

## The Quantum-Mechanical Partition Function

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A simple method is demonstrated of expanding the quantum-mechanical partition function in powers of the interaction potential between the particles of the system. The result is valid for all types of statistics and for all types of interaction, provided the interaction potential is nonsingular. The general term is expressed, in terms of known quantities, in a compact form. It is shown that the series must be considerably modified for the case in which the potential is singular. The convergence of the series is discussed briefly.

### I. INTRODUCTION

THE problem of expanding the quantum-mechanical partition function in powers of  $\hbar$  (Planck's constant) has been discussed by various authors.<sup>1-5</sup> Several methods of obtaining the original expansions, due to Wigner and Kirkwood, have now been given. As these series are, however, only useful at sufficiently high temperatures, where quantum effects are comparatively small, efforts have been made to develop an expansion convergent at low temperatures. Thus, Green<sup>4</sup> has obtained the first two terms of an expansion in powers of the interaction potential between the particles of the system. His results are in an extremely cumbersome form and are, in any case, limited to the case of Boltzmann statistics, whereas the few calculations that have actually been carried out<sup>6,7</sup> at low temperatures definitely show that the type of statistics obeyed by the particles is of considerable importance. Goldberger and Adams<sup>5</sup> obtained the general term in the series proposed by Green. The final result was, however, left in an awkward operational form and the calculations were again limited to the case of Boltzmann statistics. Finally, Siegert<sup>8</sup> showed how the series could be obtained by solving an integral equation for the partition function by an iterative procedure. In this approach it is easy to take into account, in a formal manner, the type of statistics obeyed by the particles. The general term in the series was not, however, calculated in an explicit form. A knowledge of the general term is clearly of importance if we wish to discuss, even qualitatively, the convergence of the expansion.

The purpose of the present paper is to rederive, and to discuss the validity of, the expansion of the partition function in powers of the interaction potential. It is first shown that the series may be obtained by a straightforward application of Taylor's theorem to the

partition function of the system. The calculation is quite general and is valid for all types of statistics. The general term is expressed, in terms of known quantities, in a compact form. In Sec. 3 we compare our work with that of previous authors. The equivalence of our expansion with that due to Goldberger and Adams is established. Lastly, the validity of the expansion is discussed. It is shown that the terms in the series must be considerably modified if the potential possesses any singularities. In fact, the series is only valid in this case if the particles of the system are considered to have finite (nonzero) incompressible cores. A condition is obtained for the convergence of the series.

### II. THE EXPANSION IN POWERS OF THE POTENTIAL

The partition function ( $Z$ ) of a system, is usually written as

$$Z = \sum_a \exp(-\beta \mathcal{E}_a), \quad (1.1)$$

where in Eq. (1.1),  $\beta = 1/kT$ , and the  $\mathcal{E}_a$  are the energy levels of the system. A well-known alternative form of Eq. (1.1) is

$$Z = \text{Tr}[\exp(-\beta H)], \quad (1.2)$$

where  $H$  is the Hamiltonian of the system, and  $\text{Tr}(A)$ , stands for the trace of the quantum-mechanical operator  $A$ . It is assumed, in what follows, that the Hamiltonian is independent of any spin coordinates of the particles.

The trace of any operator is invariant under change of representation. Consequently, any complete set of wave functions can be used to form the trace in Eq. (1.2).

For a system of  $N$  interacting particles, in an enclosure,  $H$  can be written  $H_0 + gV$ , where  $H_0$  is the translational energy and  $gV$  the potential energy of the mutual interactions. The partition function  $Z$  can now be thought of as a function of  $g$ . It will be shown that the Taylor series expansion of  $Z$  in powers of  $g$  is identical with the series proposed by Goldberger and Adams. We first write

$$\exp[-\beta(H_0 + gV)] = \exp(-\beta H) = \sum_{\nu=0}^{\infty} \frac{(-1)^\nu}{\nu!} \beta^\nu H^\nu. \quad (1.3)$$

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<sup>1</sup> E. P. Wigner, *Phys. Rev.* **40**, 749 (1932).

<sup>2</sup> J. G. Kirkwood, *Phys. Rev.* **44**, 31 (1933).

<sup>3</sup> J. E. Mayer and W. Band, *J. Chem. Phys.* **15**, 141 (1947).

<sup>4</sup> H. S. Green, *J. Chem. Phys.* **19**, 955 (1951).

<sup>5</sup> H. Goldberger and E. N. Adams, *J. Chem. Phys.* **20**, 240 (1952).

<sup>6</sup> De Boer, Van Kranendonk, and Compaan, *Physica* **16**, 545 (1950).

