, except for surface terms which may be neglected with respect to the volume terms as K-space becomes continuous, each K has associated with it a volume of K-space

$$d^3K = (2\pi)^3/L^3 = (2\pi)^3/V. \quad (3.10)$$

Hence we obtain

$$(1/V)\log Z =$$
$$-(2\pi)^{-3}\int \log\{1-\exp(-E_K/kT)\}d^3K \quad (3.11)$$

or else, since E_K depends only on K^2,

$$F/V = (2\pi)^{-3}kT\int_0^\infty \log\{1-\exp(-\hbar^2K^2/2mkT)\}4\pi K^2dK, \quad (3.12)$$

$$S/V = -(2\pi)^{-3}k\int_0^\infty \log\{-1\exp(-\hbar^2K^2/2mkT)\}4\pi K^2dK$$
$$+\frac{1}{(2\pi)^3}\frac{1}{T}\int_0^\infty \frac{\hbar^2K^2}{2m\{\exp(\hbar^2K^2/2mkT)-1\}}4\pi K^2dK, \quad (3.13)$$

$$\frac{E}{V} = \frac{1}{(2\pi)^3}\int_0^\infty \frac{1}{2m}\frac{\hbar^2K^2}{\exp(\hbar^2K^2/2mkT)-1}4\pi K^2dK. \quad (3.14)$$

These integrals can be computed. Actually, they are similar to the expressions which one obtains for the statistics of Einstein-Bose particles. The reason for this is, of course, that the nonrelativistic Schrödinger field is fully equivalent to a system of oscillators with symmetric states. Thus it is seen that a straightforward application of quantum statistics to the field is equivalent in the present case to an application of Bose statistics to the particles "contained" in the field. This is not quite the same thing as concluding that the particles "contained" in such a field must obey Bose statistics. Heretofore, statistics have been applied only to the particles, never to the field (except for the paper of Kaempffer[4]); only the symmetry properties for the eigenfunctions of the particles have been inferred from the quantum theory of fields.

Incidentally, the values of the above integrals are[7]

$$\frac{F}{V} = -\frac{(2\pi m)^{3/2}}{h^3}(kT)^{5/2}\sum_{n=1}^\infty \frac{1}{n^{5/2}}, \quad (3.15)$$

$$\frac{S}{V} = \frac{5}{2}\frac{(2\pi m)^{3/2}}{h^3}k^{5/2}T^{3/2}\sum_{n=1}^\infty \frac{1}{n^{5/2}}, \quad (3.16)$$

$$\frac{E}{V} = \frac{3}{2}\frac{(2\pi m)^{3/2}}{h^3}(kT)^{5/2}\sum_{n=1}^\infty \frac{1}{n^{5/2}}. \quad (3.17)$$

These expressions check with those obtained earlier by Kaempffer[4] by his more phenomenological methods.

The formulas (3.15) to (3.17) hold for all temperatures. This corresponds, thus, to an Einstein-Bose gas where there are an infinite number of particles available in a reservoir without kinetic energy.[8] Obviously, one may interprete Eq. (3.14) as (Stieltjes' integral)

$$E = \int E_K dN(K), \quad (3.18)$$

in which

$$dN(k)/V = \tfrac{1}{2}\pi^{-2}K^2dK/\{\exp(\hbar^2K^2/2mkT)-1\} \quad (3.19)$$

is the number of "particles" per unit volume between K and $K+dK$. Thus, the number of particles which are energized and thus "contained" in the field is

$$\frac{N}{V} = \frac{(2\pi m)^{\frac{3}{2}}}{h^3}(KT)^{\frac{3}{2}}\sum_{n=1}^\infty \frac{1}{n^{\frac{3}{2}}} \quad (3.20)$$

which again corresponds to the formula for an Einstein-Bose gas.

IV. THE SCHRÖDINGER-GORDON FIELD

The relativistic generalization of the case treated in the last section is the Schrödinger-Gordon field. Each field variable satisfies the equation (Wentzel,[5] p. 29)

$$(\Box-\mu^2)\psi = 0. \quad (4.1)$$

The lagrangian and the hamiltonian turn out as follows (Wentzel,[5] p. 29):

$$L = \tfrac{1}{2}\int (\dot{\psi}^2 - c^2|\text{grad}\psi|^2 - c^2\mu^2\psi^2)d^3x, \quad (4.2)$$

$$H = \tfrac{1}{2}\int \{\pi^2 + c^2|\text{grad}\psi|^2 + c^2\mu^2\psi^2\}d^3x, \quad (4.3)$$

π and ψ being regarded as canonical variables. In momentum space representation, one finds the hamiltonian

$$H = \tfrac{1}{2}\sum\{p_K{}^*p_K + \omega_K{}^2q_K{}^*q_K\}, \quad (4.4)$$

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[7] C. D. McKay, "Thermodynamics of fields," thesis, Queen's University Library, Kingston, 1951.

