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Quantum Statistics of Nonideal Systems*

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A new cluster development for the logarithm of the grand partition function of a system of interacting particles is derived. The leading term in this expansion is the pressure exerted by an ideal Bose or Fermi gas at the same temperature and absolute activity Z as the actual system. Succeeding terms involve quantum cluster integrals which themselves depend upon Z , unlike their classical analogs. The definition of these cluster integrals follows in a natural fashion using techniques illustrated by construction (in closed form) of the successive Z derivatives of the Bose and Fermi ideal gas grand partition functions. It is not possible (except in the classical limit) to eliminate Z explicitly between the pressure and density series, so that the equation of state must remain in parametric form.

I. INTRODUCTION

RECENTLY there has been considerable interest in the quantum-mechanical behavior of large systems of interacting particles. For the most part, the approach of these many-body theories has limited the analysis to properties of the ground state or low-lying excited states.¹⁻⁵ Of equal intrinsic interest for equilibrium statistical mechanics are details of the system's properties during the entire passage from the high-temperature classical realm to absolute zero, requiring knowledge of the complete energy spectrum. It is the purpose of the present note to clarify this transition from the standpoint of the cluster theory of the equation of state in a form which need make no special appeal to the usual quantum mechanical perturbation theory; our formalism is valid for arbitrarily strong interactions. In this respect primarily, the present quantum cluster development differs from

that of both Green⁶ and of Montroll and Ward.⁷ As in the corresponding classical treatment, we find it convenient to employ the powerful techniques of the grand ensemble to derive expressions for the fundamental thermodynamic quantities. In the following, it will be supposed that the reader is familiar with classical cluster theory.⁸

The next section reviews, very briefly, the fundamental properties of the canonical (CPF) and grand partition functions (GPF). In particular, the effects of quantum statistics (wave-function symmetry conditions) are separated from the interparticle force contributions by introducing a modified Hamiltonian operator. Section III develops further the basis of our cluster approach in the ideal gas case, obtaining directly the successive activity derivatives of the Fermi and Bose GPF's. In IV, the quantum mechanical cluster integrals are introduced in a way which retains the same formal structure of the activity expansion of the GPF as in classical statistics; now, however, the quantum analogs of the singly and doubly connected cluster integrals themselves depend upon the activity, reflecting statistical degeneracy. It must be pointed out that the quantum clusters as defined below are by no means unique, even if the usual classical forms are

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¹ M. Gell-Mann and K. A. Brueckner, *Phys. Rev.* **106**, 364 (1957).

² K. A. Brueckner and K. Sawada, *Phys. Rev.* **106**, 1117 (1957).

³ K. A. Brueckner and K. Sawada, *Phys. Rev.* **106**, 1128 (1957).

⁴ T. D. Lee and C. N. Yang, *Phys. Rev.* **105**, 1119 (1957).

⁵ T. D. Lee, K. Huang, and C. N. Yang, *Phys. Rev.* **106**, 1135 (1957).

⁶ H. S. Green, *J. Chem. Phys.* **20**, 1274 (1952).

⁷ E. W. Montroll and J. C. Ward, *Phys. Fluids* **1**, 55 (1958).

⁸ A comprehensive account may be found in: J. E. Mayer and M. G. Mayer, *Statistical Mechanics* (John Wiley & Sons, Inc., New York, 1940), Chap. 13.

regarded as proper high-temperature limits. Our purpose has been to emphasize the role played by particle indistinguishability, insofar as it determines a degenerate momentum distribution.

Section V examines the cluster equation of state, which must remain in parametric form except in the classical realm. In a final section certain integral equation relations satisfied by the exponential of the modified Hamiltonian are derived, and this function is expressed in terms of the wave functions for the actual (unmodified) Hamiltonian.

II. CANONICAL AND GRAND PARTITION FUNCTIONS

For the purposes of the present article it will be sufficient to suppose that the particles (of mass m) comprising our single-component, nonideal system are spinless, and interact through central forces. Generalization to include more complicated interactions, as well as particle structure, will not require fundamental revision of our procedure. The N -particle Hamiltonian is therefore written

$$H_N = H_N^{(0)} + V_N = -\frac{\hbar^2}{2m} \sum_{j=1}^N \nabla_j^2 + \sum_{j < k=1}^N v(r_{jk}). \quad (1)$$

The eigenfunctions of H_N are presumed to constitute an orthonormal set over the system volume V .

The CPF for quantum assemblies is the trace of the density matrix⁹

$$Q_N = \exp(-\beta A_N) = \text{Tr} [\exp(-\beta H_N)], \quad \beta = 1/kT; \quad (2)$$

A_N is the Helmholtz free energy. The value of the trace in (2) is independent of the representation chosen. Kirkwood^{10,11} has shown that for certain purposes, plane waves are a particularly convenient basis. Specifically, it is important to choose only those linear combinations, $\varphi^{(N)}$, of plane-wave functions which possess the same symmetry properties as the wave functions of our interacting system. Consequently, set

$$\varphi^{(N)}(\mathbf{r}, \mathbf{p}) = \frac{1}{(N!)^{1/2}} \sum_P (\pm 1)^{|P|} \exp\left[-\frac{i}{\hbar} \sum_{j=1}^N \mathbf{r}_j \cdot P \mathbf{p}_j\right], \quad (3)$$

where the upper sign refers to Bosons, the lower to Fermions. P is the permutation operator (of parity $|P|$) for the N momenta, and the summation in (3) is over all $N!$ possible permutations. Equation (10) of reference 10 provides the starting point for our analysis,

$$Q_N = \frac{1}{N! \hbar^{3N}} \int \varphi^{(N)*}(\mathbf{r}, \mathbf{p}) \times \exp(-\beta H_N) \varphi^{(N)}(\mathbf{r}, \mathbf{p}) d^{3N} \mathbf{r} d^{3N} \mathbf{p}, \quad (4)$$

by expressing the trace, (2), in the plane-wave representation. One of the permutation summations in the $\varphi^{(N)}$ in (4) is redundant,¹⁰ and may be eliminated

$$Q_N = \frac{1}{(N!)^{1/2} \hbar^{3N}} \int \varphi^{(N)*}(\mathbf{r}, \mathbf{p}) \exp(-\beta H_N) \times \exp\left(-\frac{i}{\hbar} \sum_{j=1}^N \mathbf{r}_j \cdot \mathbf{p}_j\right) d^{3N} \mathbf{r} d^{3N} \mathbf{p}. \quad (5)$$