<sup>7</sup> J. H. De Boer and E. G. D. Cohen, *Physica* **17**, 993 (1951).

<sup>8</sup> A. J. F. Siegert, *J. Chem. Phys.* **20**, 572 (1952).

If Taylor's theorem is applied to the right-hand side of Eq. (1.3), it becomes

$$\exp(-\beta H) = \sum_{n=0}^{\infty} g^n/n! \sum_{\nu=0}^{\infty} (-1)^\nu \beta^\nu/\nu! [D^n H^\nu]_{g=0}, \quad (1.4)$$

where in Eq. (1.4)  $D = \partial/\partial g$ . Combining Eq. (1.4) with Eqs. (1.2) and (1.3),<sup>9</sup>

$$Z = Z(g) = \sum_{n=0}^{\infty} g^n/n! \sum_{\nu=0}^{\infty} (-1)^\nu \beta^\nu/\nu! \text{Tr}\{[D^n H^\nu]_{g=0}\}. \quad (1.5)$$

Thus, the fundamental quantity to be calculated is  $\text{Tr}\{[D^n H^\nu]_{g=0}\}$ . To carry out this calculation the following simple relations are needed:

$$D(H) = V, \quad D^n(H) = 0, \quad n > 1, \quad \text{and} \quad [H]_{g=0} = H_0. \quad (1.6)$$

It is now easily seen, using these relations, that  $(D^n H^\nu)_{g=0}$  can be written as the sum of a number of terms of the form

$$H_0^{\nu_1} V H_0^{\nu_2} V H_0^{\nu_3} \dots H_0^{\nu_n} V H_0^{\nu_{n+1}}. \quad (1.7)$$

In the expression (1.7) the  $\nu_k$ 's are integers and can take on any values from 0 to  $\nu - n$ , subject to the condition that

$$\sum_{k=1}^{n+1} \nu_k = \nu - n.$$

As we are only concerned with the trace of (1.7), the theorem that  $\text{Tr}(AB) = \text{Tr}(BA)$  can be used to rewrite it as

$$H_0^{\nu_1} V H_0^{\nu_2} V H_0^{\nu_3} \dots H_0^{\nu_n} V, \quad (1.8)$$

with precisely the same conditions on the  $\nu_k$ . The complete expression for  $(D^n H^\nu)_{g=0}$  can now be written down:

$$(D^n H^\nu)_{g=0} = (n-1)! \nu \sum_{(\nu_k)} H_0^{\nu_1} V H_1^{\nu_2} \dots H_0^{\nu_n} V, \quad (1.9)$$

where in Eq. (1.9)  $\sum_{(\nu_k)}$  means that the summation is to be taken over all sets of integers  $\nu_k$ , satisfying the relation

$$\sum_{k=1}^n \nu_k = \nu - n.$$

The factor  $\nu$  arises from the fact that the first differentiation gives rise to  $\nu$  equal terms of the form  $H_0^{\nu-1} V$ , while the factor  $(n-1)!$  arises because at the  $k$ th stage of forming the  $n$ th differential coefficient there are  $k-1$  groups of  $H$ 's, any one of which can be chosen as the operand for the  $k$ th operator. Thus,  $(k-1)$  terms, each of which is identical with a typical term of the form (1.8), arise from the  $k$ th stage of forming  $D^n H^\nu$ . In this way, the complete factor  $(n-1)!$  is built up. The

<sup>9</sup> This step involves the interchange of the operations of trace and summation. If any difficulty arises, in any particular case, from this interchange it can be regarded as being purely formal and the remainder of the analysis will still be valid.

result, Eq. (1.9), holds for  $n \geq 1$ ; for  $n=0$  the calculations are trivial, and the term for  $n=0$  in Eq. (1.5) reduces to  $\text{Tr}[\exp(-\beta H_0)]$ . We can thus confine ourselves to the case  $n \geq 1$ .

The trace of Eq. (1.9) is now formed using free particle wave functions  $(\Psi_q)$  which satisfy the wave equation  $H_0 \Psi_q = E_q \Psi_q$ . These wave functions must be correctly symmetrized (or antisymmetrized), according to whether we are dealing with a system which obeys Bose-Einstein or Fermi-Dirac statistics. If this symmetrization were not carried out, and a single product wave function were used, then we would merely have the case of Boltzmann statistics. However, all three cases are included in the following analysis; the difference arises only in the way certain matrix elements are calculated. Thus, forming the trace of Eq. (1.9),

