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Diffraction of Neutrons by Imperfect Gases*

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The theory of cluster expansions is studied by a new method. A general procedure for obtaining the thermal average of a many-body function as a series in powers of density is derived. A recipe based on the Baker-Hausdorff theorem for reducing quantum thermal averages to their classical analogs is also described. These results are used to express the slow neutron cross sections of imperfect gases as power series in molecular density. Formulas are given for the leading contributions to both elastic and inelastic scattering.

1. INTRODUCTION

THE scattering of slow neutrons by nuclei subject to chemical forces in atomic and molecular systems can be used as a tool to study these forces. This technique is being developed as a new and welcome supplement to such well established methods as x-ray and electron diffraction. Considerable work has been done on neutron diffraction by crystals and within the past few years, the use of neutrons in the study of gases and liquids has been initiated.[1]

Methods have recently been developed[2] for the treatment of inelastic as well as elastic scattering of neutrons by gaseous systems. Since the effects of intermolecular interactions were considered quite crudely, and only in connection with the "outer effect," the results are strictly valid only in the limit of vanishing density. When scattering experiments are performed at gas densities at which the departure from ideality is manifested in other properties, corrections to the formulas previously given may be required. From the investigation of such imperfect gas corrections, one may hope to elicit information on the potentials which act between gas particles and on other aspects of the behavior of dense gases.

In the present work, we extend the methods of reference 2 to obtain the neutron cross section in a power series in the gas density, the leading term of which is the ideal gas result. For this purpose, a method is presented in the next section which both unifies and generalizes procedures previously used for deriving density expansions in simpler contexts. We shall confine our treatment to gases whose behavior approximates that of a classical ensemble of particles (a slight restriction in practice). A concise technique for obtaining classical limits of averages over systems in thermal equilibrium and quantum corrections to them is also explained in Sec. 2.

We discuss first some aspects of the scattering formalism. The excitations of a target system bombarded by a slow-neutron beam remain, as a rule, unobserved. We recall the optical theorem which relates a total cross section, summed over all scattering processes, to a coherent scattering amplitude, i.e., to an amplitude for the process which leaves the dynamical system as a whole unaltered. An analogous result is achieved in the present case where a summation is performed over the final states of the scattering medium only. In the time-dependent formulation of the diffraction problem, the relation takes the form[3]

$$\sigma(\theta)=(2\pi)^{-1}\sum_{\nu,\nu'}(A_\nu A_{\nu'}+\delta_{\nu\nu'}C_\nu^2)\times\int\int(k/k_0)e^{-i\epsilon t}\langle\chi_{\nu\nu'}\rangle dt d\epsilon, \quad (1.1)$$

$$\langle\chi_{\nu\nu'}\rangle=\langle\psi|e^{iHt}\exp(i\boldsymbol{\kappa}\cdot\mathbf{r}_\nu)e^{-iHt}\exp(-i\boldsymbol{\kappa}\cdot\mathbf{r}_{\nu'})|\psi\rangle, \quad (1.2)$$

for the differential cross section when the initial state of the scatterer is ψ.

Thus the cross section, originally computed within the formalism of the first Born approximation, may be reinterpreted in terms of a twofold collision of the neutron and the scatterer following which the scatterer returns to its initial state. Specifically, if the expression for $\langle\chi_{\nu\nu'}\rangle$ is read from right to left, we find that the scatterer, initially in state ψ, loses momentum $\boldsymbol{\kappa}$ in a collision of the neutron with nucleus ν', propagates through a time interval t, and regains the momentum $\boldsymbol{\kappa}$ in a collision involving nucleus ν. The cross section depends upon the overlap of the latter state with the state $e^{-iHt}\psi$ resulting from an uninterrupted temporal development of ψ in the course of the "collision time" t. The final states of the true scattering processes appear as intermediate states in the double scattering picture. The presence of the phase factor $e^{-i\epsilon t}$ insures that in the integration over collision times, contributions from intermediate states which disobey the conservation condition

$$\epsilon=E_i-E_f$$

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[1] G. E. Bacon, *Neutron Diffraction* (Clarendon Press, Oxford, 1955).

[2] A. C. Zemach and R. J. Glauber, Phys. Rev. **101**, 118, 129 (1956), hereafter called ZG.

[3] The reader is referred to ZG for definitions and notation. Boltzmann's constant and $\hbar$ have unit magnitude in the system of units adopted.

interfere destructively. Equation (1.1) leads to compact and powerful methods for the calculation of cross sections; in addition, the accompanying physical interpretation is of great utility in appreciating the qualitative features of the scattering.

The approximation method[2,4] based on an expansion of all or part of the expectation values (1.2) in ascending powers of t is of particular importance both because of its wide domain of validity and the comparative simplicity of the ensuing computations. The procedure is applicable when the variation in time of the expanded quantities is slow compared to the rate of oscillation of $e^{-i\epsilon t}$. We shall employ it in treating the imperfect gas problem. Work extending these calculations to denser systems such as liquids is planned.

2. CLUSTER EXPANSIONS AND THERMAL AVERAGES

We present a theory of cluster expansions which unifies and extends the formalism originated by Ursell and Mayer[5] and which provides a foundation for our later calculations.