The exponential of the Hamiltonian H_N appearing in (5) is to be interpreted as its expanded form,

$$\exp(-\beta H_N) = \sum_{j=0}^{\infty} \frac{(-\beta)^j}{j!} (H_N)^j. \quad (6)$$

We therefore make use of the identity (for an arbitrary function g of the position and momentum coordinates)

$$H_N \exp\left(-\frac{i}{\hbar} \sum_{j=1}^N \mathbf{r}_j \cdot \mathbf{p}_j\right) g(\mathbf{r}, \mathbf{p}) = \exp\left(-\frac{i}{\hbar} \sum_{j=1}^N \mathbf{r}_j \cdot \mathbf{p}_j\right) H_N' g(\mathbf{r}, \mathbf{p}), \quad (7)$$

$$H_N' = H_N^{(0)'} + V_N = \frac{1}{2m} \sum_{j=1}^N (\mathbf{p}_j - i\hbar \nabla_j)^2 + \sum_{j < k=1}^N v(r_{jk}),$$

to move the plane wave on the right of $\exp(-\beta H_N)$ in (5) to the left:

$$Q_N = (1/N! \hbar^{3N}) \int \sigma_{\pm}^{(N)}(\mathbf{r}, \mathbf{p}) F^{(N)}(\mathbf{r}, \mathbf{p}) d^{3N} \mathbf{r} d^{3N} \mathbf{p},$$

$$\sigma_{\pm}^{(N)}(\mathbf{r}, \mathbf{p}) = \sum_P (\pm 1)^{|P|} \exp\left(-\frac{i}{\hbar} \sum_{j=1}^N \mathbf{r}_j \cdot (\mathbf{p}_j - P \mathbf{p}_j)\right), \quad (8)$$

$$F^{(N)}(\mathbf{r}, \mathbf{p}) = \exp(-\beta H_N') \cdot 1.$$

The exponential of the modified Hamiltonian operator is now left to operate just on unity, defining thereby the function $F^{(N)}$.

The result (8) has simplified the statistical problem to this extent: the detailed quantum dynamics of the N -body Schrödinger equation, with the latter's complicated wave mechanical diffraction properties, are contained entirely in $F^{(N)}(\mathbf{r}, \mathbf{p})$, which is the same for both Fermi and Bose systems. We note in passing, from the last of Eq. (8), that $F^{(N)}$ satisfies a Bloch differential equation involving the modified Hamiltonian

$$\partial F^{(N)} / \partial \beta = -H_N' F^{(N)}. \quad (9)$$

In addition, $F^{(N)}$ is particularly simple in the classical limit (obtained by setting $\hbar=0$), where obviously

$$F_{cl}^{(N)}(\mathbf{r}, \mathbf{p}) = \exp\left[-\beta \left(\frac{1}{2m} \sum_{j=1}^N p_j^2 + V_N\right)\right]. \quad (10)$$

⁹ J. von Neumann, *Mathematical Foundations of Quantum Mechanics* (Princeton University Press, Princeton, 1955), Chap. V.

¹⁰ J. G. Kirkwood, *Phys. Rev.* **44**, 31 (1933).

¹¹ J. G. Kirkwood, *Phys. Rev.* **45**, 116 (1934).

Equations (9) and (10) are shown to be equivalent to a single integral equation in VI, which in principle may be employed to find $F^{(N)}$.

Statistical degeneracy, on the other hand, affects Q_N only through $\sigma_{\pm}^{(N)}$. Even if there were no pair forces acting in our system, the exchange function $\sigma_{\pm}^{(N)}$ in (8) would provide coupling between the particles; the effect is to create nonvanishing virial coefficients for degenerate ideal gases.

The GPF yields the pressure directly in terms of the chemical potential μ ,

$$G(Z) = \exp\left(\frac{\beta V}{kT}\right) = \sum_{N=0}^{\infty} Q_N Z^N, \quad Q_0=1, \quad Z = \exp(\beta\mu). \quad (11)$$

The grand ensemble average number of particles, \bar{N} , and energy, \bar{E} , are obtained by differentiating $G(Z)$,

$$\bar{N} = (\partial \ln G / \partial \ln Z)_{\beta, V}; \quad (12)$$

$$\bar{E} = -(\partial \ln G / \partial \beta)_{Z, V}. \quad (13)$$

The expression (8) for the CPF's of various orders will presently be shown particularly useful for computing $\ln G$ in a cluster series; relations (11), (12), and (13) in turn allow evaluation of all thermodynamic properties.

III. THE IDEAL GAS

Before investigating the general interacting system in quantum statistics, we examine the degenerate ideal gas, for which the particle pair potential $v(r)$ vanishes. The ideal N particle CPF then is

$$Q_N^{(0)} = \frac{1}{N! h^{3N}} \sum_P (\pm 1)^{|P|} \times \int \exp \left\{ \sum_{j=1}^N \left[-\frac{\beta p_j^2}{2m} + \frac{i}{\hbar} \mathbf{r}_j \cdot (\mathbf{p}_j - P \mathbf{p}_j) \right] \right\} \times d^{3N} \mathbf{r} d^{3N} \mathbf{p}; \quad (14)$$

the zero superscript refers to this noninteracting case.

Every permutation P of the N momenta \mathbf{p}_j may be factored into disjoint "cycles,"¹² each of which permutes a subset of the \mathbf{p}_j 's cyclically.¹³ One may show easily by induction that if P factors into l cycles, the parity of this permutation (even or odd) is the same as the parity of $N-l$. Consequently we set

$$|P| = N - l. \quad (15)$$

The ideal gas CPF, therefore, consists of a sum of $N!$ contributions, one for each distinct permutation. Every

one of these contributions may be expressed as a product of l factors, one for each cycle of the permutation to which that term corresponds. If P has l_1 one-cycles, l_2 two-cycles, \dots , then

$$l = \sum_{j=1}^N l_j,$$

and since the total number of particles is N ,

$$N = \sum_{j=1}^N j l_j, \quad (16)$$

Now $Q_N^{(0)}$ may be exhibited as a sum over such sets of integers $\{l_j\}$ subject to the restriction (16),

$$Q_N^{(0)} = \frac{1}{N! h^{3N}} \sum_{\{l_j\}} (\pm 1)^{\sum (j-1) l_j} C\{\{l_j\}\} \prod_{j=1}^N (I_j)^{l_j}, \quad (17)$$

