Variational Approach to the Many-Body Problem

R. U. AYRES
Department of Physics, Kings College, University of London, London, England
(Received January 28, 1958; revised manuscript received June 2, 1958)

Certain problems connected with the choice of trial variational functions for the quantum many-body problem are discussed. It is convenient to make use of the reduced-density-matrix formulation developed by Löwdin and Mayer, since a system whose Hamiltonian contains only 1- and 2-body interactions is characterized by the two simplest reduced density matrices $\Gamma^{(1)}$ and $\Gamma^{(2)}$. It is known that symmetry, Hermiticity, and normalizability conditions are not sufficient to ensure a physically realizable choice of the functions $\Gamma^{(1)}$ and $\Gamma^{(2)}$. However an additional nontrivial restriction is imposed by the fact that such functions must be possible variational extrema. The implications of this condition are investigated in some detail and it turns out that all the nonphysical choices of $\Gamma^{(1)}$ and $\Gamma^{(2)}$ which have been exhibited by various authors are eliminated. The condition is essentially nonquantum inasmuch as an analogous argument should be possible for a classical system. Moreover one of the consequences of this condition is that the system (classical or quantum) may exhibit macroscopic behavior, i.e., order-disorder transitions. The analysis leads to apparently reasonable choices of trial forms for $\Gamma^{(1)}$ and $\Gamma^{(2)}$, although it is still not known whether any further restriction must be imposed to complete the sufficiency argument.

1. INTRODUCTION

THE recent success in developing methods related to perturbation theory for treatment of the quantum many-body problem[1] has not as yet been matched by parallel progress in developing the variational approach. The Hartree-Fock procedure depended upon an "independent-particle" picture which breaks down drastically in most interacting systems, but no further advances have been made until quite recently.

The most promising approach seems to be via the so-called reduced density matrices, and Löwdin,[2] Mayer,[3] Blatt,[4] and others have made use of this formulation. The enormous simplification is due to the fact that if the Hamiltonian contains only 1-, 2-, 3-, $\cdots m$-particle interactions the state of the system is completely characterized by the m simplest reduced density matrices $\Gamma^{(1)}$, $\Gamma^{(2)}$, $\cdots\Gamma^{(m)}$. Evidently if only 2-particle interactions are present only $\Gamma^{(1)}$ and $\Gamma^{(2)}$ need be considered. These functions will be defined precisely later on. Since there is a $\Gamma^{(1)}$ and $\Gamma^{(2)}$ matrix for each N-particle wave function ψ with identical energies, it follows that minimizing the expectation value of the Hamiltonian with respect to $\Gamma^{(1)}$ and $\Gamma^{(2)}$ should give the ground-state energy *provided* we are certain the set of allowed Γ's is no larger than the original set of allowed ψ's. In different language, one seeks restrictive conditions which only admit functions which can be put into a $1 \leftrightarrow 1$ correspondence with the ψ's.

The conditions on the ψ's themselves are simply: symmetry (antisymmetry), Hermiticity, and square-integrability. The fact that the states must be superposable is ensured by the fact that the Schrödinger equation is linear, so that a linear combination of solutions is also a solution. Since the eigenfunctions span the space, it follows that any function which obeys all the specified conditions is a solution of the Schrödinger equation. One would like to verify that the Hilbert space is complete, i.e., that any sequence of functions in the space converges in the space. This property is generally assumed, though it has only been proved for special Hamiltonians.

Unfortunately the reduced density matrices must be handled with greater care because of the awkward fact that it is possible to find functions which have the correct symmetry (antisymmetry), Hermiticity, and normalizability properties but which definitely do not correspond to possible physical situations. The ambiguity occurs in both quantum and classical systems. Several authors[5–8] have pointed out the difficulty of ensuring physical realizability of functions $\Gamma^{(1)}$ and $\Gamma^{(2)}$, while Kirkwood recognized the problem, in a classical system, connected with choosing possible pair-distribution functions $\rho_2(r)$.

Löwdin[3] has showed that if the initial wave function is a single Slater determinant the system is completely characterized by the choice of $\Gamma^{(1)}$. In different language a slightly more general result has recently been obtained by Watanabe and Kuhn,[9] who showed that if the Hamiltonian of a system contains only 1-particle interactions the above-mentioned necessary conditions are also sufficient. However, the main problem is still unsolved: to find an additional necessary condition on the choice of $\Gamma^{(1)}$ and $\Gamma^{(2)}$ for *interacting* systems, such that all nonphysical choices are definitely eliminated.

[1] Only a small sample of the extensive literature can be mentioned; further references can be found in the following: K. Huang and C. N. Yang, Phys. Rev. **105**, 767 (1957); Lee, Huang, and Yang, Phys. Rev. **106**, 1135 (1957); K. A. Brueckner and C. A. Levinson, Phys. Rev. **97**, 1344 (1955); K. A. Brueckner, Phys. Rev. **100**, 36 (1955); H. A. Bethe, Phys. Rev. **103**, 1353 (1956); J. Goldstone, Proc. Roy. Soc. (London) **A239**, 267 (1957); K. A. Brueckner and K. Sawada, Phys. Rev. **106**, 1117, 1128, (1957); M. Gell-Mann and K. A. Brueckner, Phys. Rev. **106**, 364 (1957); K. Sawada, Phys. Rev. **106**, 372 (1957); J. Hubbard, Proc. Roy. Soc. (London) **A240**, 539 (1957).

[2] P.-O. Löwdin, Phys. Rev. **97**, 1474 (1955).

[3] J. E. Mayer, Phys. Rev. **100**, 1574 (1955).

[4] J. M. Blatt, Nuovo cimento 4, 430 (1956).

[5] M. S. Watanabe, Z. Physik **113**, 482 (1939).

[6] R. H. Tredgold, Phys. Rev. **105**, 1421 (1957).

[7] H. Koppe, Z. Physik **148**, 135 (1957).