The central problem concerns the average of a many-particle operator Q,

$$\langle\psi|Q|\psi\rangle = \int \psi^*(\mathbf{r}_1,\mathbf{r}_2,\cdots,\mathbf{r}_N)Q\psi(\mathbf{r}_1,\cdots,\mathbf{r}_N)d\mathbf{r}_1\cdots d\mathbf{r}_N, \tag{2.1}$$

in some state or thermal ensemble of states of a gaseous system. The integrand above is a separable function; i.e., when the particles divide into isolated clusters,[6] the function itself separates into factors, each a function of the coordinates of particles in one cluster. Corrections to the ideal gas limit of (2.1) which account for interparticle collisions make up a series in powers of molecular density. Series of this type are closely related to the cluster expansions of separable functions.

A situation of complete symmetry will be examined first. For brevity, we designate a set of particle coordinates $\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_N$ by $\mathbf{r}^N$ and $d\mathbf{r}_1 d\mathbf{r}_2\cdots d\mathbf{r}_N$ by $d\mathbf{r}^N$. For each integer N, let $W_N(\mathbf{r}^N)$ specify a symmetric coordinate function which is separable in the sense that if $\mathbf{r}^N$ divides into isolated clusters $\mathbf{r}'^n$ and $\mathbf{r}''^m$, $n+m=N$, then

$$W_N(\mathbf{r}^N) \to W_n(\mathbf{r}'^n)W_m(\mathbf{r}''^m). \tag{2.2}$$

We introduce a parametric function $a(\boldsymbol{\varrho})$ of a single position coordinate and write $a^{(n)}$ in abbreviation of the product $a(\boldsymbol{\varrho}_1)a(\boldsymbol{\varrho}_2)\cdots a(\boldsymbol{\varrho}_n)$. A generator $G_W(a)$ for the W functions is then defined by

$$G_W(a) = \sum_{n=0}^{\infty} \frac{1}{n!}\int a^{(n)}W_n(\boldsymbol{\varrho}^n)d\boldsymbol{\varrho}^n. \tag{2.3}$$

In this equation, W_0 is taken to be unity. Employing the technique of functional differentiation with respect to the parametric function, as expressed by

$$\frac{\delta}{\delta a(\mathbf{r})}a(\boldsymbol{\varrho}) = \delta(\mathbf{r}-\boldsymbol{\varrho}),$$

$$\frac{\delta}{\delta a(\mathbf{r})}\int a(\boldsymbol{\varrho})W(\boldsymbol{\varrho})d\boldsymbol{\varrho} = W(\mathbf{r}), \text{ etc.,}$$

we recover each W_N from the generator by the recipe:

$$W_N(\mathbf{r}^N) = \frac{\delta}{\delta a(\mathbf{r}_1)}\cdots\frac{\delta}{\delta a(\mathbf{r}_N)}G_W(a)\bigg|_{a=0}. \tag{2.4}$$

A many-particle function which vanishes when its arguments separate into isolated clusters will be termed a cluster function. The expansion of W_N in terms of cluster functions will now be derived. Let us define, as in (2.3), a generator $G_U(a)$ for a set of functions $U_N(\mathbf{r}^N)$ and consider the relation

$$G_W(a) = e^{G_U(a)}, \tag{2.5}$$

which serves as a definition of the U functions in terms of the W functions. The fundamental property of Eq. (2.5) is that each U_N so defined is a cluster function if and only if each W_N is separable. A proof of this theorem is given in the Appendix. Applying (2.4) to (2.5), we infer that

$$W_N(\mathbf{r}^N) = U_N(\mathbf{r}^N) + \textstyle\sum_N U_{N-1}U_1 + \cdots + U_1(\mathbf{r}_1)U_1(\mathbf{r}_2)\cdots U_1(\mathbf{r}_N). \tag{2.6}$$

The general term of (2.6) is

$$\textstyle\sum_N U_{N_1}U_{N_2}\cdots U_{N_n}, \quad \sum N_i = N,$$

where the symbol $\sum_N$ indicates summation over all ways of allotting N arguments to the functions which follow. For example,

$$\textstyle\sum_3 U_2U_1 = U_2(\mathbf{r}_1,\mathbf{r}_2)U_1(\mathbf{r}_3) + U_2(\mathbf{r}_1,\mathbf{r}_3)U_1(\mathbf{r}_2) + U_2(\mathbf{r}_2,\mathbf{r}_3)U_1(\mathbf{r}_1).$$

Solving (2.6) for the U functions, one obtains

$$\begin{aligned} &U_0 = 0, \quad U_1(\mathbf{r}_1) = W_1(\mathbf{r}_1),\\ &U_2(\mathbf{r}_1,\mathbf{r}_2) = W_2(\mathbf{r}_1,\mathbf{r}_2) - W_1(\mathbf{r}_1)W_1(\mathbf{r}_2),\\ &U_3(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3) = W_3(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3) - \textstyle\sum_3 W_2W_1\\ &\qquad + 2W_1(\mathbf{r}_1)W_1(\mathbf{r}_2)W_1(\mathbf{r}_3), \text{ etc.} \end{aligned} \tag{2.7}$$

We suppose hereafter that the cluster functions of interest depend on coordinate differences only. When n is sufficiently small, a connected n-particle cluster will occupy a negligible fraction of the volume V which

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[4] G. C. Wick, Phys. Rev. 94, 1228 (1954).

[5] See, for example, Hirschfelder, Curtiss, and Bird, *Molecular Theory of Gases and Liquids* (John Wiley and Sons, Inc., New York, 1955). Also, J. deBoer, dissertation, Amsterdam, 1940 (unpublished), where the expansion of thermal averages is obtained for the completely symmetrical case.