$$I_j = \int \exp \left\{ \sum_{\alpha=1}^j \left[-\frac{\beta p_{\alpha}^2}{2m} + \frac{i}{\hbar} \mathbf{r}_{\alpha} \cdot (\mathbf{p}_{\alpha} - \mathbf{p}_{\alpha-1}) \right] \right\} \times d^{3j} \mathbf{r} d^{3j} \mathbf{p},$$

$$\mathbf{p}_0 = \mathbf{p}_j,$$

where the summation over $\{l_j\}$ is subject to the restriction $\sum j l_j = N$. The combinatorial factor $C\{\{l_j\}\}$ is the number of distinct permutations which conform to the set $\{l_j\}$ of cycles of different orders. This is precisely the number of essentially different ways of arranging N objects (particles) on oriented loops (cycles) such that l_1 loops contain one object, l_2 loops contain two objects, \dots . By straightforward computation,

$$C\{\{l_j\}\} = N! / \prod_{j=1}^N l_j! (j)^{l_j}. \quad (18)$$

To develop a technique useful in construction of the quantum cluster integrals for imperfect systems, we now obtain $\partial^s G^{(0)} / \partial Z^s$ (for any integral s) by a simple approach. In Eq. (17), defer for the moment the position and momentum integrations for a set of s particles, $1 \dots s$. A particular permutation P of all N particles will have these s particles combined with $n-s$ others to provide the " s -containing" cycles. It should be realized there may be from 1 to s such cycles, depending on P . The $n-s$ particles may be chosen in

$$\binom{N-s}{n-s} = \frac{(N-s)!}{(n-s)!(N-n)!}$$

distinct ways. Taking proper account of the essentially different ways in which the s -containing cycles may be formed from a given set of n particles, and summing the non- s -containing cycles to obtain a lower order CPF, (17) leads to a difference equation satisfied by

¹² G. Birkhoff and S. MacLane, *A Survey of Modern Algebra* (Macmillan Company, New York, 1941), p. 136.

¹³ Thus, for example, if $N=7$ and if P permutes the momenta $\mathbf{p}_1 \mathbf{p}_2 \mathbf{p}_3 \mathbf{p}_4 \mathbf{p}_5 \mathbf{p}_6 \mathbf{p}_7$ to $\mathbf{p}_6 \mathbf{p}_1 \mathbf{p}_1 \mathbf{p}_2 \mathbf{p}_5 \mathbf{p}_3 \mathbf{p}_7$ so that $P \mathbf{p}_1 = \mathbf{p}_6$, $P \mathbf{p}_6 = \mathbf{p}_7$, $P \mathbf{p}_7 = \mathbf{p}_3$, $P \mathbf{p}_3 = \mathbf{p}_1$; $P \mathbf{p}_2 = \mathbf{p}_4$, $P \mathbf{p}_4 = \mathbf{p}_2$; $P \mathbf{p}_5 = \mathbf{p}_5$; then P is factored $(\mathbf{p}_1 \mathbf{p}_6 \mathbf{p}_7 \mathbf{p}_3) (\mathbf{p}_2 \mathbf{p}_4) (\mathbf{p}_5)$; i.e., a four-cycle, a two-cycle, and a one-cycle.

the ideal CPF's of various orders

$$Q_N^{(0)} = \frac{h^{-3s}}{N(N-1)\cdots(N-s+1)} \sum_{n=s}^N Q_{N-n}^{(0)} (\pm 1)^{n-s} \\ \times \sum_{\{n_j\}} \int \sigma_{\pm}^{(s)}(\mathbf{r}, \mathbf{p}) \prod_{j=1}^s \left\{ \exp \left[-\frac{n_j \beta p_j^2}{2m} \right] \right. \\ \left. \times d^3 \mathbf{p}_j d^3 \mathbf{r}_j \right\}, \quad (19)$$

where the summation over $\{n_j\}$ is subject to the restriction

$$\sum_1^s n_j = n.$$

We now pass to the grand ensemble by multiplying both sides of (19) by Z^N , and summing. The factor $[N(N-1)\cdots(N-s+1)]^{-1}$ occurring in (19) may subsequently be eliminated by an s -fold Z differentiation

$$\frac{\partial^s G^{(0)}(Z)}{\partial Z^s} = \sum_{N=s}^{\infty} Z^{N-s} h^{-3s} \sum_{n=s}^N Q_{N-n}^{(0)} (\pm 1)^{n-s} \\ \times \sum_{\substack{\{n_j\} \\ (\sum n_j = n)}} \int \sigma_{\pm}^{(s)}(\mathbf{r}, \mathbf{p}) \prod_{j=1}^s \left\{ \exp \left[-\frac{n_j \beta p_j^2}{2m} \right] \right. \\ \left. \times d^3 \mathbf{p}_j d^3 \mathbf{r}_j \right\}. \quad (20)$$

$Q_{N-n}^{(0)}$ (with the appropriate factor Z^{N-n}) on the right-hand side of (20) sums separately to give a factor $G^{(0)}(Z)$, upon suitable change of summation variables. The remaining terms may be put into closed form

$$\frac{1}{G^{(0)}(Z)} \frac{\partial^s G^{(0)}(Z)}{\partial Z^s} \\ = h^{-3s} \int \sigma_{\pm}^{(s)}(\mathbf{r}, \mathbf{p}) \prod_{j=1}^s \left\{ \frac{d^3 \mathbf{p}_j d^3 \mathbf{r}_j}{\exp[\beta p_j^2/2m] \mp Z} \right\}. \quad (21)$$

For $s=1$, the relation (21) may be integrated to yield $G^{(0)}(Z)$ in closed form (since the classical partition function must be obtained for sufficiently small Z)

$$G^{(0)}(Z) = \exp \left\{ \mp \frac{V}{h^3} \int \ln \left[1 \mp Z \exp \left(-\frac{\beta p^2}{2m} \right) \right] d^3 \mathbf{p} \right\}. \quad (22)$$

Clearly it is much simpler to find high order derivatives of $G^{(0)}(Z)$ from (21) rather than by tedious differentiation of (22).

IV. QUANTUM MECHANICAL CLUSTER INTEGRALS

For the more realistic case in which the particles of our quantum mechanical system interact via non-vanishing potentials $v(\mathbf{r})$, the fundamental quantity

$F^{(N)}$ is no longer a simple function of just the momenta as it is for the ideal gas. Since the modified Hamiltonian H_N' is a differential operator, the last of Eq. (8) shows that $F^{(N)}$ involves not only $v(\mathbf{r})$, but its derivatives as well, the latter being interpreted as the result of quantum diffraction effects.