[8] Y. Mizuno and T. Izuyama, Progr. Theoret. Phys. Japan **18**, 33 (1957).

[9] H. W. Kuhn (to be published).

This additional condition ought also to have the following properties: (a) it must be "geometrical" in the sense that the statement of the condition should be independent of the form of the Hamiltonian, though of course its detailed effect will not be—actually if all two-particle interactions vanish the condition should become redundant—and (b) it cannot be a purely quantum condition. Moreover application of the new condition ought to indicate the possibility (depending on the form of H) of *macroscopic* states of the system[10] with concomitant order-disorder transitions.

In the following the question of sufficiency will not be discussed. However it will be shown that an additional necessary condition can be derived with the required properties. The condition can be stated in a peculiarly simple way, but a correct variational calculation in terms of $\Gamma^{(1)}$ and $\Gamma^{(2)}$ is still rather difficult.

2. DENSITY MATRIX FORMULATION

Consider a system of N particles in a volume V. In general the motions of the particles will be described by a Hamiltonian of the form

$$H=\sum_i H_i+\left(\frac{1}{2!}\right)\sum_{i,j}{}' H_{ij}+\left(\frac{1}{3!}\right)\sum_{i,j,k}{}'' H_{ijk}+\cdots. \quad (1)$$

In most of the following we restrict ourselves to a model in which no three-body or higher many-body terms contribute to the Hamiltonian and in which H_i and H_{ij} are invariant under translation and independent of spin. It is also convenient to suppose that both N, $V\rightarrow\infty$, while N/V remains finite. In general these restrictions are made merely for the sake of simplicity and can be somewhat relaxed with suitable modifications of the subsequent argument. Also, to avoid cumbersome notation and frequent digressions we shall fix attention on the special case of a system obeying Fermi statistics in the ground state. The changes involved in consideration of other cases will not be discussed at any length.

The partition function can be written

$$Z=\sum_i \exp-\beta E_i=\mathrm{Tr}\{\exp[-\beta H]\}, \quad (2)$$

where $\beta=1/kT$, and the free-energy A is given by

$$A=-(1/\beta)\ln Z. \quad (3)$$

In quantum mechanics it is convenient to express (2) in terms of the density matrix

$$\Gamma^{(N)}(\mathbf{x}_1',\mathbf{x}_2',\cdots|\beta|\mathbf{x}_1,\mathbf{x}_2,\cdots)=\psi^*\{\mathbf{1}',\mathbf{2}'\cdots\}\exp(-\beta H)\psi\{\mathbf{1},\mathbf{2}\cdots\}, \quad (4)$$

where

$$Z=\sum_{\text{states}}\int\cdots\int\Gamma^{(N)}d\{\mathbf{N}\}. \quad (5)$$

[10] The author is indebted to Dr. R. H. Tredgold for making this observation.

The abbreviated notation $\mathbf{1}',\mathbf{2}',\cdots$ refers to variables (including both space and spin coordinates) $\mathbf{x}_1',\mathbf{x}_2',\cdots$, and $d\{\mathbf{N}\}=d\mathbf{x}_1d\mathbf{x}_2d\mathbf{x}_3\cdots$. The operator acts only on unprimed coordinates, then the primes are removed prior to integration. A set of reduced density matrices can be defined[2,3] by integrating $\Gamma^{(N)}$ over some of the variables, thus:

$$\Gamma^{(1)}(\mathbf{x}_1'|\beta|\mathbf{x}_1)=N\int\cdots\int\psi^*\{\mathbf{1}',\mathbf{N}-\mathbf{1}\}\times\exp(-\beta H)\psi\{\mathbf{1},\mathbf{N}-\mathbf{1}\}d\{\mathbf{N}-\mathbf{1}\}, \quad (6)$$

$$\Gamma^{(2)}(\mathbf{x}_1',\mathbf{x}_2'|\beta|\mathbf{x}_1,\mathbf{x}_2)=\frac{N(N-1)}{2}\int\cdots\int\psi^*\{\mathbf{1}',\mathbf{2}',\mathbf{N}-\mathbf{2}\}\times\exp(-\beta H)\psi\{\mathbf{1},\mathbf{2},\mathbf{N}-\mathbf{2}\}d\{\mathbf{N}-\mathbf{2}\}, \quad (7)$$

where all but one variable has been integrated in the first instance, all but two in the second, and so forth. In the ground-state ($\beta\rightarrow\infty$), (3) reduces to the usual quantum-mechanical formula

$$E_0=\underset{\beta\rightarrow\infty}{A}=\langle H\rangle=\int H_1\Gamma^{(1)}d\mathbf{x}_1+\int\int H_{12}\Gamma^{(2)}d\mathbf{x}_1d\mathbf{x}_2, \quad (8)$$

where the expansion (1) has been used. Several properties of the Γ's are immediate; for example, Hermiticity

$$\Gamma^{(1)}(\mathbf{x}_1'|\mathbf{x}_1)=\Gamma^{*(1)}(\mathbf{x}_1|\mathbf{x}_1'),$$
$$\Gamma^{(2)}(\mathbf{x}_1',\mathbf{x}_2'|\mathbf{x}_1,\mathbf{x}_2)=\Gamma^{*(2)}(\mathbf{x}_1,\mathbf{x}_2|\mathbf{x}_1',\mathbf{x}_2'), \quad (9)$$

and symmetry (antisymmetry)

$$\Gamma^{(2)}(\mathbf{x}_1',\mathbf{x}_2'|\mathbf{x}_1,\mathbf{x}_2)=\pm\Gamma^{(2)}(\mathbf{x}_2',\mathbf{x}_1'|\mathbf{x}_1,\mathbf{x}_2). \quad (10)$$