$$\text{Tr}(D^n H^\nu)_{g=0} = (n-1)! \nu \sum_{(q_j)} \sum_{(\nu_k)} E_{q_1}^{\nu_1} E_{q_2}^{\nu_2} \dots \times E_{q_n}^{\nu_n} V_{q_1 q_2} \dots V_{q_n q_1}, \quad (1.10)$$

where in Eq. (1.10), the  $E_{q_i}$  are the free particle energy levels, and the summation  $\sum_{(q_j)}$  indicates that the summation is to be taken over all sets of the  $q_j$ . The  $V_{q_i q_j}$  are the matrix elements of the interaction potential  $V$ , and are given by

$$V_{q_i q_j} = \int \Psi_{q_i}^* V \Psi_{q_j} d\mathbf{r}_1 \dots d\mathbf{r}_n. \quad (1.11)$$

The integration in Eq. (1.11) is to be taken over all the coordinates (including a summation over any spin coordinates) of the particles in the system, the limits being determined by the boundaries of the enclosure. As the  $E_{q_i}$  are the same, whether the  $\Psi_{q_i}$  are symmetrized or not, the only difference due to the statistics arises from (a) the enumeration of states  $\Psi_{q_i}$  in forming the sum  $\sum_{(q_i)}$  and (b) in the form of the matrix elements, Eq. (1.11), according as the  $\Psi_{q_i}$  are symmetrized or antisymmetrized.

The sum over the sets  $(\nu_k)$  in Eq. (1.10) can be carried out by using a generating function. Equation (1.10) is written as

$$\text{Tr}[(D^n H^\nu)_{g=0}] = \nu(n-1)! \sum_{(q_j)} V_{q_1 q_2} \dots V_{q_n q_1} \times [\text{coeff. of } z^{\nu-n} \text{ in } \prod_{i=1}^n (1 - z E_{q_i})^{-1}]. \quad (1.12)$$

The required coefficient can easily be picked out, if a technique due to Dingle<sup>10</sup> is used. The generating function is broken up into partial fractions, thus:

$$\prod_{i=1}^n (1 - z E_{q_i})^{-1} = \sum_{j=1}^n A_j (1 - z E_{q_j})^{-1}. \quad (1.13)$$

It is assumed, for the moment, that the  $E_{q_j}$  are unequal;

<sup>10</sup> R. B. Dingle, Proc. Cambridge Phil. Soc. 45, 275 (1949).

then the  $A_j$  are given by

$$A_j = \prod_{i \neq j}^n E_{q_j}^{n-1} (E_{q_j} - E_{q_i})^{-1}. \quad (1.14)$$

Combining Eqs. (1.14) and (1.13),

$$\prod_{i=1}^n (1 - z E_{q_i})^{-1} = \sum_{j=1}^n \left[ \prod_{i \neq j}^n \frac{E_{q_j}^{n-1}}{(E_{q_j} - E_{q_i})} \right] (1 - z E_{q_j})^{-1}. \quad (1.15)$$

The coefficient of  $z^{\nu-n}$  in  $(1 - z E_{q_j})^{-1}$  is  $E_{q_j}^{\nu-n}$ , so finally,

$$\text{Tr}[(D^n H^\nu)_{g=0}] = \nu(n-1)! \sum_{(q_j)} V_{q_1 q_2} \cdots V_{q_n q_1}$$

$$\times \sum_{j=1}^n E_{q_j}^{\nu-1} \prod_{i \neq j}^n (E_{q_j} - E_{q_i})^{-1}. \quad (1.16)$$

The expansion of  $Z$  may now be written down, remembering that the term for  $n=0$  requires special treatment; thus,

$$Z = Z_0 + \sum_{n=1}^{\infty} g^n Z_n, \quad (1.17)$$

where in Eq. (1.17)  $Z_0$  is given by,

$$Z_0 = \sum_q \exp(-\beta E_q), \quad (1.18)$$

and  $Z_n$  is given by,

$$Z_n = -(\beta/n) \sum_{(q_j)} V_{q_1 q_2} \cdots V_{q_n q_1}$$

$$\times \sum_j [\exp(-\beta E_{q_j}) / \prod_{i \neq j}^n (E_{q_j} - E_{q_i})]. \quad (1.19)$$

Thus, Eq. (1.19) gives an explicit expression for the  $n$ th term in the expansion of  $Z$  in powers of  $g$ , and also in powers of the matrix elements of the interaction potential. In the above derivation, it might be thought that the summation over the sets  $(q_j)$  should be restricted to unequal values of the  $q_j$ , because of terms with  $(E_{q_j} - E_{q_i})$  in the denominator. Such a restriction is, however, unnecessary as it is easily shown that the numerators of these terms also vanish for  $E_{q_i} = E_{q_j}$ . By a careful passage to the limit ( $E_{q_i} \rightarrow E_{q_j}$ ) a finite result is obtained. This result is identical with that obtained by allowing some of the  $E_{q_j}$  in Eq. (1.13) to be equal.