[8] The total number of particles is thus *not* an independent variable.

with

$$\omega_K{}^2 = c^2(\mu^2 + K^2). \tag{4.5}$$

For p_K, q_K, H a matrix representation can be found (Wentzel,[5] p. 34); the eigenvalues of H turn out to be

$$(H)_{N_K N_{K'}\ldots} = \sum_K \hbar(N_K + 1)\omega_K. \tag{4.6}$$

Thus, in the representation where **H** is a diagonal matrix, we can again define the Neumann density matrix by (3.6) and the partition function Z now becomes

$$\begin{aligned} Z &= \sum_{N_K} \exp(-\vartheta H_{N_K}) = \sum_{N_K} \exp\{-\sum_K \vartheta\hbar\omega_K(N_K + \tfrac{1}{2})\} \\ &= \prod_K \exp(-\tfrac{1}{2}\vartheta\hbar\omega_K)/\{1 - \exp(-\vartheta\hbar\omega_K)\}. \end{aligned} \tag{4.7}$$

Thus $\log Z$, which alone enters into the thermodynamic functions, becomes

$$\log Z = -\sum_K \log\{1 - \exp(-\vartheta\hbar\omega_K)\} - \tfrac{1}{2}\vartheta \sum_K \hbar\omega_K. \tag{4.8}$$

As in the last section, the sum is replaced by an integral by means of (3.10), whence we obtain

$$(1/V)\log Z = -(2\pi)^{-3}\int \{\log[1 - \exp(-\vartheta\hbar\omega_K)] + \tfrac{1}{2}\vartheta\hbar\omega_K\} d^3K \tag{4.9}$$

or else, since ω_K depends only on K^2,

$$F/V = (2\pi)^{-3}kT\int \log\{1 - \exp(-\hbar\omega_K/kT)\}4\pi K^2 dK, \tag{4.10}$$

$$S/V = -(2\pi)^{-3}k\int \log\{1 - \exp(-\hbar\omega_K/kT)\}4\pi K^2 dK + \frac{k}{(2\pi)^3}\int \frac{\hbar\omega_K}{kT}\frac{1}{\exp(\hbar\omega_K/kT) - 1}4\pi K^2 dK, \tag{4.11}$$

$$\frac{E}{V} = \frac{1}{(2\pi)^3}\int \frac{\hbar\omega_K}{\exp(\hbar\omega_K/kT) - 1}4\pi K^2 dK. \tag{4.12}$$

Herein, the last term of (4.9) has been dropped, since, although it is infinite, it is independent of the temperature (if multiplied by kT) and just gives rise to an infinite zero-point energy. Thus we need indeed the *same* renormalization as in the interpretation of a *single* field as an ensemble of particles.

The integrals can be computed; they lead to series of hankel functions of the argument (nmc^2/kT) which is usually very large. Hence the hankel functions may be replaced by their asymptotic expansions, and one obtains finally[7]

$$\frac{F}{V} = -\frac{(2\pi m)^{3/2}}{h^3}(kT)^{5/2}\sum_{n=1}^{\infty}\left\{\frac{1}{n^{5/2}}\exp\left(-n\frac{mc^2}{kT}\right) \times\left[1 + \frac{15}{8n}\frac{kT}{mc^2} + \cdots\right]\right\}, \tag{4.13}$$

$$\frac{S}{V} = \frac{(2\pi m)^{3/2}}{h^3}k^{3/2}T^{1/2}\sum_{n=1}^{\infty}\left\{\frac{1}{n^{3/2}}\exp\left(-n\frac{mc^2}{kT}\right) \times\left[1 + \frac{35}{8n}\frac{kT}{mc^2} + \cdots\right]\right\}, \tag{4.14}$$

$$\frac{E}{V} = \frac{(2\pi m)^{3/2}}{h^3}(kT)^{3/2}mc^2\sum_{n=1}^{\infty}\left\{\frac{1}{n^{3/2}}\exp\left(-n\frac{mc^2}{kT}\right) \times\left[1 + \frac{27}{8n}\frac{kT}{mc^2} + \cdots\right]\right\}. \tag{4.15}$$

