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Quantum Statistics of Almost Classical Assemblies

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The sum of states of an assembly in statistical equilibrium may be transformed into an integral in phase space, which is analogous to the classical Gibbs phase integral. With the use of an equation obtained by Bloch it is possible to expand the quantum phase integral in powers of Planck's constant h. The present method of treating the problem supplements that of Wigner and of Uhlenbeck and Gropper by furnishing a more convenient means of obtaining the h-expansion.

INTRODUCTION

It is generally assumed that an assembly, consisting of a large number of mechanical systems in statistical equilibrium, has the properties of a Gibbs canonical ensemble in respect to its probability distribution in energy. The thermodynamic properties of such an assembly may be calculated from the sum of states

$$\sigma=\sum_n e^{-\beta E_n}, \tag{1}$$

where β is the reciprocal of the product of Boltzmann's constant k and the absolute temperature T. The sum is extended over all accessible energy states E_n. When σ is known, the energy, entropy and thermodynamic potential of the assembly may be obtained from the following relations:[1]

$$\bar{E}=-d\ln\sigma/d\beta;\quad S=k(\ln\sigma-\beta(d\ln\sigma/d\beta)) \tag{1a}$$

$$A=\bar{E}-TS=-(1/\beta)\ln\sigma.$$

If the laws of classical mechanics are assumed to be valid, which would be true if Planck's constant h were allowed to approach zero, the sum of states may be conveniently transformed into an integral over the phase space of the assembly.

$$\lim_{h=0} h^N\sigma=z=\int\int e^{-\beta H(p,q)}dp\,dq, \tag{2}$$

where $H(p,\ q)$ is the classical Hamiltonian function of the momenta p and the configuration coordinates q, and N is the number of degrees of freedom of the system. The integral is extended over all of momentum and configuration space. From the Gibbs phase integral z, the energy, entropy, and thermodynamic potentials of the classical assembly may be determined except for additive constants.

For systems governed by quantum mechanics, the evaluation of σ is usually more complicated. The direct procedure would consist in determining the allowed energies of the system by means of the Schrödinger equation together with certain restrictions on the symmetry character of the wave functions, and then carrying out the summation. However, in many cases this method requires a prohibitive amount of mathematical labor. The question arises whether one could transform the sum of states into an integral in phase space analogous to the Gibbs integral z, without explicitly solving the dynamical problem. The basis for such a transformation is furnished by work of von Neumann.[2] It has been used by Bloch[3] and by Wigner[4] in the treatment of certain problems. The phase integral which is thus obtained is considerably more difficult to evaluate than the corresponding classical one. However, for systems nearly classical in their behavior, Wigner has shown that it may be expanded in powers of h, the first term of which is the Gibbs integral z.

It is the aim in the present article to carry out an expansion of σ in powers of h similar to that of

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[1] J. W. Gibbs, *Elementary Principles in Statistical Mechanics*, Yale University Press.

[2] von Neumann, Gött. Nachr. 273 (1927).

[3] Bloch, Zeits. f. Physik **74**, 295 (1932).

[4] Wigner, Phys. Rev. **40**, 749 (1932).

Wigner. By starting from an equation obtained by Bloch, it is possible to obtain for the coefficients in this expansion a recursion formula which permits a simpler calculation of the higher approximations than the method employed by Wigner. In addition, the correction to σ required by the symmetry restrictions to be placed on the wave functions in accordance with the Fermi-Dirac or the Bose-Einstein statistics is obtained. This correction, neglected by Wigner, has been calculated by Uhlenbeck and Gropper.[5] It is included here, since it seems desirable to give a general formulation of the problem yielding all of the quantum corrections which must be applied to the Gibbs phase integral for systems deviating but little from classical behavior.

Transformation of the Sum of States

We take for consideration an assembly consisting of N similar particles of mass m, moving in a conservative field of force. The potential function of the system $V(q_1\cdots q_{3N})$ will be determined by the $3N$ coordinates $q_1\cdots q_{3N}$, specifying position in configuration space. The Schrödinger equation for such a system is

$$(H-E)\psi=0,\quad H=H_0+V(q_1\cdots q_3),\quad H_0=-h^2\sum_{k=1}^{N}\frac{1}{2m}\Delta_k, \tag{3}$$

where h is Planck's constant divided by 2π, and Δ_k is the Laplacian operator in the configuration space of the particle k. The normalized wave functions will be denoted by ψ_n and the corresponding energy levels by E_n.