The quantum cluster development is introduced by the set of relations ($N=2, 3, \dots$)

$$F^{(N)}(1 \cdots N) = \prod_{j=1}^N F^{(1)}(j) + \sum_{j < k=1}^N \Phi^{(2)}(jk) \prod_{\substack{l=1 \\ l \neq j, k}}^N F^{(1)}(l) \\ + \sum_{j < k < l=1}^N \Phi^{(3)}(jkl) \prod_{\substack{m=1 \\ m \neq j, k, l}}^N F^{(1)}(m) \\ + \cdots + \Phi^{(N)}(1 \cdots N). \quad (23)$$

The first term, a product of N free particle factors $F^{(1)}$, is precisely the ideal gas $F^{(N)}$. The following members of the sum, through the $\Phi^{(2)}$, $\Phi^{(3)}$, ..., correct for interactions of pairs of particles, triplets, By successive reversion of the expressions (23), the $\Phi^{(N)}$ may be related to sums of products of the $F^{(N)}$. The general term is found to be

$$\Phi^{(n)}(1 \cdots n) = (-1)^{(n-1)} (n-1) \prod_{j=1}^n F^{(1)}(j) \\ + \sum_{s=2}^n (-1)^{n-s} \sum_{i_1 < \cdots < i_s=1}^n F^{(s)}(i_1 \cdots i_s) \\ \times \prod_{\substack{j=1 \\ j \neq i_1, \dots, i_s}}^n F^{(1)}(j), \quad (24)$$

which may be verified by substitution in (23). The first members of this sequence are readily seen to be

$$\Phi^{(2)}(jk) = F^{(2)}(jk) - F^{(1)}(j)F^{(1)}(k), \\ \Phi^{(3)}(jkl) = F^{(3)}(jkl) - F^{(2)}(jk)F^{(1)}(l) \\ - F^{(2)}(jl)F^{(1)}(k) - F^{(2)}(kl)F^{(1)}(j) \\ + 2F^{(1)}(j)F^{(1)}(k)F^{(1)}(l), \text{ etc.} \quad (25)$$

When the positions of particles $1 \cdots n$ are such that they are separated into two sets ($1 \cdots k$ and $k+1 \cdots n$, for example) such that every member of the first set is significantly farther from all members of the second set than the range of $v(\mathbf{r})$, then $F^{(n)}(1 \cdots n)$ reduces to the product of F 's for each subset $[F^{(k)}(1 \cdots k)F^{(n-k)}(k+1 \cdots n)]$. So far as Eq. (24) is concerned, this factorization property of the F 's implies that if none of the particles $1 \cdots n$ are close enough to interact through the $v(\mathbf{r})$, then $\Phi^{(n)}$ vanishes identically. It must be realized, however, that $\Phi^{(n)}$ does not necessarily vanish if $1 \cdots n$ separates into subsets each of more than just a single particle.¹⁴

The expansion (23) is now inserted for $F^{(N)}$ in the

¹⁴ $\Phi^{(4)}(1234)$ for example reduces to $\Phi^{(2)}(12)\Phi^{(2)}(34)$ when the only particle pair distances which are small are r_{12} and r_{34} .

CPF (8). The first member of the resulting sum is $Q_N^{(0)}$. Since the $\Phi^{(s)}$ are complicated functions of both the position and momentum coordinates of a set of s particles, it is advantageous to separate the integrations over these $6s$ coordinates in the terms containing a $\Phi^{(s)}$. The remaining integrations are treated in the manner of Sec. III. When it is remembered that exactly $N(N-1)\cdots(N-s+1)/s!$ terms contain a $\Phi^{(s)}$, one has finally the counterpart of the difference equation (19)

$$Q_N = Q_N^{(0)} + \sum_{s=2}^N \frac{h^{-3s}}{s!} \sum_{n=s}^N Q_{N-n}^{(0)} (\pm 1)^{n-s} \times \sum_{\substack{\{n_i\} \\ (\sum n_i = n)}} \int L^{(s)}(\mathbf{r}, \mathbf{p}) \prod_{j=1}^s \exp \left[-\frac{n_j \beta p_j^2}{2m} \right] \times d^3 \mathbf{p}_j d^3 \mathbf{r}_j, \quad (26)$$

$$L^{(s)}(\mathbf{r}, \mathbf{p}) = \sigma_{\pm}^{(s)}(\mathbf{r}, \mathbf{p}) \Phi^{(s)}(\mathbf{r}, \mathbf{p}) / [F^{(1)}(1) \cdots F^{(1)}(s)].$$

The quantity $L^{(s)}$ represents the coupling between the momenta and positions of an s -particle set induced both by forces and by exchange effects.

The techniques used to construct $G^{(0)}(Z)$ and its derivatives previously are likewise applicable to this interacting case. When (26) is multiplied on both sides by Z^N , and summed over N , each term on the right gives rise to a factor $G^{(0)}(Z)$, so that finally

$$\frac{G(Z)}{G^{(0)}(Z)} = 1 + \sum_{s=2}^{\infty} B^{(s)}(Z) Z^s, \quad (27)$$

$$B^{(s)}(Z) = \frac{h^{-3s}}{s!} \int L^{(s)}(\mathbf{r}, \mathbf{p}) \times \prod_{j=1}^s \left\{ \frac{d^3 \mathbf{p}_j d^3 \mathbf{r}_j}{\exp[\beta p_j^2/2m] \mp Z} \right\}.$$

A significant feature of the integrals $B^{(s)}(Z)$ is their momentum denominators, which exhibit clearly the quantum degeneracy induced by the Fermi or Bose statistics. These denominators are, in fact, the momentum distribution in an ideal gas at activity Z and temperature $T=1/k\beta$. In rough terms, the form (27) for the cluster integrals $B^{(s)}$ shows that the interactions among the members of an s -particle set act in a highly degenerate (though ideal) bath of other particles; this bath affects the s particles by establishing a characteristic nonclassical momentum distribution.