[6] That is, clusters whose physical separation exceeds the range of molecular forces.

encloses the gas particles. In this case, the cluster integral $\int U_N(\mathbf{r}^N)d\mathbf{r}^N$ is proportional to V. For if the integrations over $\mathbf{r}^{N-1}$ are carried out with $\mathbf{r}_N$ fixed, the effective limits of integration are set by the range of molecular forces rather than the size of the enclosure. Then the result must be independent of both V and $\mathbf{r}_N$, and the final integration over $\mathbf{r}_N$ supplies a factor of V.

We now consider separable functions $W_{M,N}(\mathbf{r}^M,\mathbf{s}^N)$ which are symmetric functions of the groups $\mathbf{r}^M$ and $\mathbf{s}^N$ separately. A second parametric function $b(\boldsymbol{\sigma})$ is required for the definition of the generator:

$$G_W(a,b)=\sum\frac{1}{m!}\frac{1}{n!}\int a^{(m)}b^{(n)}W_{m,n}(\boldsymbol{\varrho}^m,\boldsymbol{\sigma}^n)d\boldsymbol{\varrho}^m d\boldsymbol{\sigma}^n,$$

where $W_{0,0}=1$. It follows that

$$W_{M,N}(\mathbf{r}^M,\mathbf{s}^N)=\frac{\delta}{\delta a(\mathbf{r}_1)}\cdots\frac{\delta}{\delta b(\mathbf{s}_N)}G_W(a,b)\bigg|_{a=b=0}.$$

With a similar definition for the generator $G_U(a,b)$ of the cluster functions, we have

$$G_W(a,b)=e^{G_U(a,b)}. \tag{2.8}$$

The derivation of $U_{M,N}(\mathbf{r}^M,\mathbf{s}^N)$ in terms of the W functions closely resembles the method of the previous case.

The relations between the integrals of the functions at hand are also of interest. If we define

$$\begin{aligned} w_{M,N}&=\frac{1}{M!}\frac{1}{N!}\int W_{M,N}(\mathbf{r}^M,\mathbf{s}^N)d\mathbf{r}^M d\mathbf{s}^N,\\ u_{M,N}&=\frac{1}{M!}\frac{1}{N!}\int U_{M,N}(\mathbf{r}^M,\mathbf{s}^N)d\mathbf{r}^M d\mathbf{s}^N, \end{aligned} \tag{2.9}$$

and replace $a(\boldsymbol{\varrho})$ and $b(\boldsymbol{\sigma})$ by the constants a and b, respectively, then (2.8) becomes

$$\sum a^m b^n w_{m,n}=\exp(\sum a^m b^n u_{m,n}). \tag{2.10}$$

The extension to situations of still lower symmetry is obvious.

As an application of the foregoing work, we determine the density expansion for the thermal average $\langle Q(\mathbf{r})\rangle_T$ of an operator function $Q(\mathbf{r})$. The operator may depend, in general, on all molecular coordinates of the N particle assembly; the notation indicates, however, a lack of symmetry between $\mathbf{r}$ and the remaining coordinates.

We define $W_{0,N}$ as the Slater sum over a complete set of molecular states ψ_i[7]:

$$W_{0,N}(\mathbf{s}^N)=\left(\frac{2\pi}{MT}\right)^{3N/2}\sum_i\psi_i^*(\mathbf{s}^N)\times\exp[-H(\mathbf{s}^N)/T]\psi_i(\mathbf{s}^N), \tag{2.11}$$

and $W_{1,N-1}$ as the generalized Slater sum:

$$W_{1,N-1}(\mathbf{r},\mathbf{s}^{N-1})=\left(\frac{2\pi}{MT}\right)^{3N/2}\sum_i\psi_i^*(\mathbf{r},\mathbf{s}^{N-1})Q(\mathbf{r})\times\exp[-H(\mathbf{r},\mathbf{s}^{N-1})/T]\psi_i(\mathbf{r},\mathbf{s}^{N-1}). \tag{2.12}$$

Functions $W_{M,N}$ with $M\geqslant 2$ remain undefined, but no definitions are needed. The relations implicit in (2.8) and (2.10) are still of value; one simply ignores all terms containing a power of a higher than the first. Utilizing the definitions above, we find that

$$\langle Q(\mathbf{r})\rangle_T=(1/N)(w_{1,N-1}/w_{0,N}). \tag{2.13}$$

Equating coefficients of a in (2.10), we obtain

$$\begin{aligned} \sum b^n w_{1,n}&=\sum b^n u_{1,n}\exp(\sum b^k u_{0,k})\\ &=\sum b^n u_{1,n}\sum b^k w_{0,k}, \end{aligned}$$

whence

$$w_{1,N-1}=\sum_{n=0}^{N-1}u_{1,n}w_{0,N-1-n}. \tag{2.14}$$

We introduce the quantities D_n,

$$D_n=(1/V)u_{1,n}, \tag{2.15}$$

which, for small n, are essentially volume independent. The partition sums $w_{0,n}$ are connected with the fugacity z of the gas by[5]

$$w_{0,N-n}=z^n w_{0,N}. \tag{2.16}$$

The substitution of (2.14) into (2.13) yields, in virtue of (2.15) and (2.16),

$$\langle Q(\mathbf{r})\rangle_T=(V/N)\sum_{n=0}^{N-1}D_n z^{n+1}. \tag{2.17}$$

Finally, we take advantage of the equation

$$z=(N/V)\exp\left[-\sum_{n=1}^{\infty}\beta_n(N/V)^n\right], \tag{2.18}$$

which expresses the fugacity in terms of the molecular density and the irreducible cluster integrals β_n. The latter are derivable from the molecular potential. With the help of (2.18), we conclude that

$$\langle Q(\mathbf{r})\rangle_T=D_0+(N/V)(D_1-\beta_1 D_0)+(N/V)^2[D_2-2\beta_1 D_1-(\beta_2-\tfrac{1}{2}\beta_1^2)D_0]+\cdots, \tag{2.19}$$

which is the desired density series.