### III. COMPARISON WITH PREVIOUS WORK

Goldberger and Adams, in their paper,<sup>5</sup> quote the following result, due to Schwinger. If  $a$  and  $b$  are any two operators, then

$$\begin{aligned} \text{Tr}[e^{-(a+b)}] &= \text{Tr}[e^{-a}] - \text{Tr}[b e^{-a}] \\ &+ \sum_{n=2}^{\infty} \frac{(-1)^n}{n} \int_0^1 s_1^{n-1} ds_1 \int_0^1 s_2^{n-2} ds_2 \cdots \int_0^1 ds_n \\ &\times \text{Tr}(b e^{-(1-s_1)a} e^{-s_1(1-s_2)a} \cdots b e^{-s_1 \cdots s_n a}). \quad (2.1) \end{aligned}$$

If we identify  $a$  with  $\beta H_0$  and  $b$  with  $\beta V g$ , then the left-hand side of Eq. (2.1) is merely the partition function of Sec. II. Formally, it is quite clear that this expansion is identical with that given above, both being expansions in powers of  $g$ . This can easily be verified by writing the general term in the series in Eq. (2.1) as

$$\begin{aligned} Z_n' &= \frac{(-\beta)^n g^n}{n} \int_0^1 s_1^{n-1} ds_1 \cdots \int_0^1 ds_n \\ &\times \text{Tr}(V e^{-(1-s_1)\beta H_0} \cdots V e^{-s_1 s_2 \cdots s_n \beta H_0}). \quad (2.2) \end{aligned}$$

The trace in Eq. (2.2) is now formed, using the same wave functions as before; thus,

$$\begin{aligned} Z_n' &= \frac{(-\beta)^n g^n}{n} \sum_{(q_j)} V_{q_1 q_2} \cdots V_{q_n q_1} \\ &\times \int_0^1 s_1^{n-1} \exp(-\beta s_1 E_{q_1}) ds_1 \cdots \\ &\times \int_0^1 ds_n \exp(-\beta s_1 s_2 \cdots s_n E_{q_n}). \quad (2.3) \end{aligned}$$

By direct integration it is easily shown that

$$Z_n' = -\frac{\beta g^n}{n} \sum_{(q_j)} V_{q_1 q_2} \cdots V_{q_n q_1} \sum_{j=1}^n \frac{\exp(-\beta E_{q_j})}{\prod_{i \neq j} (E_{q_j} - E_{q_i})}; \quad (2.4)$$

thus  $Z_n'$  and  $g^n Z_n$  are identical. In this form, Eq. (1.19), the general term is expressed in terms of known quantities,  $E_{q_j}$  and  $V_{q_i q_j}$ . This is a considerable advantage if we wish to estimate the order of magnitude of the terms in the series. In deriving the expansion, it was assumed initially that the Hamiltonian could be split into two parts  $H_0$  and  $gV$ , one of which ( $H_0$ ) had a very simple eigenvalue equation, the solutions of which were known. However it is obvious, from the method of derivation, that the expansion is valid for any partition of a general Hamiltonian, provided that the solutions of the eigenvalue equation of one of the parts are known, and these are used to form the trace in Eq. (1.5). Another formal method of generating the series is to substitute in the usual formula, Eq. (1.1), for the partition function, the perturbation expansion for the  $g$ th energy level, and then expand the resulting expression in powers of  $g$ . The procedure requires to be justified because of possible degeneracies in the energy levels. Our procedure avoids this.

It is of interest to compare the first-order term in the above series, with the same term in the series due to Goldberger and Adams<sup>5</sup> and Green.<sup>4</sup> In both these papers the series was generated by expanding the configurational distribution function, in a power series in the interaction potential, and then integrating term by term over all the coordinates. No account was taken of quantum statistics in either case. It was pointed out

by Goldberger and Adams that the first term in their series is identical with that given by Green. However, when the term is integrated over all the coordinates, the result is trivial, namely that