Finally, our quantum analogs, $b_j(Z)$, of the classical singly connected cluster integrals are introduced as the Thiele semi-invariants¹⁵ of the $B^{(s)}(Z)$,

$$B^{(s)}(Z) = \sum_{\substack{\{n_i\} \\ (\sum n_i = s)}} \prod_{i=2}^{\infty} \frac{1}{n_i!} \left[\frac{V}{\Lambda^3(Z)} b_j(Z) \right]^{n_i} \quad (s=2, 3, \dots), \quad (28)$$

$$\frac{1}{\Lambda^3(Z)} = \frac{1}{h^3} \int \frac{d^3 \mathbf{p}}{\exp[\beta p^2/2m] \mp Z},$$

which is equivalent to¹⁵

$$b_j(Z) = \frac{\Lambda^3(Z)}{V} \sum_{\substack{\{n_i\} \\ (\sum n_i = j)}} (-1)^{\sum n_i - 1} \left(\sum_1^{\infty} n_i - 1 \right)! \times \prod_{i=1}^{\infty} \frac{[B^{(i)}(Z)]^{n_i}}{n_i!}, \quad (29)$$

$$B^{(1)}(Z) \equiv 0.$$

The "degenerate" mean de Broglie wavelength $\Lambda(Z)$ is introduced to nondimensionalize the $b_j(Z)$; it reduces to the usual value $h/(2\pi mkT)^{1/3}$ for small Z (vanishing degeneracy). It will be recognized that since the momentum and position integrations in (27) commute with the summation and product operations in (28) and (29), $b_j(Z)$ may be written

$$b_j(Z) = \frac{\Lambda^3(Z)}{V h^3 j!} \int l^{(j)}(\mathbf{r}, \mathbf{p}) \prod_{k=1}^j \left\{ \frac{d^3 \mathbf{p}_k d^3 \mathbf{r}_k}{\exp[\beta p_k^2/2m] \mp Z} \right\}. \quad (30)$$

As regards the relation between the L 's in the integrands of the B 's, (27), and the l 's in the b 's, (30), Eqs. (29), the first members of which are

$$\begin{aligned} b_2(Z) &= B^{(2)}(Z), \\ b_3(Z) &= B^{(3)}(Z), \\ b_4(Z) &= B^{(4)}(Z) - \frac{1}{2} [B^{(2)}(Z)]^2, \\ b_5(Z) &= B^{(5)}(Z) - B^{(3)}(Z) B^{(2)}(Z), \text{ etc.}, \end{aligned} \quad (31)$$

lead directly to the results

$$\begin{aligned} l_2(jk) &= L^{(2)}(jk), \\ l_3(jkl) &= L^{(3)}(jkl), \\ l_4(jklm) &= L^{(4)}(jklm) - \frac{1}{2} \langle L^{(2)}(jk) L^{(2)}(lm) \rangle, \\ l_5(jklmn) &= L^{(5)}(jklmn) - \langle L^{(3)}(jkl) L^{(2)}(mn) \rangle, \text{ etc.} \end{aligned} \quad (32)$$

The angular brackets, $\langle \rangle$, denote in (32) the symmetrical function obtained by averaging over all ways of interchanging arguments between the functions contained in the brackets; for example:

$$\begin{aligned} \langle L^{(2)}(jk) L^{(2)}(lm) \rangle &= \frac{1}{3} [L^{(2)}(jk) L^{(2)}(lm) + L^{(2)}(jl) L^{(2)}(km) \\ &\quad + L^{(2)}(jm) L^{(2)}(kl)]. \end{aligned} \quad (33)$$

The properties of the semi-invariant relations (28) and (29) lead now to the major result of this section

$$\ln \frac{G(Z)}{G^{(0)}(Z)} = \beta V (p - p^{(0)}) = \frac{V}{\Lambda^3(Z)} \sum_{j=2}^{\infty} b_j(Z) Z^j, \quad (34)$$

¹⁵ H. Cramér, *Mathematical Methods of Statistics* (Princeton University Press, Princeton, 1946), p. 185.

which is the desired expansion of the logarithm of the GPF.

At this point, it is instructive to examine the behavior of the quantum cluster integrals $B^{(s)}(Z)$ and $b_j(Z)$ in the classical region. Here it is necessary to consider only the identity permutation in $\sigma_{\pm}^{(s)}$. On account of the simple form of $F_{cl}^{(n)}$, (10), $L^{(s)}$ becomes independent of the momentum coordinates, so that one is left with just

$$B_{cl}^{(s)} = (\Lambda^{-3s}/s!) \int L_{cl}^{(s)}(\mathbf{r}) d^3\mathbf{r}, \quad (35)$$

$$b_{j,cl} = (\Lambda^{-3(j-1)}/V_j!) \int l_{cl}^{(j)}(\mathbf{r}) d^3\mathbf{r}.$$

We hasten to emphasize that coupling of momentum and position coordinates in the cluster integral integrands in the nonclassical region means that generally the $B^{(s)}$ and b_j are much more complicated than the special cases (35) might indicate.

For $N=2, 3, \dots$, Eq. (23) may be rewritten (in the classical limit)

$$\frac{F_{cl}^{(N)}(1 \dots N)}{F^{(1)}(1) \dots F^{(1)}(N)} = \exp \left[-\beta \sum_{j < k=1}^N v(r_{jk}) \right]$$

$$= 1 + \sum_{j < k=1}^N L_{cl}^{(2)}(jk) + \sum_{j < k < l=1}^N L_{cl}^{(3)}(jkl) + \dots + L_{cl}^{(N)}(1 \dots N). \quad (36)$$

Equation (36), which determines the $L_{cl}^{(s)}$ uniquely, may be compared now with the Mayer f expansion

$$\exp[-\beta \sum_{j < k=1}^N v(r_{jk})] = \prod_{j < k=1}^N [1 + f(r_{jk})]$$

$$= 1 + \sum_{j < k=1}^N \{f(r_{jk})\} + \sum_{j < k < l=1}^N \{f(r_{jk})f(r_{kl}) + \dots\} + \dots + \{\dots\}, \quad (37)$$

$$f(r_{jk}) = \exp[-\beta v(r_{jk})] - 1.$$

It will be recalled that the curly brackets in (37) collect successively distinct products of f functions involving the position coordinates of two, three, ... different particles. Examining both (36) and (37) for each $N > 1$ in turn, one finds that $L_{cl}^{(s)}(i_1 \dots i_s)$ must be precisely the curly bracket for arguments $i_1 \dots i_s$, thereby establishing the relation of the present develop-

ment to the Mayer theory. Specifically, one may use the f -product interpretation of $L_{cl}^{(s)}$ to assign cluster diagrams to the corresponding contributions to $B_{cl}^{(s)}$. Subsequently, $l_{cl}^{(j)}$ is identified in the usual fashion as the reducible (singly connected) cluster sum for j particles; in contrast to $\Phi^{(s)}$, $l_{cl}^{(j)}$ vanishes if any pair of its arguments are separated by a distance large compared with the range of intermolecular forces.