The total number of particles "contained" in the field at a given temperature is, similarly to (3.19),

$$\frac{N}{V} = \frac{(2\pi m)^{3/2}}{h^3}(kT)^{3/2}\sum_{n=1}^{\infty}\left\{\frac{1}{n^{3/2}}\exp\left(-n\frac{mc^2}{kT}\right) \times\left[1 + \frac{15}{8n}\frac{kT}{mc^2} + \cdots\right]\right\}. \tag{4.16}$$

It is an interesting observation that, in the present case, one cannot obtain the formulas of Sec. III by letting c approach infinity. Thus, the statistics of the Schrödinger-Gordon field is quite different from that one of the nonrelativistic field. In the particle-picture, one can interpret Eqs. (4.13)–(4.16) as an expression of the fact that the number of *existing* particles is in thermal equilibrium with the surroundings. If the temperature is raised, then the kinetic energy of the particles already present in the field is raised, in addition to more particles being created. Thus, part of the thermal energy is contained in the rest mass of the particles. It is only natural that the nonrelativistic equations cannot describe such a case. There, in the particle-picture the particles are assumed to be already created and to be only raised from an "unobservable" state without any kinetic energy into a state which is observable.

Since the Schrödinger-Gordon equation is supposed to hold for mesons, one should expect that Eqs. (4.13) to (4.16) are valid for the meson field. The number of mesons present per unit volume should be in thermal equilibrium with the surroundings according to (4.16); if the temperature is lowered, the mesons must disintegrate and not merely disappear into an "unobservable" state. At room temperature (68°F) the meson density is very small (for μ-mesons):

$$N = 10^{-1.89\times 10^9}\ \text{cm}^{-3}. \tag{4.17}$$

One may object that one cannot speak of the disintegration of the mesons without considering their decay products. However, it should be kept in mind that the mesons, in the present formalism, are annihilated and do not decay into other particles. This is a consequence of the Schrödinger-Gordon equation. Therefore, if certain particles in nature do not disintegrate but only disappear into an unobservable state when the temperature is lowered, one should note that the Schrödinger-Gordon equation cannot be the right equation for them; or else one has to invent some explanation why more mesons are present than are given by Eq. (4.17). We are grateful to Professor Schrödinger for suggesting that one might get such an explanation by saying that the mesons do not disintegrate, but are absorbed by the nucleons. The nucleons themselves are certainly not in thermal equilibrium. There are much too many of them left. Unless one considers the transformation of nucleons into electromagnetic radiation impossible, one must be astonished that there is so much matter with rest mass $\neq 0$ left in the universe, and one must regard it as a relic of 2 or 3 billion years ago that has not yet reached equilibrium.

Finally, we could perhaps remark that in this section, too, the counting prescriptions of Einstein and Bose hold, for the N_K's run from 0 to ∞ and each combination is enumerated just once. Nevertheless, the thermodynamic functions are quite different from those in ordinary Bose statistics.

V. SPINOR FIELDS

In this section we shall treat fields "containing" particles which obey the exclusion principle.

The *nonrelativistic* case for such fields is obtained by taking the ordinary Schrödinger equation (3.1), but assuming anticommutation, rather than commutation, rules for ψ and its conjugate. This leaves the matrix representation (3.4) for H unchanged, but the matrix $\mathbf{N}_K$ has now the form

$$\mathbf{N}_K = \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}. \tag{5.1}$$

Hence, the partition function Z becomes

$$Z = \text{trace}\exp(-\vartheta\mathbf{H}) = \sum_{N_K=0,1} \exp(-\vartheta \textstyle\sum_K N_K E_K) \tag{5.2}$$

and

$$\begin{aligned}\log Z &= \textstyle\sum_K \log \sum_{N_K} \exp(-N_K E_K/kT) \\ &= \textstyle\sum_K \log\{1+\exp(-E_K/kT)\},\end{aligned} \tag{5.3}$$

which differs from (3.8) only in some signs. The eigenvalues E_K are given by (3.5), as before. In a similar way to Sec. III one can proceed to calculate the thermodynamic functions and obtains the following expressions as for a Fermi-Dirac gas:

$$F/V = -(2\pi m)^{3/2}h^{-3}(kT)^{5/2}\textstyle\sum\{(-1)^{n+1}/n^{5/2}\}, \tag{5.4}$$

$$S/V = (5/2)(2\pi m)^{3/2}h^{-3}k^{5/2}T^{3/2}\textstyle\sum\{(-1)^{n+1}/n^{5/2}\}, \tag{5.5}$$

$$E/V = (3/2)(2\pi m)^{3/2}h^{-3}(kT)^{5/2}\textstyle\sum\{(-1)^{n+1}/n^{5/2}\}. \tag{5.6}$$