$$gZ_1 \propto Z_0. \tag{2.5}$$

This result follows at once from our expansion, for

$$gZ_1 = -\beta g \sum_q V_{qq} \exp(-\beta E_q), \tag{2.6}$$

and in the case of classical statistics  $V_{qq}$  is independent of  $q$ , and thus Eq. (2.6) at once reduces to Eq. (2.5). However, in the case of quantum statistics  $V_{qq}$  is not independent of  $q$ , and Eq. (2.6) is no longer trivial. In a later paper Green<sup>11</sup> has derived the general term in the form of an extremely complicated integral. This result is again limited to the case of classical (Boltzmann) statistics. It would seem, however, that if the series proves to be useful, it will be in the region of low temperatures, where the Kirkwood expansion is too slowly convergent to be of any use. In this region there is reason to believe that quantum statistics exert a marked influence on the properties of a system. Thus, the two isotopes of helium show markedly different properties at low temperatures. Likewise, De Boer's calculations<sup>6,7</sup> on the light isotope of helium again show up the importance of the statistics obeyed by the particles. Indeed, the discussion of the second term in the series, Eq. (2.6), completely confirms our statement.

It might seem, at first sight, that each term in the series is proportional to  $\beta$ . However, the general term  $Z_n$  consists of a sum of terms of the form  $R_{(q_k)}$ , where  $(q_k)$  is the set of all summation indices  $q_1 \cdots q_n$ . It is easily shown that if any term  $R_{(q_k)}$  has  $r$  of these indices equal then it is proportional to  $\beta^r$ . Consequently, each term  $Z_n$  contains "sub terms" proportional to all powers of  $\beta$  up to  $\beta^n$ . This is contrary to Green's suggestion<sup>4</sup> that each successive term would be proportional to  $\beta$ .

#### IV. THE VALIDITY OF THE EXPANSION

In this section, the existence of the individual terms ( $Z_n$ ) will be investigated first, and then the more difficult problem of the convergence of the series will be discussed.

In the deduction of the series, no account was taken of any singularities in the potential function  $V$ . In many cases, however,  $V$  will possess singularities, for instance, if it represents the interaction potential of a number of particles. This type of potential was assumed in Sec. II. The importance of such singularities is illustrated by considering the classical partition function. This is proportional to  $\int_S \exp(-\beta V) dQ$ , where  $S$  is the whole of configuration space, and  $Q$  stands for all the coordinates. If the exponential is expanded in powers of  $V$ , and  $V$  has any singularities, then there will be an  $n$  such that all integrals of the type

$\int_S (\beta V)^n dQ$  ( $n \geq n$ ) will diverge. Consequently, this expansion of the classical partition function is invalid. This state of affairs can easily be remedied, if the only kinds of singularity that  $V$  possesses are such that it becomes positively infinite. If this is assumed, then the range of integration ( $S$ ) can be split up into two parts  $S_1$  and  $S_2$ , such that  $S_1$  constitutes the region where  $V$  is bounded, and  $S_2$  consists of the remainder of configuration space. Then it is seen at once that the integral over the region  $S_2$  vanishes, because  $\exp(-\beta V)$  is identically zero in this region. The partition function is now proportional to  $\int_{S_1} \exp(-\beta V) dQ$  and as  $V$  is bounded in the set of points  $S_1$  all integrals of the type  $\int_{S_1} (\beta V)^n dQ$  will be finite. Thus, if we wish to expand the partition function in powers of  $V$ , the range of integration of each term must exclude the points at which  $V$  is singular.

It will now be shown that precisely the same conclusion holds in the case of the quantum-mechanical partition function. First, it is easily seen that similar divergent integrals will occur in the quantum-mechanical case. For the expansion of  $\exp(-\beta H)$  consists of a sum of terms of the form  $H_0^p V \cdots H_0^n V$ . Clearly, if any one of these operators is expanded, then there will always be one term of the type  $V^n H_0^{p-n}$ . When the trace of this term is formed, the integral that results will diverge for sufficiently large  $n$ . To avoid this difficulty, a similar method to that used above is employed. The following assumptions are first made about  $V$ : (a) if any pair of particles with position vectors  $\mathbf{r}_i$  and  $\mathbf{r}_j$  take up a configuration such that  $|\mathbf{r}_i - \mathbf{r}_j| \leq 2r_0$ , then  $V$  is to become positively infinite; (b) otherwise,  $V$  is to be continuous and bounded everywhere. The entire configuration space ( $S$ ) of the system is again divided into two parts,  $S_1$  which consists of  $S$  apart from the  $N(N-1)/2$  regions such that  $|\mathbf{r}_i - \mathbf{r}_j| \leq 2r_0$ , while  $S_2$  constitutes the remainder of  $S$ . These assumptions about the potential energy include all the types of interactions that are commonly met with in statistical mechanics. Thus, if  $V$  has no singularities  $r_0$  is zero and  $S_2$  is merely the null set. If  $V$  is singular at isolated points, then  $r_0$  is again zero, and to proceed with the analysis,  $r_0$  is replaced by  $\epsilon$ , which is set equal to zero at the end of the calculations. Finally, if there are regions in which  $V$  is singular, then  $r_0$  is finite. This would occur for the case in which the particles are supposed to have incompressible cores of radius  $r_0$ .