By definition $\Gamma^{(1)}$ is obtained from $\Gamma^{(2)}$ as follows:

$$\Gamma^{(1)}(\mathbf{x}_1'|\mathbf{x}_1)=\frac{2}{N-1}\int\Gamma^{(2)}d\mathbf{x}_2. \quad (11)$$

The normalization (square-integrability) condition is essentially that

$$\int\cdots\int\Gamma^{(N)}d\{\mathbf{N}\}=\frac{1}{N}\int\Gamma^{(1)}d\mathbf{x}_1=1, \quad (12)$$

which implies that the diagonal element of $\Gamma^{(1)}$ (obtained by removing the prime) is a constant:

$$\Gamma_{\text{diag}}{}^{(1)}(\mathbf{x}_1|\mathbf{x}_1)=N/V. \quad (13)$$

Under the simple conditions specified at the outset (H_1, H_{12}, position- and spin-independent, N, $V\rightarrow\infty$) it is appropriate to introduce variables $R=|\mathbf{x}_1'-\mathbf{x}_1|$, $r=|\mathbf{x}_2-\mathbf{x}_1|$ and notice that the Hamiltonian depends only on these; all others are cyclic and can be integrated

out. Thus we can define

$$\Gamma^{(1)}(\mathbf{x}_1'|\mathbf{x}_1)=(N/V)\rho_1(R), \tag{14}$$

where $\rho_1(0)=1$ by (13). Similarly

$$\Gamma_{\text{diag}}{}^{(2)}(\mathbf{x}_1,\mathbf{x}_2)=\tfrac{1}{2}(N/V)^2\rho_2(r), \tag{15}$$

where $\rho_2(r)$ is essentially the pair-distribution function which also appears in classical statistical mechanics. The function $\rho_1(R)$ has no particular physical significance, but its 3-dimensional Fourier transform $n(k)$ is easily interpretable, *viz.*,

$$R\rho_1(R)=2\frac{V}{N}\int_0^\infty kn(k)\,\sin 2\pi kR dk, \tag{16}$$

$$kn(k)=2\frac{N}{V}\int_0^\infty R\rho_1(R)\,\sin 2\pi kR dR. \tag{17}$$

Evidently[11] $n(k)$ is the coefficient belonging to a given plane-wave component in momentum space, or the distribution function of the particles in k space. The expression (8) now becomes, after considerable manipulation, assuming $H_1=-\hbar^2/2m\nabla^2$,

$$\frac{1}{N}\langle H\rangle=\epsilon=2\pi\frac{\hbar^2}{m}\left(\frac{V}{N}\right)\int_0^\infty k^4 n(k)dk + 2\pi\left(\frac{N}{V}\right)\int_0^\infty u(r)\rho_2(r)r^2 dr. \tag{18}$$

Evidently ϵ is the energy per particle, and $u(r)$ is the pair-interaction. The right-hand term is the potential energy and is (formally) the same in a classical or quantum system, though of course $\rho_2(r)$ will depend somehow on the statistics. As far as the ground state is concerned, the same may be said for the left-hand (kinetic energy) term, the differences depending on the form of $n(k)$ ($h\to 0$ for a classical system).

3. DIMENSIONLESS VARIABLES

In order to express the energy in Rydberg units and keep the various integrals dimensionless the following change of variables is indicated:

$$\xi=r/r_B, \qquad \xi_0=l/r_B, \tag{19}$$

$$\tau=\sigma=2\pi kr_B, \quad \sigma_0=2\pi k_F r_B, \tag{20}$$

where r_B is the Bohr radius and k_F is the Fermi momentum. (Naturally k_F does not appear in the discussion of a Bose-Einstein or Maxwell-Boltzmann system.) Evidently l is the mean separation of particles in the system,

$$\frac{4\pi}{3}l^3=\frac{V}{N}, \tag{21}$$

and

$$\frac{8\pi}{3}k_F{}^3=\frac{N}{V}. \tag{22}$$

We now rewrite (16) and (17),

$$\tau n(\tau)=\frac{3}{\xi_0{}^3}\int_0^\infty \xi\rho_1(\xi)\,\sin\xi\tau d\xi, \tag{23}$$

$$\xi\rho_1(\xi)=\frac{2}{3\pi}\xi_0{}^3\int_0^\infty \tau n(\tau)\,\sin\xi\tau d\tau. \tag{24}$$

It can be shown that (10) and (11) imply for a Fermi system that

$$0\le n(k)=n(\tau)\le 2, \tag{25}$$

which is similar to the usual statement of the Pauli principle, *viz.*, at most two particles (with opposite spins) can occupy a single momentum-state. For Bose and classical systems the inequality is relaxed to $0\le n(\tau)$.

Similarly, (13) and (14) imply [using (24)] the integral condition

$$1=\frac{2}{3\pi}\xi_0{}^3\int_0^\infty \tau^2 n(\tau)d\tau+\frac{n(0)}{N}. \tag{26}$$

In the Fermi case the last term is of order $2/N$ and may be ignored but the correction is important in the other cases since the integral does not count $n(0)$ which may be of order N. For a system containing a finite number of particles (26) is simply equivalent to the sum

$$\sum_{k=0}^{\infty} n_k=N. \tag{27}$$

Further conditions involve the pair-distribution function $\rho_2(r)$. The simplest [derivable from the basic relations (9)–(11)] is

$$0\le\rho_2(r)=\rho_2(\xi), \tag{28}$$

which means that a probability density must be nonnegative. It is now convenient to split $\rho_2(r)$ into a part which depends only on the statistics and a part which vanishes when $u(r)$, the pair interaction, disappears. For the ideal Fermi gas [$u(r)=0$] it can be shown that

$$\rho_{20}(r)=\rho_{20}(\xi)=1-\tfrac{1}{2}\rho_{10}{}^2(\xi), \tag{29}$$

and it is natural to extend (29) as follows[12]:

$$\rho_2(\xi)=[1-\tfrac{1}{2}\rho_1{}^2(\xi)][1-K(\xi)], \tag{30}$$

[11] The fact that the Hamiltonian is invariant under translation makes the angular coordinates cyclic, so $n(\mathbf{k})$ is spherically symmetric: Therefore k in (16) and (17) is the absolute magnitude of $\mathbf{k}$.