The sum of states may be expressed as an integral in configuration space, in the following manner.

$$\sigma=\sum_n e^{-\beta E_n}=\sum_n\int\cdots\int\psi_n{}^*e^{-\beta H}\psi_n dq_1\cdots dq_{3N}, \tag{4}$$

where the operator $e^{-\beta H}$ is defined by the series[6]

$$e^{-\beta H}=\sum_{l=0}^{\infty}\frac{(-\beta)^l}{l!}H^l. \tag{5}$$

Eq. (4) follows simply from the relation, $H^l\psi_n=E_n{}^l\psi_n$, and from the fact that the functions ψ_n are normalized. The integral (4) has much in common with the Gibbs phase integral z. Thus it will be remembered that the transformation determinant of the volume element $dp_1\cdots dp_{3N}$, $dq_1\cdots dq_{3N}$ in the classical integral (2) is unity for any canonical transformation of the momentum and configuration coordinates. The quantum mechanical analogue of the classical canonical transformation consists in a transformation of the orthogonal function set ψ_n. From (4) it is seen that σ is the diagonal sum of the matrix $[e^{-\beta H}]$, the elements of which are given by

$$[e^{-\beta H}]_{n'n}=\int\psi_{n'}{}^*e^{-\beta H}\psi_n dq. \tag{6}$$

Since the diagonal sum of such a matrix is invariant under a transformation of the ψ's, one may employ not only the characteristic functions ψ_n of the operator H in its evaluation, but any other convenient set of orthogonal functions having the same symmetry properties as the ψ_n's. This corresponds to the fact that one may employ any convenient canonically conjugate set of momentum and space coordinates in the evaluation of the classical Gibbs phase integral.

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[5] Uhlenbeck and Gropper, Phys. Rev. **41**, 79 (1932).

[6] One may write $e^{-\beta H}$ as $e^{-\beta(H_0+V)}$ where H_0 is the kinetic energy operator. However, since H_0 and V do not commute, $e^{-\beta H}$ is not equal to $e^{-\beta H_0}e^{-\beta V}$ or $e^{-\beta V}e^{-\beta H_0}$.

We wish to replace the energy summation in the integral (4) by an integration in momentum space. For this purpose we choose the characteristic functions $\varphi(p, q)$ of the kinetic energy operator H_0.[7] These functions together with the corresponding continuous energy levels are easily found to be

$$\varphi(p, q) = \exp\left[\frac{i}{h}\sum_{k=1}^{N}\mathbf{p}_k\cdot\mathbf{r}_k\right], \quad T(p) = \sum_{k=1}^{N}\mathbf{p}_k^2/2m, \tag{7}$$

where $\mathbf{p}_k$ is the momentum vector and $\mathbf{r}_k$ is the radius vector in the phase space of the particle k. It will be assumed that the characteristic functions ψ_n of the operator H are either symmetric or antisymmetric in the coordinates of the N particles. The first assumption corresponds to the Bose-Einstein and the second to the Fermi-Dirac statistics. Linear combinations of the functions $\varphi(p, q)$, which are symmetric or antisymmetric must be constructed before they are suitable for an expansion of the functions ψ_n. The required linear combinations are the following:

$$\Phi(p, q) = \frac{1}{(N!)^{\frac{1}{2}}}\sum_{P}(\pm 1)^{(P)}\exp\left[\frac{i}{h}P\sum_{k=1}^{N}\mathbf{p}_k\cdot\mathbf{r}_k\right]. \tag{8}$$