The partition function  $Z$  is given by

$$Z(\beta) = \int_S \sum_q \phi_q^*(Q) \phi_q(Q) \exp(-\beta E_q) dQ, \tag{4.1}$$

where in Eq. (4.1)  $\phi_q(Q)$  is the  $q$ th eigensolution of the eigenvalue equation  $H\phi_q = E_q\phi_q$ , and  $Q$  stands for the set of all coordinates. The  $\phi_q$  must, of course, be suitably symmetrized. Define  $I(Q)$  by the equation,

$$I(Q) = \sum_q \phi_q^*(Q) \phi_q(Q) \exp(-\beta E_q). \tag{4.2}$$

<sup>11</sup> H. S. Green, J. Chem. Phys. 20, 1274 (1952).

Then,  $I(Q)dQ$  is the probability that at a temperature  $T$  the coordinates  $(Q)$  of the system have values lying between  $Q$  and  $Q+dQ$ . This statement follows immediately from the definition that  $\phi_q^*(Q)\phi_q(Q)dQ$  is the probability that the coordinates of the system have values lying between  $Q$  and  $Q+dQ$ , when the system is in the state  $\phi_q(Q)$ . Now, it follows from a theorem due to Pauli<sup>12</sup> that  $\phi_q^*(Q)\phi_q(Q)\tau(Q)\rightarrow 0$  as we approach any of the singularities of  $V$ , where  $dQ$  has been written as  $\tau(Q)dr_1\cdots dr_N$ ,  $\tau(Q)$  being the weight factor for  $dQ$ . If this were not so, then the Hamiltonian of the system would no longer be Hermitian. Thus, in the set of points  $S_2$   $I(Q)dQ$  is identically zero. That this must be so is obvious in the case of particles with incompressible cores, for the wave functions must be made to vanish in the region of the core. However, this type of potential requires special consideration; we will, therefore, suppose, for the moment, that the potential is only singular at isolated points. The function  $I(Q)$  can be written in the form

$$I(Q) = \sum_q \phi_q^*(Q) \exp(-\beta H) \phi_q(Q). \quad (4.3)$$

The wave functions  $\phi_q$  are now expanded in terms of the complete orthonormal (suitably symmetrized) set of free particle wave functions  $\Psi_n(Q)$ , and it is easily shown that Eq. (4.3) becomes

$$I(Q) = \sum_n \Psi_n^*(Q) \exp(-\beta H) \Psi_n(Q). \quad (4.4)$$

When Eqs. (4.4) and (4.1) are combined, it is found that

$$Z(\beta) = \int_{S_1+S_2} I(Q)dQ = \int_{S_1} \sum_n \Psi_n^*(Q) \exp(-\beta H) \Psi_n(Q). \quad (4.5)$$

If  $\text{Tr}'(A)$  stands for the trace of  $A$ , with the restriction that all the integrals are to be taken *only* over the set  $S_1$ , then Eq. (4.5) becomes

$$Z(\beta) = \text{Tr}'(\exp -\beta H). \quad (4.6)$$

It is easily proved that the following results still hold:

$$\text{Tr}'(AB) = \text{Tr}'(BA), \quad (4.7)$$

and

$$\text{Tr}'(ABC\cdots H) = \sum_{(qk)} A'_{q_1q_2} B'_{q_2q_3} \cdots H'_{qnq_1}, \quad (4.8)$$

where in Eq. (4.8) the  $A'_{q_1q_2}$ , etc., are defined by equations of the type

$$A'_{q_1q_2} = \int_{S_1} \Psi_{q_1}^* A \Psi_{q_2} dQ. \quad (4.9)$$

We shall call matrix elements such as this "restricted matrix elements." If these results are used, then the whole of the previous analysis can be carried through again, the usual matrix elements  $V_{q_iq_j}$  being replaced at each step by the restricted matrix elements  $V'_{q_iq_j}$ . The zero-order term ( $Z_0$ ) requires special attention. For

when the trace of  $\exp(-\beta H_0)$  is formed, the normalization integral  $\int_{S_2} \Psi_n^* \Psi_n dQ$  has to be replaced by the integral  $\int_{S_1} \Psi_n^* \Psi_n dQ$ . This integral is, however, unity, because the set  $S_2$  is a set of zero measure and the integrand is bounded in  $S_2$ . We thus have

$$Z = Z_0 + \sum_{n=1}^{\infty} g^n Z_n', \quad (4.10)$$

where in Eq. (4.10),

$$Z_0 = \sum_q \exp(-\beta E_q) \quad (4.11)$$

and

$$Z_n' = -(\beta/n) \sum_{(qk)} V'_{q_1q_2} \cdots V'_{qnq_1} \times \sum_j [\exp(-\beta E_{q_j}) / \prod_{i \neq j} (E_{q_i} - E_{q_j})]. \quad (4.12)$$