In a later paper we shall examine at some length the utilization of cluster diagrams in the quantum mechanical case. In particular, it is possible to employ the classical identity (37) to re-establish, in a unique fashion, the previously obtained expressions for our quantum mechanical functions Φ , L , and l .

V. THE CLUSTER EQUATION OF STATE

The activity series (34) may be rewritten

$$\frac{\Lambda^3(Z)p}{kT} = \frac{\Lambda^3(Z)p^{(0)}}{kT} - Z + \sum_{j=1}^{\infty} b_j(Z)Z^j, \quad b_1(Z) \equiv 1. \quad (38)$$

This expansion is superficially similar to the corresponding classical expression involving singly connected classical cluster integrals as coefficients. The quantum statistical situation, however, is complicated by the fact that the $b_j(Z)$ are, themselves, dependent on Z . Therefore, we find it no longer possible to undergo the usual elimination of Z between (38) and the expression (12) for the density $\rho = \bar{N}/V$, to obtain a virial expansion of the pressure. We shall, nevertheless, examine to what extent Kahn's classical approach¹⁶ may be modified to cope with the quantum mechanical problem.

The quantum statistical relatives of the irreducible (doubly connected) cluster integrals are implicitly defined by the same relations encountered in the classical theory ($j=2, 3, \dots$)

$$j^2 b_j(Z) = \sum_{\substack{\{n_k\} \\ \sum k n_k = j-1}} \prod_{k=1}^{j-1} \frac{[j \beta_k(Z)]^{n_k}}{n_k!}. \quad (39)$$

The inversion of Eq. (39) is found to be¹⁷

$$\beta_k(Z) = \sum_{\substack{\{m_j\} \\ \sum (j-1)m_j = k}} (-1)^{\sum m_j - 1} \left[\frac{(k-1 + \sum 2^{k+1} m_j)!}{k!} \right] \times \prod_{j=2}^{k+1} \frac{[j b_j(Z)]^{m_j}}{m_j!}. \quad (40)$$

In particular, one finds

$$\begin{aligned} \beta_1(Z) &= 2b_2(Z), \\ \beta_2(Z) &= 3b_3(Z) - 6[b_2(Z)]^2, \\ \beta_3(Z) &= 4b_4(Z) - 24b_3(Z)b_2(Z) \\ &\quad + (80/3)[b_2(Z)]^3, \text{ etc.} \end{aligned} \quad (41)$$

¹⁶ B. Kahn, dissertation, Utrecht, 1938 (unpublished).

¹⁷ J. E. Mayer, J. Chem. Phys. **10**, 629 (1942).

Although it is true that in the classical realm our $\beta_k(Z)$ (the "irreducible" cluster integrals) are proportional to the virial coefficients for the nonideal system, they are, on the other hand, very complicated functions of the mean density ρ when quantum degeneracy appears. It is for this reason that they include many-body effects determined by the thermodynamic state of the entire interacting system.

An auxiliary variable y is introduced by setting

$$Z = y \exp[-\tau(y)], \quad \tau(y) = \sum_{k=1}^{\infty} \beta_k y^k. \quad (42)$$

On account of the definitions (39), Lagrange's theorem¹⁸ allows (42) to be inverted

$$y(Z) = \sum_{j=1}^{\infty} j \beta_j Z^j. \quad (43)$$

The sum occurring in (38) may be rewritten as an integral, making use of (42)

$$\sum_{j=1}^{\infty} b_j Z^j = \int_0^Z \frac{y(\alpha)}{\alpha} d\alpha. \quad (44)$$

$$\rho(\beta, \mu) = \left(\frac{\partial p(\beta, \mu)}{\partial \mu} \right)_{\beta, V} = \rho^{(0)}(\beta, \mu) - \frac{3(p - p^{(0)})}{\Lambda(Z)} \left(\frac{\partial \Lambda(Z)}{\partial \mu} \right)_{\beta, V} + \frac{kT}{\Lambda^3(Z)} \left\{ \left(\frac{\partial y}{\partial \mu} \right)_{\beta, V} - \frac{Z}{kT} - \sum_{k=1}^{\infty} k y \left[\frac{y}{k+1} \left(\frac{\partial \beta_k(Z)}{\partial \mu} \right)_{\beta, V} + \beta_k(Z) \left(\frac{\partial y}{\partial \mu} \right)_{\beta, V} \right] \right\}, \quad (47)$$

obtained by differentiating (46).

As already remarked, the equation of state must remain in parametric form. Having chosen values for the chemical potential μ and $\beta = 1/kT$, the quantities Z and [by (43)] y are numerically determined. Substitution of these values into (46) and (47) yield the simultaneous values of p and ρ .

VI. THE MODIFIED HAMILTONIAN

Determination of the quantum cluster integrals $b_j(Z)$ and $\beta_k(Z)$ requires knowledge of the $F^{(n)}$ of various orders. The behavior of these functions may be displayed in a number of ways. One can, for example, easily obtain a series development of $F^{(n)}$ in ascending orders in Planck's constant \hbar (the general term of which would be given recursively); alternatively $F^{(n)}$ would admit of a perturbation expansion in the interaction potentials. In the present section, though, we shall illustrate properties of the $F^{(n)}$ in a manner appropriate to all temperatures (not merely the near classical region) as well as all interaction strengths.

We have already seen that $F^{(n)}$ satisfies a Bloch equation, (9). Without significant loss of generality,

If we replace Z by α in (42), (44) is seen to be

$$\begin{aligned} \sum_{j=1}^{\infty} b_j Z^j &= \int_{\alpha=0}^{\alpha=Z} \exp[\tau(y(\alpha))] \\ &\quad \times d\{y(\alpha) \exp[-\tau(y(\alpha))]\} \\ &= \int_0^{y(Z)} \left[1 - y \frac{\partial \tau}{\partial y} \right] dy \\ &= y - \sum_{k=1}^{\infty} \frac{k}{k+1} \beta_k(Z) y^{k+1}, \end{aligned} \quad (45)$$

where reference has been made to the definition of τ , (42). The pressure is therefore

$$\frac{\Lambda^3(Z)p}{kT} = \frac{\Lambda^3(Z)p^{(0)}}{kT} - Z + y - \sum_{k=1}^{\infty} \frac{k}{k+1} \beta_k(Z) y^{k+1}. \quad (46)$$

Referring to (11) and (12), the mean density ρ is the μ derivative of p at constant temperature and volume,

it may be assumed that the pair potentials $v(r)$ are bounded, though possibly very large in magnitude. At sufficiently high temperatures, then, $F^{(n)}$ is asymptotic to the classical ideal gas form

$$F^{(n)}(\mathbf{r}, \mathbf{p}; \beta) = \exp[-\beta p^2/2m]. \quad (48)$$

$F^{(n)}$ is completely determined by this boundary condition in conjunction with the Bloch differential equation. Consequently, (9) and (48) may be combined to give a single integral equation

$$\begin{aligned} F^{(n)}(\mathbf{r}, \mathbf{p}; \beta) &= \exp[-\beta p^2/2m] \\ &\quad - \int_0^{\beta} \exp[(\beta' - \beta) H_n^{(0)'}] V_n(\mathbf{r}) F^{(n)}(\mathbf{r}, \mathbf{p}; \beta') d\beta', \end{aligned} \quad (49)$$

from which (9) may be recovered by differentiation.