The summation is extended over the $N!$ functions generated by allowing the permutation operator P to redistribute the $\mathbf{r}_k$'s among the $\mathbf{p}_k$'s in the sum $\sum_{k=1}^{N}\mathbf{p}_k\cdot\mathbf{r}_k$. The order of the permutation is denoted by (P). When it is even the factor $(\pm 1)^{(P)}$ has the value $+1$, and when odd the value ± 1. The functions ψ_n are then expanded in terms of the orthogonal set $\Phi(p, q)$ by means of Fourier integrals, and the sum over the index n carried out by means of the completeness relation

$$\sum_{n}\psi_n^*(q')\psi_n(q) = \delta(q'-q), \tag{9}$$

where $\delta(q'-q)$ is the Dirac delta-function. Eq. (4) then becomes

$$\sigma = \frac{1}{(2\pi h)^{3N}N!}\sum_{P'P}(\pm 1)^{(P'+P)}\int_{-\infty}^{+\infty}\cdots\int_{-\infty}^{+\infty}\exp\left[-\frac{i}{h}P'\sum_{k=1}^{N}\mathbf{p}_k\cdot\mathbf{r}_k\right]e^{-\beta H}\exp\left[\frac{i}{h}P\sum_{k=1}^{N}\mathbf{p}_k\cdot\mathbf{r}_k\right]dp_1\cdots dq_{3N}. \tag{10}$$

This integral is the quantum mechanical analogue of the Gibbs phase integral.

The evaluation of the quantum phase integral (10) depends upon a determination of the following functions

$$u(P) = e^{-\beta H}\varphi(P); \quad \varphi(P) = \exp\left[\frac{i}{h}P\sum_{k=1}^{N}\mathbf{p}_k\cdot\mathbf{r}_k\right]. \tag{11}$$

One notes that as β approaches zero, u must approach φ. Moreover differentiation of both sides of Eq. (11) with respect to β leads to the Bloch equation

$$Hu + \partial u/\partial\beta = 0, \quad \lim_{\beta=0} u = \varphi. \tag{12}$$

This equation, which may be regarded as a fundamental equation of quantum statistics, is identical in form with the Schrödinger equation containing the time, differing from it only in the appearance of β instead of it/h. Bloch[3] noting that its solutions may be obtained from the Kennard transformation functions by replacing it/h by β, has obtained exact solutions of Eq. (12) for certain special problems. We will attempt here an approximate solution of Eq. (12), which depends upon an expansion in powers of Planck's constant h. While the method resembles in principle the Wentzel-Brillouin-Kramers solution of the wave equation, its details are quite different. Let us suppose that

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[7] The quantities $\mathbf{p}_k$ and $\mathbf{r}_k$ in the wave function are to be regarded as vectors in ordinary three-dimensional space. The components of $\mathbf{p}_k$ are of course numbers, not operators.

$$u = w\varphi(P)e^{-\beta H(p,\,q)}, \tag{13}$$

where $H(p, q)$ is the ordinary classical Hamiltonian function, $T+V$. With the aid of Eq. (12) and the relations $H_0\varphi(P) = T\varphi(P)$ and

$$-ih\sum_{k=1}^{N} \nabla_k\varphi(P)\cdot\nabla_k = \varphi(P)\left(P\sum_{k=1}^{N} \mathbf{p}_k\cdot\nabla_k\right)$$

one finds that w must satisfy the following equation:

$$\frac{\partial w}{\partial\beta} - e^{+\beta V}\left\{\frac{ih}{m}\left(P\sum_{k=1}^{N}\mathbf{p}_k\cdot\nabla_k e^{-\beta V}w\right) + \frac{h^2}{2m}\sum_{k=1}^{N}\Delta_k e^{-\beta V}w\right\} = 0; \quad \lim_{\beta=0} w = 1. \tag{14}$$

Because of the boundary condition at $\beta = 0$, Eq. (14) may be conveniently written as an integral equation

$$w = 1 + \frac{ih}{m}\int_0^\beta e^{Vt}\left[P\sum_{k=1}^{N}\mathbf{p}_k\cdot\nabla_k e^{-Vt}w\right]dt + \frac{h^2}{2m}\int_0^\beta e^{Vt}\sum_{k=1}^{N}\Delta_k(e^{-Vt}w)dt. \tag{15}$$