[12] The form (30) is quite general for the diagonal element of ρ_2, but a more extensive argument is needed to find an off-diagonal form (which would be necessary if the interaction H_{12} were a noncommuting operator, e.g., a Fermi pseudo-potential). Briefly, the argument (due to Mayer[3]) is as follows: the total ρ_2 is a product

where to satisfy (28) we simply require

$$K(\xi)\leq 1. \tag{31}$$

Finally, the relation (11) leads to

$$1=\frac{1}{3\pi}\xi_0^3\int_0^\infty \tau^2 n^2(\tau)d\tau + \frac{3}{\xi_0^3}\int_0^\infty [1-\tfrac{1}{2}\rho_1^2(\xi)]K(\xi)\xi^2 d\xi, \tag{32}$$

where the argument of footnote (12) has been used, together with Parzeval's theorem.

The energy per particle in Rydberg units becomes [from (18)]

$$\epsilon=\frac{2\xi_0^3}{3\pi}\int_0^\infty \tau^4 n(\tau)d\tau+\frac{3}{\xi_0^3}\int_0^\infty u(\xi) \times[1-\tfrac{1}{2}\rho_1^2(\xi)][1-K(\xi)]\xi^2 d\xi. \tag{33}$$

4. ADDITIONAL NECESSARY CONDITION ON THE CHOICE OF $\Gamma^{(1)}$ AND $\Gamma^{(2)}$

It has been pointed out already that the choice of possible functions $\Gamma^{(1)}$ and $\Gamma^{(2)}$ must be restricted to those which can be put in $1\leftrightarrow 1$ correspondence with the set of all possible many-particle wave functions. In the Boltzmann case one seeks a correspondence with the N-particle density functions ρ_N. We now note that the variation of the expectation value of the Hamiltonian actually generates such an isomorphism. Clearly all possible N-particle wave functions can be obtained in principle by successive variations; degeneracies are easily removed by using orthogonality conditions. Similarly all possible $\Gamma^{(1)}$ and $\Gamma^{(2)}$ functions are obtainable by variations (once we know the complete set of necessary conditions on the variation).

It is obvious that one of the necessary conditions on the choice of $\Gamma^{(1)}$ and $\Gamma^{(2)}$ is that they be *possible* variational extrema. However it is not so obvious that any functions satisfying the conditions (25), (26), (28), and (32) are thereby excluded, i.e., that the set of possible variational extrema is smaller than the set defined by the conditions stated. This question is worth investigating in some detail.

We begin by asserting that the four restrictions above, *in toto*, define bounded subsets of all possible functions $n(\tau)$ and $K(\xi)$. Moreover, the bounded subsets are *convex*.[13] (Both properties are generalizations to infinite-dimensional function-space of simple geometrical concepts which are easily visualized in the case of a circle on a plane; convexity means any point on a straight line connecting two points in the circle is itself in the circle; the boundary is simply the set of points which do not lie on straight lines connecting any but boundary points). To verify the assertion one must exhibit the restrictive conditions in a form such that functions inside and outside the bounded sets are explicitly distinguished from each other. From the inequality (25) [since $n^2(\tau)\leq 2n(\tau)$ for all τ] combined with (26) and (32) one obtains new inequalities

$$\frac{1}{3\pi}\xi_0^3\int_0^\infty \tau^2 n^2(\tau)d\tau\leq 1, \tag{34}$$

and

$$\frac{3}{\xi_0^3}\int_0^\infty [1-\tfrac{1}{2}\rho_1^2(\xi)]K(\xi)\xi^2 d\xi\leq 1. \tag{35}$$

The form of $n(\tau)$ for an ideal (noninteracting) Fermi gas in the ground state is well known, namely

$$\begin{aligned} n_0(\tau)&=2 \quad \text{for} \quad 0\leq\tau\leq\sigma_0 \\ &=0 \quad \text{for} \quad \sigma_0<\tau, \end{aligned} \tag{36}$$

from which, by (24)

$$\rho_{10}(\xi)=3\frac{j_1(\xi\sigma_0)}{\xi\sigma_0}=\left(\frac{9\pi}{2\xi^3\sigma_0^3}\right)^{\frac{1}{2}}J_{\frac{3}{2}}(\xi\sigma_0), \tag{37}$$

where $j_1(s)$ is the spherical Bessel function of order unity. If any particles are excited above the Fermi level σ_0, $n(\tau)$ will spread out, and by an elementary property of Fourier transforms $\rho_1(\xi)$ will tend on the contrary to bunch up near the origin. Thus, regardless of interaction (or temperature β),

$$\lim_{\xi\to\infty}|\rho_1(\xi)|\leq|\rho_{10}(\xi)|\leq\frac{|\cos\xi\sigma_0|}{(\xi\sigma_0)^2}. \tag{38}$$

A similar asymptotic convergence condition exists for $K(\xi)$ [note that for large ξ, $1-\frac{1}{2}\rho_1^2(\xi)\to 1$], namely

$$\lim_{\xi\to\infty}|K(\xi)|\leq\frac{1}{\xi^{2+\delta_0}}\frac{1}{\ln\xi}, \tag{39}$$

---

of spin terms and spatial terms; since there are three symmetric combinations of two spin functions and one antisymmetric combination, the spatial part must have a triple weight for the antisymmetric function and a single weight for the symmetric function, thus:

$$\rho_2(\text{space})=\tfrac{3}{4}\rho_{2a}+\tfrac{1}{4}\rho_{2s},$$

where to satisfy (9) and (10), ρ_{2s} and ρ_{2a} may be written

$$\rho_{2s,a}=[f(|\mathbf{x}_1'-\mathbf{x}_1|)f(|\mathbf{x}_2'-\mathbf{x}_2|)\pm f(|\mathbf{x}_1'-\mathbf{x}_2|)f(|\mathbf{x}_2'-\mathbf{x}_1|)] \times[1-g(|\mathbf{x}_1'-\mathbf{x}_2'|)][1-g(|\mathbf{x}_1-\mathbf{x}_2|)].$$