Thus the particle-picture of such a field corresponds to that one of the nonrelativistic Schrödinger field; except that for the particles, Fermi instead of Bose statistics is applied. Again, by raising the temperature, some particles are lifted out of an infinite reservoir with no kinetic energy.[8]

More interesting is the *relativistic* case. The hamiltonian of the quantized Dirac equation is in a suitable matrix representation (Wentzel,[5] p. 162; Schiff,[6] p. 352)

$$\mathbf{H} = \sum_{K,s} \mathbf{N}_{Ks} E_{Ks} \tag{5.7}$$

with $\mathbf{N}_{Ks}$ as given by (5.1). The eigenvalues E_{Ks} of the Dirac equation are (Schiff,[6] p. 351)

$$E_{Ks} = +(\hbar^2c^2K^2+m^2c^4)^{\frac{1}{2}} \quad \text{for } s=1, 2, \tag{5.8a}$$

$$E_{Ks} = -(\hbar^2c^2K^2+m^2c^4)^{\frac{1}{2}} \quad \text{for } s=3, 4 \tag{5.8b}$$

and thus may be positive or negative.

Thus we can find the partition function Z:

$$\begin{aligned}Z &= \textstyle\sum_{N_{Ks}} \exp(-\vartheta \sum_{Ks} N_{Ks}E_{Ks}) \\ &= \textstyle\prod_{Ks}\{1+(\exp-\vartheta E_{Ks})\}\end{aligned} \tag{5.9}$$

and

$$\log Z = \textstyle\sum_{Ks} \log\{1+(\exp-\vartheta E_{Ks})\} \tag{5.10}$$

and the thermodynamic functions

$$\begin{aligned}F &= -kT\log Z \\ &= -kT\textstyle\sum_{Ks}\log\{1+\exp(-E_{Ks}/kT)\},\end{aligned} \tag{5.11}$$

$$\begin{aligned}S = k\textstyle\sum_{Ks}\{(E_{Ks}/kT)/[\exp(E_{Ks}/kT)+1] \\ +\log[1+\exp(-E_{Ks}/kT)]\},\end{aligned} \tag{5.12}$$

$$E = \textstyle\sum_{Ks} E_{Ks}/\{\exp(E_{Ks}/kT)+1\}. \tag{5.13}$$

If we set

$$E = \textstyle\sum N(K, s)E_{Ks}, \tag{5.14}$$

it follows that

$$N(K, s) = 1/\{\exp(E_{Ks}/kT)+1\}. \tag{5.15}$$

Thus, so far, the thermodynamic functions are the same as in the nonrelativistic case for electrons, except for the summation over s which arises from the spin of the particles.

However, we observed that now half of the eigenvalues E_{Ks} are negative, whereas heretofore the energy eigenvalues have always been positive. For low temperatures such that

$$|E_{Ks}| \gg kT \tag{5.16}$$

we obtain in the particle-picture that

$$N(K, s) \cong 1 \tag{5.17}$$

for all negative energy eigenvalues. This means that in thermal equilibrium at low temperatures all the negative energy states are occupied. Thus we obtain that the "normal" state of the field at low temperatures is exactly the vacuum state as postulated by Dirac in his hole theory, which serves to substantiate the present formalism.

The summation over the negative states makes the sums in (5.10) to (5.15) divergent; naturally, there is an infinite number of particles present in the negative states. Only the deviation from the vacuum state is physically interesting.

Thus one has to renormalize everything so that it is zero for $T=0$. It is seen that all one has to do is to take the sums only for the positive eigenvalues of the energy and to double their value. Furthermore, the summation over the spins gives an additional factor 2. Thus we have

$$F=-4kT\sum_K \log\{1+\exp(-E_K/kT)\}, \tag{5.18}$$

$$S=4k\sum_K\{\log(1+\exp(-E_K/kT)+(E_K/kT)[\exp(E_K/kT)+1]^{-1}\}, \tag{5.19}$$

$$E=4\sum_K E_K/\{\exp(E_K/kT)+1\}, \tag{5.20}$$

$$N=4\sum_K 1/\{\exp(E_K/kT)+1\}. \tag{5.21}$$

The sums can be approximated by integrals and the latter expanded into asymptotic expressions. One then obtains[7] the following formulas which are analogous to the expressions (4.13) to (4.16):