In terms of the molecular potential $V(\mathbf{r}_i-\mathbf{r}_j)$, the classical expressions for the first two irreducible cluster integrals are

$$\beta_1=\int f(\mathbf{r})d\mathbf{r}, \tag{2.20}$$

$$\beta_2=\tfrac{1}{2}\int f(\mathbf{r})f(\mathbf{r}-\mathbf{s})f(\mathbf{s})d\mathbf{r}d\mathbf{s}, \tag{2.21}$$

where $f(\mathbf{r})=e^{-V(\mathbf{r})/T}-1$.

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[7] We omit consideration of quantum statistics in this paper. The Slater sums require an additional factor of $N!$ if the wave functions represent Bose or Fermi systems.

For later use, we compute the thermal average $\langle Q(\mathbf{r},\mathbf{r}')\rangle_T$ where no symmetry is assumed between $\mathbf{r}$ and $\mathbf{r}'$ or between these coordinates and the others. We define $W_{0,0,N}$ by the expression (2.11), and $W_{1,1,N-2}$ by

$$W_{1,1,N-2}=\left(\frac{2\pi}{MT}\right)^{3N/2}\sum\nolimits_i\psi_i^*(\mathbf{r},\mathbf{r}',\mathbf{s}^{N-2})Q(\mathbf{r},\mathbf{r}')$$
$$\times\exp[-H(\mathbf{r},\mathbf{r}',\mathbf{s}^{N-2})/T]\psi_i(\mathbf{r},\mathbf{r}',\mathbf{s}^{N-2}).$$

Additional functions $W_{0,1,N-1}$ and $W_{1,0,N-1}$ are inferred from the assumed separability of $W_{1,1,N-1}$. The cluster expansion of $W_{1,1,N-2}$ is obtained using generators which depend on three parametric functions, and integrals $w_{1,1,N-2}$, etc. are defined in analogy to (2.9). The equation corresponding to (2.10) is

$$\sum a^mb^nc^kw_{m,n,k}=\exp(\sum a^mb^nc^ku_{m,n,k}),\qquad(2.22)$$

so that

$$w_{1,1,N-2}=\sum_{n=0}^{N-2}\left[u_{1,1,n}+\sum_{m=0}^{n}u_{1,0,m}u_{0,1,n-m}\right]w_{0,0,N-2-n}.$$

With the definitions

$$I_n=(1/V)u_{1,1,n},$$
$$I_n^{(1)}=(1/V)u_{1,0,n},\quad I_n^{(2)}=(1/V)u_{0,1,n},$$

we get

$$\langle Q(\mathbf{r},\mathbf{r}')\rangle_T$$
$$=[N(N-1)]^{-1}w_{1,1,N-2}/w_{0,0,N}$$
$$=V[N(N-1)]^{-1}\sum_{n=0}^{N-2}(I_n+V\sum_{m=0}^{n}I_m^{(1)}I_{n-m}^{(2)})z^{n+2},$$

therefore,

$$\langle Q(\mathbf{r},\mathbf{r}')\rangle_T=(1/V)I_0+(N/V^2)(I_1-2\beta_1I_0)+\cdots$$
$$+I_0^{(1)}I_0^{(2)}+(N/V)[I_0^{(1)}I_1^{(2)}$$
$$+I_1^{(1)}I_0^{(2)}-2\beta_1I_0^{(1)}I_0^{(2)}]+\cdots.\qquad(2.23)$$

To arrive at (2.23) from the preceding line, we have equated $N/(N-1)$ to unity.

The generator equations and the process of functional differentiation were of value in proving the cluster property of the U functions. We observe, however, that for the calculation of terms in the density series, the simpler relations among integrals, as expressed by (2.10) and (2.22), are sufficient.

At high temperatures, the thermal averages and Slater sums approximate their classical analogs. In concluding this section, we show how the Baker-Hausdorff theorem may be used to effect the passage to the classical limit in an elementary way. The quoted theorem is an operator identity which states that if

$$e^Ae^B=e^C,\qquad(2.24)$$

then C is given by a series,

$$C=A+B+\tfrac{1}{2}[A,B]+\tfrac{1}{12}[A-B,[A,B]]$$
$$-(1/24)[B,[A,[A,B]]]+\cdots,\qquad(2.25)$$

whose higher terms are successive commutators of A and B. The terms given here may be verified by substitution into (2.24).