Inserting the above in (12), taking the limit $N\to\infty$, and assuming f and g are the same for both symmetric and antisymmetric parts, one can make the identification $f=\rho_1$. Evidently there is no loss of generality in writing $(1-g)^2=1-K$ where $K\leq 1$. For a Bose system the analogous argument must be carried out in its entirety, but this will not be done here. In the case of Boltzmann statistics, of course, $\rho_{2s}(r)=1$ (see 29). The argument can also be used to obtain a plausible form for $\rho_3(r_{12},r_{23},r_{31})$, if desired.

[13] Since we are discussing physics and not pure mathematics, no details will be given here. Complete discussions of these properties can be found in the mathematical literature, for example Charnes, Cooper, and Henderson, *Introduction to Linear Programming* (John Wiley and Sons, Inc., New York, 1953), and *Linear Inequalities and Related Systems*, symposium, edited by H. W. Kuhn and A. W. Tucker (Princeton University Press, Princeton, New Jersey, 1956). In most cases it is quite easy to verify the subsequent steps in the argument.

if $K(\xi)$ oscillates sinusoidally with eventually decreasing maxima, or

$$\lim_{\xi\to\infty}|K(\xi)|\leq\frac{1}{\xi^{3+\delta_1}}\frac{1}{\ln\xi} \tag{40}$$

if $K(\xi)$ is a non-oscillating function.[14] The numbers δ_0, δ_1 must be non-negative; however the limiting case $\delta_0\to 0$, $\delta_1\to 0$ requires special consideration. It is true that (39) and (40) do not necessarily take account of every possibility. For example, oscillating functions can be constructed in which positive (or negative) contributions are dominant. However all such functions can be decomposed into linear combinations of "pure" functions of the type described.

From the physical point of view (39) and (40) are rather suggestive. An oscillating function $K(\xi)$ would be indicative of long-range order in the system, and vice versa for the non-oscillating function, while the intermediate case of short-range order might correspond to a linear superposition. However, this line of speculation will not be followed up here, since it is still somewhat premature.

It is evident that the convergence conditions (38), (39), and (40) do at least display explicit boundaries for the sets which we shall label Λ_1 and Λ_2 of possible functions $\rho_1(\xi)$ and $K(\xi)$ respectively. That is to say, functions which do not converge at least as well as the limiting cases specified (as $\xi\to\infty$) are forbidden. It is easy to verify that the sets are convex; any linear combination of functions satisfying an asymptotic condition will itself satisfy the condition. On the other hand at least one of the sets Λ_1 and Λ_2 might conceivably still be too large, since in certain circumstances it is conceivable that the condition (32) might fail to be satisfied by *any* pair of functions $\rho_1(\xi)$ and $K(\xi)$ (regardless of behavior for $\xi\to 0$) which attained the limiting asymptotic behavior allowed by (38), and (39) or (40). However there are very good reasons for believing that this situation does not arise when there is no long-range order.

The fact that not all members of the sets Λ_1 and Λ_2 are possible variational extrema is now established by the following theorem[15]: *if a linear functional is defined over a set of functions (e.g., vectors) which are restricted to a convex set, then the functional only attains its extreme values on the boundary of the set.* This means only functions $\rho_1(\xi)$ which lie on the boundary of Λ_1 and functions $K(\xi)$ which lie on the boundary of Λ_2 are possible extrema.[16] The sets themselves are defined by (38) and (39) or (40) if it is possible to choose bounding functions from both sets simultaneously, while still satisfying (32). If this is not possible some other, more stringent, convergence condition would be needed; this could happen in a system which permitted contributions to $n(\tau)$ from arbitrarily large τ, whence $\rho_1(\xi)$ would be required to converge faster than any power of ξ (*viz.*, as an exponential or Gaussian). However, we consider the disordered state henceforth, to avoid any possible ambiguity.

It must be emphasized that in speaking of a function with minimum convergence only the *asymptotic* behavior is involved. The sets Λ_1 and Λ_2 include all functions with the proper asymptotic behavior; however, this is too lenient, since conditions in the region of small ξ must also be satisfied. By using (24) and comparing with (26), we have

$$\rho_1(0)=1. \tag{41}$$

Similarly, by examining (33), it is clear that if the interaction $u(\xi)$ is repulsive and stronger than $1/\xi^3$ at the origin, then

$$K(0)=1 \tag{42}$$

is necessary to ensure that the quantity being varied remains finite. Even for a weaker repulsion[17] the fact that the energy be minimum (instead of maximum) requires $K(0)$ to be positive, and combined with (31) this means that

$$0\leq K(0)\leq 1. \tag{43}$$

5. TRIAL FUNCTION FOR $n(\tau)$—CONNECTION WITH LAGRANGE FORMALISM

It is the usual practice in a variational calculation to pick a trial function with a number of variable parameters, only using physical reasoning to minimize the number of parameters needed by clever choice of trial forms. However, it is desirable to proceed as far as possible by strictly analytical methods. It will be seen that an integral equation for $n(\tau)$ can be derived subject only to the assumption that $K(\xi)$ does not depend on $n(\tau)$ explicitly. This will certainly be true to at least one order of approximation.

[14] It is sufficient to treat (39) and (40) as being *approximately* correct. It is perhaps suggestive to think of the ξ-axis as being broken up into discrete intervals, which are either all of one sign or alternating in sign, and then examine the conditions for summability of discrete series. However this argument requires great care. The approximate correctness of (39) and (40) can be demonstrated by direct integration. Note that (35) also gives a weak condition on convergence at $\xi\to 0$; however a stronger condition will be derived later.