$$\frac{F}{V}=-4\frac{(2\pi m)^{3/2}}{h^3}(kT)^{5/2}\sum_1^\infty\frac{1}{n^{5/2}}\exp\left(-n\frac{mc^2}{kT}\right)\times(-1)^{n+1}\left\{1+\frac{15}{8n}\frac{kT}{mc^2}+\cdots\right\}, \tag{5.22}$$

$$\frac{S}{V}=\frac{4}{T}\frac{(2\pi m)^{3/2}}{h^3}(kT)^{3/2}mc^2\sum_1^\infty\frac{1}{n^{3/2}}\exp\left(-n\frac{mc^2}{kT}\right)\times(-1)^{n+1}\left\{1+\frac{35}{8n}\frac{kT}{mc^2}+\cdots\right\}, \tag{5.23}$$

$$\frac{E}{V}=4\frac{(2\pi m)^{3/2}}{h^3}(kT)^{3/2}mc^2\sum_1^\infty\frac{1}{n^{3/2}}\exp\left(-n\frac{mc^2}{kT}\right)\times(-1)^{n+1}\left\{1+\frac{27}{8n}\frac{kT}{mc^2}+\cdots\right\}, \tag{5.24}$$

$$\frac{N}{V}=4\frac{(2\pi m)^{3/2}}{h^3}(kT)^{3/2}\sum_1^\infty\frac{1}{n^{3/2}}\exp\left(-n\frac{mc^2}{kT}\right)\times(-1)^{n+1}\left\{1+\frac{15}{8n}\frac{kT}{mc^2}+\cdots\right\}. \tag{5.25}$$

These relativistic formulas correspond to the nonrelativistic ones in a similar way to the one outlined when we were dealing with the Schrödinger-Gordon equation. Again, it is not possible to obtain the nonrelativistic expressions by letting c approach infinity. In the particle-picture, one would say that (5.22) to (5.25) describe the thermal equilibrium of electron-positron gas mixture which contains an equal number of particles of either kind. Thus, the energy of creation for each pair of electrons and positrons is contained in the thermal energy of the field.

At room temperature (68°F), the equilibrium state is almost Dirac's vacuum state. The number of particles per unit volume deviating from the vacuum state is

$$N/V=10^{-8.63\times10^6}\ \mathrm{cm}^{-3}. \tag{5.26}$$

VI. THE ELECTROMAGNETIC FIELD

As the last application of the formalism outlined in this paper we take the electromagnetic field. One expects to obtain the Stefan-Boltzmann expressions for which, thus, a new derivation is supplied.

The hamiltonian of the electromagnetic field may be represented in the following symbolic form (Wentzel,[5] p. 117)

$$\mathbf{H}=\sum_K \hbar c|K|(\mathbf{N}_K^{(1)}+\mathbf{N}_K^{(2)}+1). \tag{6.1}$$

Hence the partition function Z becomes

$$Z=\sum_{N_K^{(1)},\,N_K^{(2)}}\exp\{-\vartheta\sum_K(N_K^{(1)}+N_K^{(2)}+1)\hbar c|K|\} \tag{6.2}$$

or

$$\log Z=-2\sum_K\log\{1-\exp(-\vartheta\hbar c|K|)\}-\vartheta\sum_K\hbar c|K|. \tag{6.3}$$

Equation (6.3) is the same expression as for the Schrödinger-Gordon field, except for the factor 2 and

$$\omega_K=\hbar c|K|. \tag{6.4}$$

Hence we obtain the same expressions as in (4.10) to (4.12) except for that factor 2 and $m=0$. The integrals can be calculated,[7] and yield

$$\frac{F}{V}=\frac{kT}{\pi^2}\int_0^\infty\log\left\{1-\exp\left(-\frac{\hbar cK}{kT}\right)\right\}K^2dK=-\frac{8}{45}\frac{\pi^5k^4T^4}{h^3c^3}, \tag{6.5}$$

$$\frac{S}{V}=\frac{k}{\pi^2}\int_0^\infty\left\{\frac{\hbar cK}{kT}\Big/\left[\exp\left(\frac{\hbar cK}{kT}\right)-1\right]-\log\left[1-\exp\left(-\frac{\hbar cK}{kT}\right)\right]\right\}K^2dK=\frac{32}{45}\frac{\pi^5k^4}{h^3c^3}T^3, \tag{6.6}$$

$$E/V=(1/\pi^2)\int_0^\infty K^3\hbar c dK/\{\exp(\hbar cK/kT)-1\}=\frac{8}{15}\frac{\pi^5k^4}{h^3c^3}T^4, \tag{6.7}$$

which is indeed what was expected.