To illustrate the principle, we examine a two-particle system with the Hamiltonian

$$H=(p_1^2+p_2^2)/2M+V(\mathbf{r}_1-\mathbf{r}_2).\qquad(2.26)$$

The corresponding classical Hamiltonian H_c is formed by replacing the operator momenta in (2.26) by c numbers $\mathbf{q}_1$ and $\mathbf{q}_2$. Let $Z(\mathbf{r}_1,\mathbf{r}_2)$ denote the generalized Slater sum[7] over a complete set of states,

$$Z(\mathbf{r}_1,\mathbf{r}_2)=\left(\frac{2\pi}{MT}\right)^3\sum\nolimits_i\psi_i(\mathbf{r}_1,\mathbf{r}_2)$$
$$\times Q(\mathbf{r}_1,\mathbf{r}_2,\mathbf{p}_1,\mathbf{p}_2)e^{-H/T}\psi_i(\mathbf{r}_1,\mathbf{r}_2),\qquad(2.27)$$

whose integral, properly normalized, represents the thermal average of the operator Q. If a suitable classical analog $Q_c(\mathbf{r}_1,\mathbf{r}_2,\mathbf{q}_1,\mathbf{q}_2)$ of Q can be defined, we expect (2.27) to reduce, at high temperatures, to $Z_c(\mathbf{r}_1,\mathbf{r}_2)$ where

$$Z_c(\mathbf{r}_1,\mathbf{r}_2)=(2\pi MT)^{-3}\int Q_c(\mathbf{r}_1,\mathbf{r}_2,\mathbf{q}_1,\mathbf{q}_2)e^{-H_c/T}d\mathbf{q}_1d\mathbf{q}_2.$$

Since the complete set of states ψ_i is arbitrary, we choose plane waves,

$$\psi_{q1,q2}(\mathbf{r}_1,\mathbf{r}_2)=V^{-1}\exp(i\mathbf{q}_1\cdot\mathbf{r}_1+i\mathbf{q}_2\cdot\mathbf{r}_2),$$

and replace the summation in (2.27) by $V^2(2\pi)^{-6}\int d\mathbf{q}_1d\mathbf{q}_2$ in the usual way. In virtue of the translation property,

$$e^{-i(\mathbf{q}_i\cdot\mathbf{r}_i)}\mathbf{p}_ie^{i(\mathbf{q}_i\cdot\mathbf{r}_i)}=\mathbf{p}_i+\mathbf{q}_i,\quad i=1,\,2.$$

Equation (2.27) assumes the form

$$Z(\mathbf{r}_1,\mathbf{r}_2)=(2\pi MT)^{-3}$$
$$\times\int Q(\mathbf{r}_1,\,\mathbf{r}_2,\,\mathbf{p}_1+\mathbf{q}_1,\,\mathbf{p}_2+\mathbf{q}_2)e^Bd\mathbf{q}_1d\mathbf{q}_2,\qquad(2.28)$$

where

$$B=-(p_1+q_1)^2/2MT-(p_2+q_2^2)/2MT-V/T.$$

The operator momenta appearing as arguments of Q in (2.28) are now to be commuted to the extreme left where they disappear, leaving a function $Q_c(\mathbf{r}_1,\mathbf{r}_2,\mathbf{q}_1,\mathbf{q}_2)$. The occurrences of $\mathbf{p}_1$ and $\mathbf{p}_2$ in the exponential are to be commuted to the extreme right with the aid of (2.24). Thus if we set $A=H_c/T$, then[8]

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[8] The expansion (2.30) has been obtained by other methods by J. G. Kirkwood, Phys. Rev. 44, 31 (1933); see also J. E. Mayer and W. Band, J. Chem. Phys. 15, 141 (1947).

$$e^B=e^{-H_c/T}\exp\left[\frac{-\nabla^2V}{2MT^2}+\frac{(\nabla V)^2}{3MT^3}-\frac{i(\mathbf{q}_1-\mathbf{q}_2)\cdot\boldsymbol{\nabla}V}{2MT^2}\right.$$
$$\left.+\frac{[(\mathbf{q}_1-\mathbf{q}_2)\cdot\nabla]^2V}{6M^2T^3}+\cdots\right] \tag{2.29}$$

$$=e^{-H_c/T}\left[1-\frac{\nabla^2V}{2MT^2}+\frac{(\boldsymbol{\nabla}V)^2}{3MT^3}\right.$$
$$-\frac{i(\mathbf{q}_1-\mathbf{q}_2)\cdot\boldsymbol{\nabla}V}{2MT^2}+\frac{[(\mathbf{q}_1-\mathbf{q}_2)\cdot\boldsymbol{\nabla}]^2V}{6M^2T^3}$$
$$\left.-\frac{[(\mathbf{q}_1-\mathbf{q}_2)\cdot\boldsymbol{\nabla}V]^2}{8M^2T^4}+\cdots\right]. \tag{2.30}$$

The gradients are with respect to $\mathbf{r}_1$.

In the calculation of the bracketed series in (2.29) via (2.25), each additional commutation supplies another gradient applied to V. Thus, e^B is equal to $\exp(-H_c/T)$ multiplied by a series of powers of the gradient. Each gradient carries with it a factor of $\hbar$, although this is not explicit in our notation. Then the series proceeds in powers of $\hbar$. The use of (2.30) in (2.28) yields the classical limit with quantum corrections. Since, however, Q_c may itself contain a dependence on $\hbar$, the so-called quantum corrections are not always smaller than all contributions from the leading term, even in the limit of large T. (Compare the treatment of interference scattering in Sec. 4 where these corrections cancel against other terms.) The effects of quantum statistics may also be computed by this formalism without difficulty.