In the case in which  $V$  is singular only at isolated points, the set  $S_1$  is defined by the parameter  $\epsilon$ . Thus each of the  $Z_n$  is a function of  $\epsilon$ . Clearly as  $\epsilon \rightarrow 0$  each of the  $Z_n' \rightarrow \infty$  for sufficiently large  $n$ , and no individual term in the series has any significance. In fact, it is only possible to pass to the limit after the series (or part of it at least) has been summed. Consequently, in this case, the series cannot be used term by term.

We next consider the terms in the expansion when the potential represents the interactions between particles that have incompressible cores. For this type of potential the transformation of  $I(Q)$  from Eq. (4.3) to Eq. (4.4) is no longer valid. If we write  $\phi_q(Q) = \sum_n a_{nq} \Psi_n$ , then the transformation can only be carried out if  $\sum_q a_{nq} a_{n'q}^* = \delta_{n, n'}$ , that is, if

$$\sum_q \int_{S_1} \int_{S_1} \phi_q \phi_q^* \Psi_n(Q') \Psi_{n'}^*(Q) dQ dQ' = \delta_{n, n'}. \quad (4.13)$$

Now  $\sum_q \phi_q(Q) \phi_q^*(Q') = \delta(Q - Q')$  in  $S_1$ , and since the wave functions  $\phi_q(Q)$  vanish identically in the set  $S_2$ ,  $\sum_q \phi_q(Q) \phi_q^*(Q') = 0$  in  $S_2$ . Consequently, we must have

$$\begin{aligned} \delta_{n, n'} &= \int_{S_1} \int_{S_1} \delta(Q - Q') \Psi_n(Q') \Psi_{n'}^*(Q) dQ dQ' \\ &= \int_{S_1} \Psi_n(Q) \Psi_{n'}^*(Q) dQ. \end{aligned} \quad (4.14)$$

This last relation is obviously not true because the  $\Psi_n$  are orthonormal over the whole of the configuration space,  $S_1$  and  $S_2$ . This difficulty can, however, be overcome, if the  $\phi_q$  are expanded in terms of the complete orthonormal set  $\chi_n(Q)$ , where the  $\chi$  are the solutions of the wave equation for a system of  $N$  perfectly elastic spheres of radius  $r_0$ . These wave functions vanish identically in the set  $S_2$ , and obey the normalization condition that

$$\delta_{n, n'} = \int_{S_1} \chi_n(Q) \chi_{n'}^*(Q) dQ. \quad (4.15)$$

<sup>12</sup> W. Pauli, *Handbuch der Physik* (Springer, Berlin, 1933), second edition, Vol. 24, pp. 123-24.

With these wave functions instead of the  $\Psi_n$ , the transformation from Eq. (4.3) to Eq. (4.4) is obviously valid. Moreover, these wave functions satisfy the free particle wave equation  $H_0\chi_n(Q) = E_n\chi_n(Q)$ , in the set  $S_1$ . This means that the whole of the analysis of Sec. II is valid provided we replace the free particle wave functions  $\Psi_n(Q)$  by the wave functions  $\chi_n(Q)$ . Thus, the expansion given by Eq. (1.17) is formally correct, if  $V_{q_iq_j}$  is redefined by the equation:

$$V_{q_iq_j} = \int_{S_1} \chi_{q_i}^*(Q) V \chi_{q_j}(Q) dQ. \quad (4.16)$$

We must also take into account the fact the summations over the indices ( $q_j$ ) are over all distinct accessible states. Now, the number of these states  $G_{q_j}$  that are associated with any energy level  $E_{q_j}$  will be different, according to whether we are dealing with free particle wave functions or elastic sphere wave functions. Consequently, even though the first term  $Z_0$  appears to be identical in these two cases, it is, in fact, entirely different. It is clear from Eq. (4.16) that the  $V_{q_iq_j}$  are finite.