That part of the integrand of (49) containing $H_n^{(0)'}$ may be transformed

$$\begin{aligned} \exp\left[-\frac{(\beta' - \beta)}{2m} (i\mathbf{p} + \hbar \nabla)^2\right] &= \frac{1}{\pi^{3n/2}} \int d^{3n} \mathbf{k} \\ &\quad \times \exp\left[-k^2 - 2\mathbf{k} \cdot (i\mathbf{p} + \hbar \nabla) \left(\frac{\beta - \beta'}{2m}\right)^{\frac{1}{2}}\right]. \end{aligned} \quad (50)$$

¹⁸ E. T. Whittaker and G. N. Watson, *A Course of Modern Analysis* (Cambridge University Press, New York, 1942), p. 133.

The exponential gradient operator on the right side of (50) is the Taylor's operator; when operating on functions of the $3n$ -dimensional configuration vector \mathbf{r} , it makes the replacement

$$\mathbf{r} \rightarrow \mathbf{r}' = \mathbf{r} - 2\hbar[(\beta - \beta')/2m]^{1/2} \mathbf{k}. \quad (51)$$

The integral equation (49) is consequently modified to read

$$\begin{aligned} F^{(n)}(\mathbf{r}, \mathbf{p}; \beta) = & \exp\left[-\frac{\beta p^2}{2m}\right] - \frac{1}{\pi^{3n/2}} \int_0^\beta d\beta' \int d^{3n} \mathbf{k} \\ & \times \exp\left[-k^2 - 2i\left(\frac{\beta - \beta'}{2m}\right)^{1/2} \mathbf{k} \cdot \mathbf{p}\right] V_n(\mathbf{r}') \\ & \times F^{(n)}(\mathbf{r}', \mathbf{p}; \beta'). \end{aligned} \quad (52)$$

The variables of integration are now changed from \mathbf{k}, β' to \mathbf{r}', x , where

$$x = \beta/(\beta - \beta'); \quad (53)$$

after the correct transformation Jacobian is computed, (52) leads to the result

$$\begin{aligned} F^{(n)}(\mathbf{r}, \mathbf{p}; \beta) = & \exp\left[-\frac{\beta p^2}{2m}\right] - \beta \left(\frac{m}{2\pi\hbar^2\beta}\right)^{3n/2} \int d^{3n} \mathbf{r}' \int_1^\infty dx x^{3n/2-2} \\ & \times \exp\left[-\frac{m|\mathbf{r}' - \mathbf{r}|^2 x}{2\hbar^2\beta} + \frac{i}{\hbar} \mathbf{p} \cdot (\mathbf{r}' - \mathbf{r})\right] V_n(\mathbf{r}') \\ & \times F^{(n)}[\mathbf{r}', \mathbf{p}; \beta(1 - 1/x)]. \end{aligned} \quad (54)$$

Thus an integral equation for $F^{(n)}$ has been derived whose solution, in principle at least, should represent this function over the entire temperature range from absolute zero to the classical region.

The formal similarity of the Bloch equation (9) to the time-dependent Schrödinger equation, upon replacing β by $i\hbar/t$ (t is the time variable), has long been recognized. In consequence, the well-developed formalism of time-dependent perturbation theory in quantum mechanics is applicable to determination of the $F^{(n)}$ as an alternate method of analysis, by considering temperature differences to be equivalent to imaginary time intervals. It is our purpose only to use the structure of perturbation theory to re-establish the general result (54). This viewpoint is in contrast to that of Montroll and Ward⁷ who evaluate their quantum cluster integrals in perturbation series.

In order to examine the relation between the Bloch and Schrödinger equations, we first define a transformation function $K^{(n)}$ which, as an integral kernel, serves to connect the values of $F^{(n)}$ at different tem-

peratures and particle configurations

$$F^{(n)}(\mathbf{r}_2, \mathbf{p}; \beta_2) = \int d^{3n} \mathbf{r}_1 K^{(n)}(2|1) F^{(n)}(\mathbf{r}_1, \mathbf{p}; \beta_1), \quad (\beta_2 > \beta_1); \quad (55)$$

$$K^{(n)}(2|1) = 0 \quad (\beta_1 > \beta_2); \quad (56)$$

$$K^{(n)}(2|1) \equiv K^{(n)}(\mathbf{r}_2, \mathbf{p}; \beta_2 | \mathbf{r}_1, \mathbf{p}; \beta_1).$$

It is possible to show¹⁹ that $K^{(n)}$ satisfies the differential equation

$$[(\partial/\partial\beta_2) + H_n'(2)] K^{(n)}(2|1) = \delta(\mathbf{r}_2 - \mathbf{r}_1) \delta(\beta_2 - \beta_1) \quad (57)$$

subject to the boundary condition (56). This latter implies

$$\lim_{\epsilon \rightarrow 0+} K^{(n)}(\mathbf{r}_2, \mathbf{p}; \beta_1 + \epsilon | \mathbf{r}_1, \mathbf{p}; \beta_1) = \delta(\mathbf{r}_2 - \mathbf{r}_1), \quad (58)$$

so that (55) reduces, as it must, to an identity when $\beta_2 = \beta_1$.