3. ELASTIC SCATTERING

In the absence of extensive experimental information on neutron scattering by imperfect gases, we shall be content to mark out the general features of the problem rather than essay an exhaustive treatment of different examples. For this purpose, we neglect the role of internal degrees of freedom which formed the principal concern of ZG. A temperature sufficiently high to permit an approximately classical evaluation of thermal averages (including lowest order quantum corrections) will be assumed.

The initial term arising from the time expansion procedure is treated in the present section. This forms the static approximation which is valid when the scattering is predominantly elastic. The direct scattering is then found to be independent of molecular coordinates. Accordingly, imperfect gas corrections to elastic scattering must be sought in the interference terms.

Let $\sigma_{1,2}(\theta)$ represent one of the two terms of the elastic cross section due to interference between molecules (1) and (2):

$$\sigma_{1,2}(\theta)=A^2\langle\chi_{1,2}\rangle_T=A^2\langle\exp[i\boldsymbol{\kappa}\cdot(\mathbf{r}_1-\mathbf{r}_2)]\rangle_T, \tag{3.1}$$

where $\boldsymbol{\kappa}$ is evaluated with $k=k_0$. Then the elastic interference cross section per molecule is given by

$$\sigma_{\text{int}}^{(0)}(\theta)=\sum_{n=2}^{N}\sigma_{1,n}(\theta). \tag{3.2}$$

We suppose that molecular interaction is due to a spherically symmetric two-particle potential $V(\mathbf{r}_i-\mathbf{r}_j)$. We shall frequently write $\mathbf{r}_{ij}$ for $\mathbf{r}_i-\mathbf{r}_j$ and V_{ij} for $V(\mathbf{r}_i-\mathbf{r}_j)$. Averaging classically, we have

$$\langle\chi_{1,2}\rangle_T=\frac{\int\exp\left(-\frac{\sum V_{ij}}{T}+i\boldsymbol{\kappa}\cdot\mathbf{r}_{12}\right)}{\int\exp\left(-\frac{\sum V_{ij}}{T}\right)d\mathbf{r}^N}. \tag{3.3}$$

Quantum corrections to (3.3) are considered together with inelastic corrections in the next section. Equation (3.3) leads to the Zernike-Prins formula[9] and the final result below can be obtained from the known density expansion of the pair distribution function. The treatment here illustrates the methods of Sec. 2 and serves as an introduction to the work of the next section.

The first two terms in the density series for (3.3) will be determined. We define the separable functions:

$$W_{1,0,0}(\mathbf{r}_1)=\exp(i\boldsymbol{\kappa}\cdot\mathbf{r}_1),\quad W_{0,1,0}(\mathbf{r}_2)=\exp(-i\boldsymbol{\kappa}\cdot\mathbf{r}_2),$$
$$W_{1,1,0}(\mathbf{r}_1,\mathbf{r}_2)=e^{-V_{12}/T}\exp(i\boldsymbol{\kappa}\cdot\mathbf{r}_{12}),$$

and

$$W_{1,0,1}(\mathbf{r}_1,\mathbf{r}_3)=e^{-V_{13}/T}\exp(i\boldsymbol{\kappa}\cdot\mathbf{r}_1),$$
$$W_{0,1,1}(\mathbf{r}_2,\mathbf{r}_3)=e^{-V_{23}/T}\exp(-i\boldsymbol{\kappa}\cdot\mathbf{r}_2),$$
$$W_{1,1,1}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)=e^{-(V_{12}+V_{23}+V_{31})/T}\exp(i\boldsymbol{\kappa}\cdot\mathbf{r}_{12}).$$

The u integrals are now deduced from (2.22). Thus,

$$u_{1,1,0}=w_{1,1,0}-w_{0,1,0}w_{1,0,0}$$
$$=\int(e^{-V_{12}/T}-1)\exp(i\boldsymbol{\kappa}\cdot\mathbf{r}_{12})d\mathbf{r}_1d\mathbf{r}_2 \tag{3.4}$$

$$u_{1,1,1}=w_{1,1,1}-w_{1,1,0}w_{0,0,1}-w_{1,0,1}w_{0,1,0}$$
$$-w_{0,1,1}w_{1,0,0}+2w_{1,0,0}w_{0,1,0}w_{0,0,1}$$
$$=\int[e^{-(V_{12}+V_{23}+V_{31})/T}-e^{-V_{12}/T}-e^{-V_{23}/T}$$
$$-e^{-V_{13}/T}+2]\exp(i\boldsymbol{\kappa}\cdot\mathbf{r}_{12})d\mathbf{r}_1d\mathbf{r}_2,\text{ etc.} \tag{3.5}$$

The terms $I_n^{(1)}$ and $I_n^{(2)}$ are seen to be proportional to the integrals

$$V^{-1}\int\exp(i\boldsymbol{\kappa}\cdot\mathbf{r}_1)d\mathbf{r}_1,\quad V^{-1}\int\exp(-i\boldsymbol{\kappa}\cdot\mathbf{r}_2)d\mathbf{r}_2, \tag{3.6}$$

respectively, and may be dropped. For when the volume of integration is macroscopically large, one

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[9] J. deBoer, in *Reports on Progress in Physics* (The Physical Society, London, 1949), Vol. 12, p. 305; N. S. Gingrich, Revs. Modern Phys. **15**, 90 (1943).

readily confirms that for scattering angles differing even minutely from the precise forward direction, the integrals (3.6) are vanishingly small.