Solution of Eq. (15) by successive approximations yields

$$w = \sum_{l=0}^{\infty} h^l w_l,$$

$$w_0 = 1, \quad w_1 = -\frac{i\beta^2}{2m}\left(P\sum_{k=1}^{N}\mathbf{p}_k\cdot\nabla_k V\right),$$

$$w_2 = -\frac{1}{2m}\left\{\frac{\beta^2}{2}\sum_{k=1}^{N}\Delta_k V - \frac{\beta^3}{3}\left[\sum_{k=1}^{N}(\nabla_k V)^2 + \frac{1}{m}\left(P\sum_{k=1}^{N}\mathbf{p}_k\cdot\nabla_k\right)^2 V\right] + \frac{\beta^4}{4m}\left(P\sum_{k=1}^{N}\mathbf{p}_k\cdot\nabla_k V\right)^2\right\}. \tag{16}$$

The general term w_l may be calculated by means of the following formula

$$w_l = \frac{1}{m}\int_0^\beta e^{Vt}\left\{\frac{1}{2}\sum_{k=1}^{N}\Delta_k(e^{-Vt}w_{l-2}) + i\left(P\sum_{k=1}^{N}\mathbf{p}_k\cdot\nabla_k e^{-Vt}w_{l-1}\right)\right\}dt. \tag{17}$$

This recursion formula permits a calculation of any term in the series (16) by simple operations of differentiation and integration on the two preceding terms.

The functions $u(P)$ may now be written

$$u(P) = \varphi(P)e^{-\beta H(p,\,q)}\sum_{l=0}^{\infty} h^l w_l(P) \tag{18}$$

and the quantum phase integral becomes

$$\sigma = \frac{1}{(2\pi h)^{3N}N!}\int\cdots\int e^{-\beta H(p,\,q)}\sum_{P',\,P}(\pm 1)^{(P'+P)}\exp\left[\frac{i}{h}(P-P')\sum_{k=1}^{N}\mathbf{p}_k\cdot\mathbf{r}_k\right]\sum_{l=0}^{\infty}h^l w_l(P)dp_1\cdots dq_{3N}. \tag{19}$$

For convenience, the sum over P and P' may be arranged so that the first member contains all terms in which P' and P are the same permutation, the second those in which P' and P differ only with respect to a single pair of particles, etc. Certain simplifications are then possible. Each of the $N!$ terms in which $P' = P$, when integrated over the p's, gives the same result, since $H(p, q)$ is symmetrical in the p's and it cannot matter which p is associated with a given q. One may therefore replace the function $w_l(P)$ by its value w_l for the identity permutation. For terms in which P' and P

differ by the permutation of two particles similar simplifications may be made, and it is only necessary to use two functions $w_l(jk)$ and $w_l(kj)$, corresponding to the two permutations of the pair jk, regardless of what pair of momentum coordinates happens to be involved. The integral (19) then becomes

$$\sigma=\frac{1}{(2\pi h)^{3N}}\int\cdots\int e^{-\beta H(p,\,q)}\Bigg\{\sum_{l=0}^{\infty}w_l h^l$$

$$\pm\frac{1}{2}\sum_{k\neq j}^{N}\left[\exp\left[\frac{i}{h}(\mathbf{p}_j-\mathbf{p}_k)\cdot(\mathbf{r}_j-\mathbf{r}_k)\right]\sum_{l=0}^{\infty}h^l w_l(jk)+\exp\left[-\frac{i}{h}(\mathbf{p}_j-\mathbf{p}_k)\cdot(\mathbf{r}_j-\mathbf{r}_k)\right]\sum_{l=0}^{\infty}h^l w_l(kj)\right]$$

$$+\cdots\Bigg\}dp_1\cdots dp_{3N}\cdots dq_{3N}. \quad (20)$$

When the values of w_l calculated with the aid of Eq. (17) are inserted in Eq. (20) and the integration over the momentum coordinates is carried out, there results

$$\sigma=\frac{(2\pi mkT)^{3N/2}}{(2\pi h)^{3N}}\int_{-\infty}^{+\infty}\cdots\int_{-\infty}^{+\infty}e^{-\beta V}\Bigg\{\left[1-\frac{h^2\beta^2}{12m}\sum_{k=1}^{N}\left(\Delta_k V-\frac{\beta}{2}(\nabla_k V)^2\right)+\cdots\right]$$

$$\pm\sum_{j\neq k}e^{-mr_{jk}^2/\beta h^2}\left[1+\frac{\beta}{2}\mathbf{r}_{jk}\cdot(\nabla_j V-\nabla_k V)+\cdots\right]+\cdots\Bigg\}dq_1\cdots dq_{3N};\quad \mathbf{r}_{jk}=\mathbf{r}_j-\mathbf{r}_k. \quad (21)$$