It is known that (56) and (57) are equivalent to the integral equation

$$\begin{aligned} K^{(n)}(2|1) = & K_0^{(n)}(2|1) - \int d^{3n} \mathbf{r}_3 \\ & \times \int_{\beta_1}^{\beta_2} d\beta_3 K_0^{(n)}(2|3) V_n(3) K^{(n)}(3|1), \end{aligned} \quad (59)$$

where $K_0^{(n)}$ is the free particle transformation function defined by

$$\begin{aligned} [(\partial/\partial\beta_2) + H_n^{(0)'}(2)] K_0^{(n)}(2|1) = & \delta(\mathbf{r}_2 - \mathbf{r}_1) \delta(\beta_2 - \beta_1), \end{aligned} \quad (60)$$

and the boundary condition (56). If $\mu_\alpha(\mathbf{r})$ are the orthonormal eigenfunctions of the modified Hamiltonian H_n' , with associated eigenvalues E_α' , then ($\beta_2 > \beta_1$) the solution to (59) may be expressed in the form

$$K^{(n)}(2|1) = \sum_{\alpha=0}^{\infty} \mu_\alpha(\mathbf{r}_2) \mu_\alpha^*(\mathbf{r}_1) \exp[-(\beta_2 - \beta_1) E_\alpha']. \quad (61)$$

This result (61) leads to an immediate evaluation of $K_0^{(n)}$ since the eigenfunctions of $H_n^{(0)'}$ are plane waves

$$\frac{1}{2m} (\mathbf{p} - i\hbar\nabla)^2 \exp\left[\frac{i}{\hbar} \mathbf{q} \cdot \mathbf{r}\right] = E_q' \exp\left[\frac{i}{\hbar} \mathbf{q} \cdot \mathbf{r}\right], \quad (62)$$

$$E_q' = (\mathbf{p} + \mathbf{q})^2/2m.$$

Replacing as usual the α summation (61) by an inte-

¹⁹ See S. S. Schweber, H. A. Bethe, and F. de Hoffmann, *Mesons and Fields* (Row, Peterson and Company, Evanston, 1956), pp. 54-58, for a review of perturbation theory in this form, including justification of the results concerning $K^{(n)}$ which we quote here without proof.

gration over \mathbf{q} , we see that

$$\begin{aligned}
 K_0^{(n)}(2|1) &= \left(\frac{V}{h^3}\right)^n \frac{1}{V^n} \int d^{3n}\mathbf{q} \\
 &\quad \times \exp\left[-\frac{(\beta_2-\beta_1)}{2m}(\mathbf{p}+\mathbf{q})^2 + \frac{i}{\hbar}(\mathbf{r}_2-\mathbf{r}_1)\cdot\mathbf{q}\right] \\
 &= \left[\frac{m}{2\pi\hbar^2(\beta_2-\beta_1)}\right]^{3n/2} \\
 &\quad \times \exp\left[-\frac{m(\mathbf{r}_2-\mathbf{r}_1)^2}{2\hbar^2(\beta_2-\beta_1)} - \frac{i}{\hbar}\mathbf{p}\cdot(\mathbf{r}_2-\mathbf{r}_1)\right]. \quad (63)
 \end{aligned}$$

Upon multiplying both sides of (59) by

$$F^{(n)}(\mathbf{r}_1, \mathbf{p}; \beta_1 = 0)$$

and integrating with respect to \mathbf{r}_1 over V , we obtain

$$\begin{aligned}
 F^{(n)}(\mathbf{r}_2, \mathbf{p}; \beta_2) &= \exp[-\beta p^2/2m] - \int d^{3n}\mathbf{r}_3 \\
 &\quad \times \int_0^{\beta_2} d\beta_3 K_0^{(n)}(2|3) V_n(3) F^{(n)}(\mathbf{r}_3, \mathbf{p}; \beta_1). \quad (64)
 \end{aligned}$$

Now if (63) is inserted in (64) for the free particle transformation function $K_0^{(n)}$, and if we make the substitutions

$$\begin{aligned}
 \beta_2 &= \beta, \\
 \beta_3 &= \beta', \\
 \beta - \beta' &= \beta/x,
 \end{aligned} \quad (65)$$

the integral equation (54) is exactly reproduced, demonstrating thereby the relation between the two approaches outlined in this section.

Finally, it is a simple matter to express $F^{(n)}$ in terms of the eigenfunctions $\psi_\alpha^{(n)}(\mathbf{r})$ of the unmodified Hamiltonian H_n . By making use of the identity (7), one has that

$$\begin{aligned}
 F^{(n)}(\mathbf{r}, \mathbf{p}; \beta) &= \exp[-(i/\hbar)\mathbf{p}\cdot\mathbf{r}] \\
 &\quad \times \{\exp(-\beta H_n) \exp[(i/\hbar)\mathbf{p}\cdot\mathbf{r}]\}. \quad (66)
 \end{aligned}$$

If $E_\alpha^{(n)}$ denotes the energy eigenvalue corresponding to the wave function $\psi_\alpha^{(n)}(\mathbf{r})$, then it is easy to see that

$$\begin{aligned}
 F^{(n)}(\mathbf{r}, \mathbf{p}; \beta) &= \exp\left(-\frac{i}{\hbar}\mathbf{p}\cdot\mathbf{r}\right) \\
 &\quad \times \sum_{\alpha=0}^{\infty} \chi_\alpha^{(n)}(\mathbf{p}) \psi_\alpha^{(n)}(\mathbf{r}) \exp(-\beta E_\alpha^{(n)}), \quad (67)
 \end{aligned}$$

when the completeness property of the entire set of $\psi_\alpha^{(n)}$ is utilized in expansion of the plane-wave in (66)

$$\begin{aligned}
 \exp\left(\frac{i}{\hbar}\mathbf{p}\cdot\mathbf{r}\right) &= \sum_{\alpha=0}^{\infty} \chi_\alpha^{(n)}(\mathbf{p}) \psi_\alpha^{(n)}(\mathbf{r}), \\
 \chi_\alpha^{(n)}(\mathbf{p}) &= \int \psi_\alpha^{(n)*}(\mathbf{r}') \exp[(i/\hbar)\mathbf{p}\cdot\mathbf{r}'] d^{3n}\mathbf{r}'. \quad (68)
 \end{aligned}$$

At sufficiently low temperatures, only the lowest eigenvalues $E_\alpha^{(n)}$ (i.e., the ground state and low-lying excited states) contribute appreciably to the sum (67), and in certain cases it may be convenient to establish the properties of $F^{(n)}$ from known behavior of the wave functions $\psi_\alpha^{(n)}$. For intermediate temperatures, where a large number of energy levels in (67) are involved, it will undoubtedly be necessary to solve the integral equation (54) in detail. A later communication will deal with application of known solutions of the quantum mechanical two-body problem to computation of thermodynamic properties of systems in interaction.