We get, by (3.4),

$$I_0=\int f(\mathbf{r})\exp(i\boldsymbol{\kappa}\cdot\mathbf{r})d\mathbf{r}.$$

Further, by (3.5) and (2.20) we have

$$I_1=\int e^{-V(\mathbf{r})/T}f(\mathbf{r}-\mathbf{s})f(\mathbf{s})\exp(i\boldsymbol{\kappa}\cdot\mathbf{r})d\mathbf{r}d\mathbf{s}+2\beta_1 I_0.$$

It follows from (2.23) and (3.2) that

$$\sigma_{\mathrm{int}}{}^{(0)}(\theta)=A^2\left\{\left(\frac{N}{V}\right)\int f(\mathbf{r})\exp(i\boldsymbol{\kappa}\cdot\mathbf{r})d\mathbf{r}\right.$$
$$\left.+\left(\frac{N}{V}\right)^2\int e^{-V(\mathbf{r})/T}f(\mathbf{r}-\mathbf{s})f(\mathbf{s})\exp(i\boldsymbol{\kappa}\cdot\mathbf{r})d\mathbf{r}d\mathbf{s}+\cdots\right\}.$$

Using the notation

$$\langle F(\mathbf{r}^N)\rangle_r=\int F(\mathbf{r}^N)\exp(i\boldsymbol{\kappa}\cdot\mathbf{r})d\mathbf{r}^N\bigg/\int F(\mathbf{r}^N)d\mathbf{r}^N,$$

and the definitions (2.20), (2.21), we obtain for the interference cross section in the present approximation:

$$\sigma_{\mathrm{int}}{}^{(0)}(\theta)=A^2\{(N/V)\beta_1\langle f(\mathbf{r})\rangle_r+(N/V)^2(2\beta_2+\beta_1{}^2)\times\langle e^{V(\mathbf{r})/T}f(\mathbf{r}-\mathbf{s})f(\mathbf{s})\rangle_r+\cdots\}. \quad (3.7)$$

The expressions in angular brackets above are essentially weighted averages of $\exp(i\boldsymbol{\kappa}\cdot\mathbf{r})$. They are equal to unity for $\kappa=0$ (forward scattering) and oscillate with decreasing amplitude as κ increases. For molecular potentials of the Lennard-Jones type, these functions can be computed, for example, by the method Kihara employed for the virial coefficients.[10]

Quantitative statements are more easily made if the molecules are assumed to be hard spheres. In terms of the hard sphere diameter d, we have $\beta_1=-(4\pi/3)d^3$, $\beta_2=-(5\pi^2/12)d^6$. The coefficients of the angular brackets are conveniently expressed in terms of the ratio Ω/V where $\Omega=(4\pi/3)Nd^3$ is the total "interaction volume." If a hard sphere is introduced into a rare gas of N hard spheres, V_0 is essentially the volume from which the first sphere is excluded in virtue of the particle interactions. The coefficients of the first and second angular brackets are then $-(\Omega/V)$ and $(17/32)(\Omega/V)^2$, respectively. The first term of (3.7) is simply the Debye formula for the outer effect. The second bracket is reducible to the form

$$\langle e^{-V(\mathbf{r})/T}f(\mathbf{r}-\mathbf{s})f(\mathbf{s})\rangle_r$$
$$=\frac{6}{25}\int_1^2(\kappa d)^{-1}\sin(\kappa dz)(z^4-12z^2+16z)dz,$$

which, if desired, can be integrated in terms of elementary functions.

The terms which appear in the density expansion for the cross section are quite similar to the cluster integrals and the virial coefficients. Their evaluation presents difficulties of a comparable order of magnitude and the domain of convergence is probably equivalent to that of the virial expansion.

4. INELASTIC CORRECTIONS

We have observed that apart from the first term the terms of the density series for the expectation values $\langle\chi_{\nu\nu}\rangle_T$ yield only inelastic corrections to the direct scattering. To investigate the relative importance of the succeeding part we examine the portion which is linear in (N/V) and compute the leading terms obtained by the time expansion method.

The development of $\langle\chi_{\nu\nu}\rangle_T$ in powers of t gives rise to terms of two types. From the classical evaluation of the thermal averages, we obtain spatial integrals of ∇^2V, $(\nabla V)^2$, and higher derivatives, multiplied by certain powers of t. The latter cause the appearance of inverse powers of $\mathcal{E}_0$, the energy of the incident neutron, in the cross section. In addition, we have the quantum corrections to the classical averaging process which contain similar integrals over derivatives of the potential, divided by powers of T. Since the two kinds of terms may be of comparable magnitude, it is necessary to consider them together in a consistent calculation. It is then natural to order the various quantities according to the number of derivatives applied to the potential that they contain and to study, in a first approximation, the initial terms of the resulting series. This ordering is, in fact, an arrangement in powers of $\hbar$ and so constitutes a semiclassical expansion.

This procedure is quite analogous to the familiar method for approximating the partition function which was discussed earlier, and may be expected to have the same validity; that is, the series in powers of $\nabla^2V/\mathcal{E}_0$, ∇^2V/T, etc., is presumably asymptotic, and its leading terms yield an adequate approximation when $\mathcal{E}_0$ and T are not much lower than ordinary thermal energies.