The first three terms of the series $\sum_{l=0}^{\infty} h^l w_l$ have been retained in the part of σ involving identical permutations, and the first two terms in the part involving permutations differing with respect to two particles. The first part agrees with the result obtained by Wigner and the second with that obtained by Uhlenbeck and Gropper.[5a] Since they become rather cumbersome, the higher approximations are not written down. They may, however, be calculated by simple processes of differentiation and integration with the aid of the recursion formula (17). In an actual problem, their form may usually be kept simpler by inserting an explicit expression for the potential V at the beginning.

In the case of relatively weak coupling between the particles as between the molecules of a gas at low pressures, the arrangement of terms in the sum over permutations in Eq. (19) actually corresponds to their order of magnitude. Because of the factors $e^{-mr_{12}^2/\beta h^2}$, the ratio of each member to the preceding one will be v/V, where v is of the order of magnitude of the second virial coefficient of the gas and V the total volume of the vessel in which it is confined. The walls of the vessel may be represented by means of high potential barriers which cause $e^{-\beta V}$ to vanish in regions of configuration space outside the vessel. In practice, if one neglects small wall corrections, this is equivalent to restricting the integrations in configuration space to regions inside the vessel.

Probability Distribution in Phase Space

In the preceding section, the sum of states has been transformed into the phase integral of a function $F(p, q)$ having the form $e^{-ipq/h}e^{-\beta H}e^{ipq/h}$. The relation which this function bears to the probability distribution in phase space has not yet been investigated, and indeed from a purely thermodynamic point of view is unessential. It may be shown, however, that $F(p, q)$, when integrated over momenta, yields a probability in configuration, and when integrated over configuration space, a probability in momentum, consistent both with a canonical distribution in energy and with the Schrödinger equation.

A discussion of the probability distribution in phase space is facilitated by the use of the

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[5a] A trivial oversight of making the derivative of x^2 equal to x instead of $2x$, causes the coefficient of $r_{jk}\cdot(\nabla_j V-\nabla_k V)$ in their formula to be $\beta/4$ instead of $\beta/2$.

following function, which differs but little from Wigner's[8] $P(x, p)$

$$P(p, q)=(2\pi h)^{-1}\int_{-\infty}^{\infty+} e^{ip(q'-q)/h}\psi^*(q')\psi(q)dq', \quad (22)$$

where ψ satisfies the Schrödinger equation

$$H\psi-ih(\partial\psi/\partial t)=0. \quad (23)$$

When $P(p, q)$ is integrated with respect to p, it yields the probability in configuration space $\psi^*(q)\psi(q)$ and when integrated with respect to q the corresponding probability in momentum space $(2\pi h)^{-1}\Phi^*(p)\Phi(p)$ where

$$\Phi(p)=\int_{-\infty}^{+\infty} e^{-ipq/h}\psi(q)dq. \quad (24)$$

The above relations are equally valid whether the system is made up of a pure state or of a mixture of states.

For an arbitrary distribution in energy

$$\psi=\sum_n C_n\psi_n e^{2\pi i\nu_n t+i\varphi_n}, \quad (25)$$

where Ψ_n satisfies the Schrödinger equation $(H-E_n)\psi_n=0$; $\nu_n=-E_n/2\pi h$, and φ_n is an arbitrary phase angle. The probability in configuration space is

$$P(q)=\psi^*\psi=\sum_{n',\,n} C_{n'}{}^*C_n\psi_{n'}{}^*\psi_n e^{2\pi i\nu_{n'n}t+i(\varphi_n-\varphi_{n'})} \quad (26)$$