[15] For discussion and proof see Charnes, Cooper, and Henderson, reference 13.

[16] Care must be exercised to avoid too free an application to function spaces intuitive ideas from ordinary geometry. In parricular, it may be worthwhile to point out that it is quite possible to choose functions from the "interior" of Λ_2 which give rise to energies below the true energy (for examples, see references 6–8). This subclass of functions $K(\xi)$ have the common property of vanishing *identically* as $\xi\to 0$, and also possess no extreme point. It is not difficult to construct a sequence of functions from this subclass leading to unboundedly negative (or positive) energies, regardless of interaction. The significant point is the lack of an extreme point, not the absolute magnitude of the "energies" obtained.

[17] The fact that electrons, in the S state, for example, have a finite probability of instantaneously occupying the same point in space [implying $K(0)<1$] is confirmed by E. A. Hylleraas [Z. Physik **48**, 469 (1928); **54**, 347 (1929), and elsewhere] and also in a special case by R. H. Tredgold and J. S. Evans (unpublished).

The only difficulty in principle in carrying out a variation of the energy with respect to $n(\tau)$ is in taking account of the inequality (25) (analogous to the "nonholonomic" constraints of classical mechanics). The simple conditions (26) and (32) are introduced via Lagrange multipliers γ_1 and γ_2. The method employed is to remove the constraint by making an appropriate functional transformation which automatically satisfies the inequality; *viz.*, let

$$n(\tau)=2\exp[-\varphi^2(\tau)], \tag{44}$$

where $\varphi(\tau)$ is only required to be real. Any function satisfying (25) can be written in the form (44) (although there is no claim that (44) is unique). Varying $n(\tau)$ in the usual way gives

$$\begin{aligned}\delta n(\tau)&=-2\varphi(\tau)\{2\exp[-\varphi^2(\tau)]\}\delta\varphi(\tau)\\&=-2n(\tau)\varphi(\tau)\delta\varphi(\tau).\end{aligned} \tag{45}$$

Since $\varphi(\tau)$ is free to vary, we can take $\delta\varphi(\tau)>0$ for all τ, but it is seen that $\delta n(\tau)$ vanishes identically when either $n(\tau)=0$ or $\varphi(\tau)=0$ $[n(\tau)=2]$. Thus $\delta n(\tau)$ must be zero whenever $n(\tau)$ attains either of its constraining limits; this is quite a general property of such constraints. Evidently the variation of the energy vanishes whenever $\delta n(\tau)=0$, whence $n(\tau)=2$, $n(\tau)=0$ are extrema of the variation, although neither can hold true for all τ. It is easy to see that the behavior of $n(\tau)$ in the intervening region is determined by the integral equation

$$n_i(\tau)=\frac{1}{\gamma_1}\Big[\tau^2-\gamma_2-\frac{3}{\xi_0^3\tau}\int_0^\infty \xi\rho_1(\xi)\times\sin\xi\tau\{u(\xi)[1-K(\xi)]-\gamma_1K(\xi)\}d\xi\Big], \tag{46}$$

whence

$$n(\tau)=\begin{cases}=2 & \text{for } 0\le\tau\le\tau_2\\ =n_i(\tau) & \text{for } \tau_2\le\tau\le\tau_0,\\ =0 & \text{for } \tau_0<\tau\end{cases} \tag{47}$$

where γ_1 and γ_2 are Lagrange multipliers to be determined by satisfying (26) and (32), and τ_2 and τ_0 are defined by requiring $n_i(\tau)$ to satisfy (25), that is

$$n_i(\tau_2)=2,\quad n_i(\tau_0)=0. \tag{48}$$

If $K(\xi)$ is known $n(\tau)$ is determined uniquely, although the computations are formidable.

Fortunately one can introduce several simplifications immediately. A good deal of calculation is saved by using the (quantum mechanical) virial theorem,[18] in the form

$$pV=\frac{4\xi_0^3}{9\pi}\int_0^\infty\tau^4n(\tau)d\tau-\frac{1}{\xi_0^3}\int_0^\infty\xi\frac{\partial u}{\partial\xi}\times[1-\tfrac{1}{2}\rho_1^2(\xi)][1-K(\xi)]\xi^2d\xi. \tag{49}$$

Upon varying both sides, the pressure p never appears. If γ_1 and γ_2 are eliminated by using the pair of Eqs. (48), one obtains

$$n_i(\tau)=\frac{3}{\xi_0^3}\int_0^\infty\xi\rho_1(\xi)\Big[\frac{\sin\xi\tau}{\tau}-\frac{\sin\xi\tau_0}{\tau_0}\Big]K(\xi)d\xi+\Big[2-\frac{3}{\xi_0^3}\int_0^\infty\xi\rho_1(\xi)\Big[\frac{\sin\xi\tau_2}{\tau_2}-\frac{\sin\xi\tau_0}{\tau_0}\Big]K(\xi)d\xi\Big]\times\Big[\int_0^\infty\xi\rho_1(\xi)\Big[\frac{\sin\xi\tau}{\tau}-\frac{\sin\tau_0}{\tau_0}\Big][1-K(\xi)]\Big[u(\xi)+\frac{\xi}{2}\frac{\partial u}{\partial\xi}\Big]d\xi\Big]\Big/\int_0^\infty\xi\rho_1(\xi)\Big[\frac{\sin\xi\tau_2}{\tau_2}-\frac{\sin\xi\tau_0}{\tau_0}\Big][1-K(\xi)]\Big[u(\xi)+\frac{\xi}{2}\frac{\partial u}{\partial\xi}\Big]d\xi. \tag{50}$$