It should be mentioned that the methods of Goldberger and Adams, and of Siegert, both require to be modified for this type of potential. Consider, for instance, the method of Goldberger and Adams. When the trace is formed in Eq. (2.2), it is not permissible to use free particle wave functions for the same reason as we have given above. The simplest suitable set is the set of elastic sphere wave functions  $\chi_n(Q)$ . When these wave functions are used, the series again becomes identical with that given in this paper. A similar consideration applies to the integral equation derived by Siegert.

It still remains to discuss the convergence of the sum in Eq. (4.12). Write

$$Z_n = -(\beta^n/n) \sum_{(q_k)} V_{q_1q_2} \cdots V_{q_nq_1} F_{(q_k)}, \quad (4.17)$$

where, if Eq. (2.3) is used,

$$F_{(q_k)} = \int_0^1 s_1^{n-1} ds_1 \int_0^1 s_2^{n-2} ds_2 \cdots \int_0^1 ds_n \times \exp[-\beta(s_1 E_{q_1} + s_2(1-s_1)E_{q_2} \cdots s_1 \cdots s_n E_{q_n})]. \quad (4.18)$$

From this equation it is seen that  $F_{(q_k)} > 0$  for all ( $q_k$ ) and  $\beta$ , and is moreover monotonically decreasing in all the summation indices  $q_k$ . If any one term in the multiple sum in Eq. (4.17) is considered, then it is easily shown that  $F_{(q_k)} \leq \exp[-\beta(E_{q_k})_m]$  where  $(E_{q_k})_m$  is the smallest value that  $E_{q_k}$  takes on for this particular term. If it is now assumed that the following multiple series  $S_n$ , where  $S_n$  is given by

$$S_n = -\beta^n \sum_{q_1} \left[ \sum'_{(q_k) \geq q_1} V_{q_1q_2} \cdots V_{q_nq_1} \right] \exp(-\beta E_{q_1}), \quad (4.19)$$

converges, then it follows that the multiple series in Eq. (4.17) also converges. This is essentially because the  $F_{(q_k)}$  are monotonic in all their indices  $q_k$  and are

bounded by  $\exp(-\beta(E_{q_k})_m)$  as  $q_k \rightarrow \infty$ . The symbol  $\sum'_{(q_k) \geq q_1}$ , in Eq. (4.18), means that the sum is to be over all sets of indices ( $q_k$ ), omitting always the index  $q_1$ , and that the values of the other  $q_k$  are to be such that  $q_k \geq q_1$ . This seems to be as far as one can go rigorously. However, the unrestricted sum  $\sum_{(q_k)} V_{q_1q_2} \cdots V_{q_nq_1}$  converges because the integral for  $V_{q_1q_1}$  converges—this follows from the assumptions that were made about the potential  $V$ . This makes it very reasonable to suppose that the restricted sum converges as well, particularly as the unrestricted sum always converges, no matter in what order the summations are performed. Because of the factor  $\exp(-\beta E_{q_1})$  the summation over the index  $q_1$  will converge, provided the restricted sum is of order less than  $\exp(-\beta E_{q_1})$ .

The much more difficult question of the convergence of the series as a whole has still to be discussed. The classical analog of the series, Eq. (4.10), converges for all finite value of  $g$ —always granted the assumptions we have made about  $V$ . Unfortunately, it does not seem possible to establish a similar result in the quantum-mechanical case. However, the following remarks seem to be worth noting. Firstly, the convergence of the perturbation expansion in powers of  $g$  for the energy levels  $\mathcal{E}_q$  does not guarantee the convergence of our series. Conversely, the convergence of our series does not guarantee the convergence of the perturbation expansion of any energy level  $\mathcal{E}_q$ . This is because in each case it is necessary to rearrange a double sum. Finally, it is quite easily shown that the series will be absolutely convergent for all finite  $g$ , if the series  $\sum'_{(q_k)} V_{q_1q_2} \cdots V_{q_nq_1}$  is absolutely convergent for all  $q_1$ . This appears to be so restrictive on the potential  $V$  that it is unlikely to be very useful.

The following conclusions can be drawn from the preceding analysis. Firstly, if the interaction potential has no singularities (of the type discussed), then the original series [Eq. (1.17)] is valid. The existence of the individual terms being almost certainly guaranteed by the convergence of the integral for  $V_{q_1q_2}$ . Secondly, if the potential has regions in which it is positively infinite, then the original series must be modified and must be replaced by the series given by Eq. (1.17) and (4.16). In this case the existence of the individual terms again depends on the convergence of  $V_{q_1q_2}$ . If the potential is, however, singular at isolated points, then eventually the terms in the series become infinite, and the expansion is invalid. Finally, even in the cases in which the individual terms exist, we are unable to deduce any really useful criterion for the convergence of the series.

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