To give this probability a physical meaning it is necessary to form an average over the arbitrary phases φ_n,[9] and one finds

$$\overline{P(q)}=\sum_n C_n{}^*C_n\psi_n{}^*\psi_n \quad (27)$$

with a similar expression for $\overline{P(p)}$, the probability in momentum space

$$\overline{P(p)}=\sum_n C_n{}^*C_n\Phi_n{}^*\Phi_n, \quad (28)$$

where Φ_n may be calculated with the aid of Eq. (24). The probability distribution function in energy is

$$P(E_n)=C_n{}^*C_n\,|\,\sum_n C_n{}^*C_n. \quad (29)$$

For a canonical distribution $P(E_n)=e^{\beta(A-E_n)}$ where A is the thermodynamic potential $\bar{E}-TS$. Thus one may write

$$C_n{}^*C_n=e^{-\beta E_n}$$
$$\sigma=e^{-\beta A}=\sum_n C_n{}^*C_n=\sum_n e^{-\beta E_n}. \quad (30)$$

The probability functions $\overline{P(q)}$ and $\overline{P(p)}$ become for a canonical distribution

$$\overline{P(q)}=\sigma^{-1}\sum_n\psi_n{}^*e^{-\beta E_n}\psi_n,$$
$$\overline{P(p)}=\sigma^{-1}\sum_n\Phi_n{}^*e^{-\beta E_n}\Phi_n. \quad (31)$$

They may be obtained by integration from the function

$$\overline{P(p, q)}=(2\pi h\sigma)^{-1}\int_{-\infty}^{+\infty}\sum_n e^{ip(q'-q)/h}\psi_n{}^*(q')e^{-\beta E_n}\psi_n(q)dq'. \quad (32)$$

When integrated with respect to p, $\overline{P(p, q)}$ gives the probability in configuration $\overline{P(q)}$, and when integrated with respect to q, the probability in momentum $\overline{P(p)}$. If one remembers that $e^{-\beta E_n}\psi_n=e^{-\beta H}\psi_n$ and expands ψ_n in the functions $e^{ipq/h}$ by means of a Fourier integral, there is obtained

$$\overline{P(p, q)}=(2\pi h\sigma)^{-1}\int\int_{-\infty}^{+\infty}\int\left\{\left[\sum_n\psi_n{}^*(q')\psi_n(q'')\right]e^{i(pq'-p'q'')/h}e^{-ipq/h}e^{-\beta H}e^{ip'q/h}\right\}dp'dq''dq'. \quad (33)$$

When the sum over n is carried out by means of the completeness relation (9) and the indicated integrations are performed, Eq. (33) reduces to

$$\overline{P(p, q)}=(2\pi h\sigma)^{-1}e^{-ipq/h}e^{-\beta H}e^{ipq/h}. \quad (34)$$

Thus the normalized probability function $\overline{P(p, q)}$ is proportional to the integrand $e^{-ipq/h}e^{-\beta H}e^{ipq/h}$ employed in the representation of the sum of states.

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[8] Wigner, reference 4, Eq. (5).

[9] For a discussion of this point see J. C. Slater, Phys. Rev. **38**, 237 (1931).

The expansion of $\overline{P(p, q)}$ in powers of h does not agree exactly with Wigner's expansion of $P(p, x)$. Thus his expansion contains no odd powers of h, while the expansion of $\overline{P(p, q)}$ does. However, when integrated over momenta, the two functions appear to lead to the same result for the probability in configuration. They also give the same result for the probability in momentum space, when the potential function V becomes positive and infinite on the boundary of a finite region in configuration space. The difference between $\overline{P(p, q)}$ and $P(p, x)$ may possibly be connected with the average over the arbitrary phases of the wave functions, which seems physically necessary. However, it should be remembered that because of the uncertainty principle, neither function has a physical meaning until it is integrated either over momentum space or over configuration space. Thus, it would not be surprising if one could construct a number of different functions of p and q, all of which would give the correct results for the momentum and configuration probabilities after integration over p or q.

The practical value of the method outlined in this article depends of course on the convergence of the expansion of $e^{-ipq/h}e^{-\beta H}e^{ipq/h}$ in powers of h. Its convergence will depend upon the properties of the integral Eq. (15). A detailed investigation of this equation would be desirable, but will not be undertaken here. However, from a physical standpoint, it seems likely that the expansion may be employed with confidence when kT is large relative to the spacing of the energy levels of the assembly, provided that the term system coalesces into a continuous spectrum as the potential function V approaches zero.

In conclusion, the writer wishes to express his indebtedness to Dr. F. London, Dr. F. Bloch, and to Dr. E. Wigner for the opportunity to discuss with them some of the questions treated here.