Further simplification ensues in the interesting case when $u(\xi)=1/\xi$, whence by (49) we can write

$$n_i(\tau)=\frac{3}{\xi_0^3}\int_0^\infty\xi\rho_1(\xi)\Big[\frac{\sin\xi\tau}{\tau}-\frac{\sin\xi\tau_0}{\tau_0}\Big]K(\xi)d\xi+\Big[2-\frac{3}{\xi_0^3}\int_0^\infty\xi\rho_1(\xi)\Big]\frac{\sin\xi\tau_2}{\tau_2}-\frac{\sin\xi\tau_0}{\tau_0}\Big[K(\xi)d\xi\Big]\times\Big[\frac{\tau^2-\tau_0^2}{\tau_2^2-\tau_0^2}\Big]. \tag{51}$$

It is clear from examining either (50) or (51) directly that (48) is satisfied. The condition (26) can be used to determine τ_2 in terms of τ_0 still, without specifying $K(\xi)$. Provided $\tau_0>\tau_2$, this calculation gives

$$\tau_2=2\sigma_0-\tau_0+\cdots, \tag{52}$$

which is also intuitively reasonable. However an exact calculation is not feasible at this stage. If $K(\xi)$ happened to take a particularly simple form it might be possible to obtain one or two iterations of $n_i(\tau)$ [beginning either with $\rho_{10}(\xi)$ corresponding to the ideal gas, or with some other convenient first approximation], but in general numerical methods would be required.

6. TRIAL FUNCTION FOR $K(\xi)$

Superficial examination of the relations involving $K(\xi)$ shows immediately that a straightforward applica-

[18] While (49) is useful it is not a condition affecting the form of $n(\tau)$; actually it introduces no new information.

tion of Lagrange's method cannot be expected to succeed. The difficulty is that $K(\xi)$ always appears linearly, and from the general theory of variational problems it appears that in this case more than one, usually infinitely many variational extrema must exist.[19] Nevertheless these may belong to a well-defined subclass of the original set of functions (i.e., a "boundary," see Sec. 4). The abstract connection between the Lagrange method for problems of this type and the so-called "simplex" method for finding extrema of systems subject to linear inequalities is discussed by Goldman and Tucker.[20] It will be shown in the following how the Lagrange method can be used even in the linear case to extract useful information and confirm the conclusion already reached.

The trick is to find a set of integral conditions approximating (35) which also imply (39) or (40). Evidently (35) does not distinguish between oscillating and non-oscillating functions $K(\xi)$; this can be remedied by raising $K(\xi)$ to some power greater than unity. It can be shown that the following conditions lead to (39) or (40), respectively:

$$\int_\eta^\infty \xi^2 K(\xi)[\xi^2 f(\xi) K(\xi)]^{p-1} d\xi < \infty, \tag{53}$$

$$\int_\eta^\infty \xi^2 K(\xi)[\xi^3 K(\xi)]^{p-1} d\xi < \infty, \tag{54}$$

where p takes all positive integral values and $f(\xi)$ is any sinusoidal function with the periodicity of $K(\xi)$ (by definition) though it need not be continuous or even finite at points where $K(\xi)=0$. The behavior of the integrals at $\xi=0$ is explicitly ignored by taking $\eta>0$ [see (43)], a step which is justified if we only look for the asymptotic form of $K(\xi)$. Note that when $p=1$, Eqs. (53) and (54) are identical and no distinction is made between the convergence conditions (39) and (40). Hence we deliberately choose $p>1$. A Lagrange variation can now be carried out formally, introducing multipliers γ_1, γ_2 corresponding to (32) and (53) or (54). Let $K^\infty(\xi)$ denote $\lim_{\xi\to\infty} K(\xi)$, from which we have

$$K_p{}^\infty(\xi) = \gamma_1 \frac{\{u(\xi)[1-\frac{1}{2}\rho_1{}^2(\xi)]-\gamma_2\}^{1/(p-1)}}{\xi^2 f(\xi)}, \tag{55}$$

$$K_p{}^\infty(\xi) = \gamma_1 \frac{\{u(\xi)[1-\frac{1}{2}\rho_1{}^2(\xi)]-\gamma_2\}^{1/(p-1)}}{\xi^3}, \tag{56}$$

respectively. The oscillation or non-oscillation is explicitly shown by the presence of $f(\xi)$.[21] For all p, (53) or (54) cannot be satisfied except by $\gamma_2=0$, whence a single multiplier is left, to be determined by (32). To find a true extremum one must eliminate the parameter p which entered more or less by the back door in the first place. Evidently the limiting case when

$$\partial K_p{}^\infty(\xi)/\partial p = 0 \tag{57}$$

defines the function $K^\infty(\xi)$ which is p independent. This occurs for $p\to\infty$, which in turn defines the slowest converging function which satisfies either (39) or (40) when $\delta_0, \delta_1 \to 0$.

Hence our trial functions must be bounded by

$$\lim_{p\to\infty} K_p{}^\infty \leq K^\infty(\xi) < \frac{1}{\xi^2 f(\xi) \ln\xi}, \tag{58}$$

$$\lim_{p\to\infty} K_p{}^\infty \leq K^\infty(\xi) < \frac{1}{\xi^3 \ln\xi}. \tag{59}$$

The limiting processes must be taken in a rather subtle way, but functions can be exhibited which satisfy (58) for arbitrarily large p. That is, there exist functions converging faster than $1/\xi^3$ such that the integral (35) does not diverge, but which converge slower than $1/\xi^{3+\delta}$ for any $\delta>0$; in fact (as expected) there are still infinitely many such functions, for example

$$K^\infty(\xi) = \gamma_1 \frac{1}{\xi^3 \ln^q(\xi)}, \tag{60}$$

where $q>1$.