VII. CONCLUSION

In spite of many applications of quantum statistics to field theories, a consistent treatment of this subject had not yet been given before. In the foregoing sections we have shown that Klein's[3] formalism of quantum statistics can be applied to field theories without the need of much alteration. In some instances the thermodynamic functions were very similar to those for an ensemble of like particles; in others modifications had to be made.

The statistics of the nonrelativistic fields correspond to ordinary Bose and Fermi statistics of an ensemble of identical particles and thus agree with the results obtained by Kaempffer.[4] The relativistic cases, however, are different and yield new expressions where the number of existent particles is in equilibrium with the surrounding thermal conditions. It is considered as a considerable support for the present formalism that the thermal equilibrium at low temperatures of the Dirac electron field is automatically the "vacuum" state as described in the hole theory. Finally, the fact that the application of our formalism to the electromagnetic field leads back to Planck's radiation theory had to be expected.

It seems to us that the treatment given here is much more straightforward and direct than the approach of Debye[1] and Kaempffer[4] to the statistics of waves. We should like to emphasize once more that here we are not primarily concerned with the particles that are "contained" in the field, but with the statistics of the field only. The notion of "particles" is used only for convenience because it turned out that the calculation of the traces of the matrices representing the distribution functions is most easily performed in the N-representation which permits one to talk about "particles."

In conclusion, we should like to acknowledge our indebtedness to colleagues and students who have shown much interest in the progress of this work. We are especially grateful to Professor Bergmann in Syracuse and Professor Preston in Toronto for valuable discussions and helpful advice. Professors Green and Schrödinger in Dublin have read and criticized the manuscript and made pertinent suggestions; we wish to thank them. We are also indebted to the Reuben Wells Leonard Foundation for awarding a fellowship to one of us (C.D.M.) which made this research possible.

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A Calculation of the Electron Affinity of Sodium*

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A wave function of the form $\Phi=\varphi(r_1, r_2)(1+cr_{12})$ is assumed for the (3s) electrons of Na$^-$, to take into account the polarization effect of the added electron, an effect neglected by the Hartree method. On this basis the electron affinity of sodium is calculated to be +1.2 ev and therefore the negative ion is stable. The decrease in energy relative to the Hartree result is mainly due to the increased separation and consequent lowered interaction potential energy of the (3s) electrons. Since the (4s) electrons of K$^-$ should be strongly polarized, the electron affinity of potassium can be estimated to be about +0.7 ev.

I. INTRODUCTION AND THEORY

ALTHOUGH the negative sodium ion Na$^-$ probably can exist as a stable structure, calculation of its energy by the method of the self-consistent field[1] leads to a negative electron affinity, indicating an unstable ion (to the accuracy of the approximation). The reason is that the Hartree-Fock method cannot take into account the polarization effect of the added electron, an effect which contributes very largely to the stability of a negative ion.[2]

To take account of the polarization of the two outer shell electrons, it is necessary to adopt a wave function which depends on the interelectronic distance r_{12} between the outer electrons, as well as on their distances r_1, r_2 from the nucleus. The simplest wave function of this kind is

$$\Psi=U(r_3, \cdots, r_N)\Phi(r_1, r_2, r_{12}), \tag{1}$$

where the inner ten electrons are represented by the numbers 3, $\cdots$, N($N=12$ for Na$^-$), and the outer two electrons are labeled 1 and 2. If the wave function U of the Na$^+$ core is chosen as a product of one-electron functions, it follows from the variation principle that U is essentially the self-consistent field function.[3] Similarly, if exchange is included U becomes the Hartree-Fock function, a determinant of one-electron functions. We are led in either case to an equation for Φ, which

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[1] D. R. Hartree and W. Hartree, Proc. Cambridge Phil. Soc. 34, 550 (1938).

[2] This question is discussed by D. R. Hartree, Rep. on Prog. in Phys. 11, 113 (1948) and E. Conwell, Phys. Rev. 74, 268 (1948).

[3] There is a slight difference between U and the s.c.f. function because Φ is not the Hartree function. However, the distinction is only a theoretical one, since the wave function U is negligibly influenced by the outer wave functions.