It is, of course, necessary to choose $K(\xi)$ for all ξ, not just in the limit $\xi\to\infty$. There are convincing quasi-physical arguments to the effect that $K(\xi)$ should be analytic.[22] One would normally assume this in any case. However, it must be pointed out that in most cases even an analytic function is not uniquely determined by its asymptotic form.[23] Therefore it seems likely that one must, at this stage, revert to the usual procedure and pick a trial function having the correct asymptotic form and containing several variable parameters. Unfortunately very substantial analytic difficulties still must be overcome in order to calculate the energy. Work in this direction is in progress.

7. CONCLUSION

The restriction we have imposed, namely that $\Gamma^{(1)}$ and $\Gamma^{(2)}$ can only be chosen from among possible variational extrema, turns out to be rather powerful. In the first place the precise form of the Hamiltonian is not involved. Secondly, a similar restriction must exist for a classical system, and one infers that there would be a comparable reduction in the number of allowed possi-

[19] See, for example Caratheodory, *Variatzungsrechnung* (B. G. Teubner, Leipzig, 1935).

[20] A. J. Goldman and A. W. Tucker, in *Linear Inequalities and Related Systems*, reference 13.

[21] In this connection it must be noted that $f(\xi)$ will be different for different possible lattice structures.

[22] Except possibly at the origin ($\xi=0$).

[23] Exceptional cases do exist, however; see Phil. Trans. **213**, 274–313 (1911) or E. T. Whittaker and G. N. Watson, *Modern Analysis* (Cambridge University Press, London, 1935).

bilities. Third, the possibility of macroscopic states of the system is clearly indicated, although all detailed information about an ordered state is implicit in the undetermined function $f(\xi)$. It is conceivable that information about other types of macroscopic order (e.g., in momentum-space) would also be available from detailed knowledge of $n(\tau)$. The next step is, of course, to calculate the energy of an electron gas at high density with one or more appropriate trial functions for $K(\xi)$ in order to test the accuracy of the method against a known result. This will be done in a succeeding paper.

ACKNOWLEDGMENTS

The author wishes to acknowledge the kind help and valuable suggestions and criticisms from a number of people, particularly Professor T. Tanaka of Kyusyu University, Japan, Dr. M. Fisher of Kings College, London, Dr. R. Mazo and Professor J. E. Mayer of the Institute for Nuclear Studies, Chicago, Dr. M. S. Watanabe of I.B.M. Research Laboratories, Ossining, New York, and most particularly to Dr. R. H. Tredgold of U.C.N.W., Bangor, Wales without whose penetrating criticisms nothing whatsoever would have been achieved.

PHYSICAL REVIEW VOLUME 111, NUMBER 6 SEPTEMBER 15, 1958

Quantum Statistical Theory of Electron Correlation*

ROBERT D. COWAN, *Los Alamos Scientific Laboratory, University of California, Los Alamos, New Mexico*

AND

JOHN G. KIRKWOOD, *Sterling Chemistry Laboratory, Yale University, New Haven, Connecticut*

(Received April 18, 1958)

The average electrostatic potential distribution about a given electron is calculated for a system of point-charge electrons embedded in a neutralizing continuum of positive charge. The calculation is classical, involving a Poisson equation of the Debye-Hückel type, except that the electron density is treated by means of Fermi-Dirac statistics as in the Thomas-Fermi theory of the atom. The calculated energy due to electrostatic interactions agrees with the quantum-mechanical exchange plus correlation energy over the observed range of metal valence-electron densities, $2 \leqq r_s \leqq 6$, but is too small at larger and smaller densities. (r_s is the electron-sphere radius in units of the Bohr radius.) The equilibrium density ($T=p=0$) occurs at $r_s=4.3$, at which point the compressibility is 69 per megabar. The electronic specific heat is linear in T at low temperatures and varies from 0.9 to 0.74 of the Sommerfeld value over the observed metal density range.

1. INTRODUCTION

A DEBYE–HÜCKEL, Thomas-Fermi (DHTF) theory of plasmas and liquid metals has recently been developed by Plock and Kirkwood.[1] The theory is similar to the Debye-Hückel theory of electrolyte solutions,[2] except that the charged particles are nuclei and electrons rather than positive and negative ions, and the behavior of the electrons is described in terms of Fermi-Dirac rather than Boltzmann statistics. The method of treating the electrons is similar to that of the Thomas-Fermi theory of the atom,[3] but the DHTF theory automatically introduces a certain degree of correlation among the electrons due to their mutual electrostatic repulsion. It would be interesting to know how the correlation energy given by this theory would compare with that calculated quantum mechanically. However, the only quantum-mechanical calculation with which a comparison can readily be made is for the case of free electrons moving in a uniform sea of positive charge; consequently, the DHTF theory is modified correspondingly in the discussion which follows.

2. THEORY

In the DHTF theory the thermodynamic functions are evaluated by considering the Debye charging process. For this purpose it is necessary to examine a hypothetical system in which each particle carries an arbitrary fraction λ of its true physical charge. Consider, then, a system consisting of electrons of (average) density n_0 each with a charge $-\lambda e$, embedded in a uniform neutralizing sea of positive charge of density

$$\lambda\rho_0=\lambda e n_0. \tag{1}$$

Let $\psi_\lambda(r)$ be the average electrostatic potential at a distance r from any specific electron (due to *all* charges, including the electron in question). Then the potential energy of a second electron a distance r from the first is $-\lambda e\psi_\lambda(r)$, and the density of electrons at r is given

* Work performed under the auspices of the U. S. Atomic Energy Commission.

[1] R. J. Plock, thesis, Yale University, 1956; R. D. Cowan and J. G. Kirkwood, J. Chem. Phys. **29**, 264 (1958).

[2] P. Debye and E. Hückel, Physik Z. **24**, 185 (1923); see also R. Fowler and E. A. Guggenheim, *Statistical Thermodynamics* (Cambridge University Press, Cambridge, 1956), Secs. 904–913.

[3] L. H. Thomas, Proc. Cambridge Phil. Soc. **23**, 542 (1927); E. Fermi, Z. Physik **48**, 73 (1928).