We consider now the direct scattering by a gas particle specified by the coordinate $\mathbf{r}_1$. We seek to determine the linear term in the density expansion of the thermal average of the operator

$$e^{iHt}\exp(i\boldsymbol{\kappa}\cdot\mathbf{r}_1)e^{-iHt}\exp(-i\boldsymbol{\kappa}\cdot\mathbf{r}_1)=e^{iHt}e^{-iH_{(1)}'t}. \quad (4.1)$$

The operator $H_{(1)}'$, as defined in ZG, is obtained from H by replacing the momentum $\mathbf{p}_1$ with $\mathbf{p}_1-\boldsymbol{\kappa}$. If the particle at $\mathbf{r}_1$ is free, we have, simply, $H=p_1{}^2/2M$ and (4.1) reduces to a quantity we denote by $\chi_0(t)$:

$$\chi_0(t)=\exp[it(2\mathbf{p}_1\cdot\boldsymbol{\kappa}-\kappa^2)/2M]. \quad (4.2)$$

But if the first particle interacts with a second through a potential, then

$$H=p_1{}^2/2M+p_2{}^2/2M+V(\mathbf{r}_1-\mathbf{r}_2), \quad (4.3)$$

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[10] T. Kihara, J. Phys. Soc. Japan **3**, 265 (1948); **6**, 184 (1951).

whence

$$H_{(1)}'=(\mathbf{p}_1-\boldsymbol{\kappa})^2/2M+p_2^2/2M+V(\mathbf{r}_1-\mathbf{r}_2).$$

In the latter case, (4.1) is a function of greater complexity which we shall call $\chi_1(t)$. Hereafter, the symbol H will be reserved for the two-particle Hamiltonian (4.3) and we shall write H_0 for $(p_1^2+p_2^2)/2M$.

Following the prescription of Sec. 3, we have

$$D_0=\left(\frac{1}{V}\right)\left(\frac{2\pi}{MT}\right)^{\frac{3}{2}}\int\left\{\sum_i \psi_i^*(\mathbf{r}_1)\chi_0(t)\right.$$
$$\left.\times\exp\left(-\frac{p_1^2}{2MT}\right)\psi_i(\mathbf{r}_1)\right\}d\mathbf{r}_1,$$

$$D_1=\left(\frac{1}{V}\right)\left(\frac{2\pi}{MT}\right)^{3}\int\{\sum_i \psi_i^*(\mathbf{r}_1,\mathbf{r}_2)$$
$$\times[\chi_1(t)e^{-H/T}-\chi_0(t)e^{-H_0/T}]\psi_i(\mathbf{r}_1,\mathbf{r}_2)\}d\mathbf{r}_1d\mathbf{r}_2.$$

Then the latter equation can be rewritten

$$D_1=\beta_1D_0+\left(\frac{1}{V}\right)\left(\frac{2\pi}{MT}\right)^{3}\int\{\sum_i \psi_i^*(\mathbf{r}_1,\mathbf{r}_2)[\chi_1(t)e^{-H/T}$$
$$-(1+\beta_1)\chi_0e^{-H_0/T}]\psi_i(\mathbf{r}_1,\mathbf{r}_2)\}d\mathbf{r}_1d\mathbf{r}_2, \quad (4.4)$$

where β_1 is the quantum version of the first irreducible cluster integral:

$$\beta_1=\left(\frac{1}{V}\right)\left(\frac{2\pi}{MT}\right)^{3}\int\{\textstyle\sum_i \psi_i^*(\mathbf{r}_1,\mathbf{r}_2)$$
$$\times[e^{-H/T}-e^{-H_0/T}]\psi_i(\mathbf{r}_1,\mathbf{r}_2)\}d\mathbf{r}_1d\mathbf{r}_2.$$

The identity (2.25) allows us to express $\chi_1(t)$ as the exponential of a series in ascending powers of t. A factor of $\chi_0(t)$ can then be separated from $\chi_1(t)$ by a second application of (2.25) so that

$$\begin{aligned}\chi_1(t)&=e^{+iHt}e^{-iH_{(1)}'t}\\&=\chi_0(t)[1+c_2(-it)^2+c_3(-it)^3\\&\qquad+c_4(-it)^4+\cdots], \quad (4.5)\end{aligned}$$

where

$$c_2=\tfrac{1}{2}i(\boldsymbol{\kappa}\cdot\nabla V)/M,$$
$$c_3=[-2(\boldsymbol{\kappa}\cdot\nabla)^2V+(\boldsymbol{\kappa}\cdot\nabla)(\mathbf{p}_1-\mathbf{p}_2)\cdot\nabla V]/6M^2,$$
$$c_4=-\tfrac{1}{8}(\boldsymbol{\kappa}\cdot\nabla V)^2/M^2.$$

The gradients occurring above are with respect to $\mathbf{r}_1$. In computing the coefficients c_i, we have discarded terms containing more than two derivatives. We now insert (4.5) into (4.4), use momentum eigenfunctions for the $\psi_i(\mathbf{r}_1,\mathbf{r}_2)$ and reduce $e^{-H/T}$ to the form (2.30). Upon integration over momentum and space coordinates, we find

$$D_1-\beta_1D_0=\sum_{n=2}^{4}c_n'(-it)^n\exp\left[\frac{-it\kappa^2}{2M}-\frac{t^2T\kappa^2}{2M}\right], \quad (4.6)$$

where

$$c_2'=(\kappa^2/18M^2T)\mathcal{V}_1-(\kappa^2/24M^2T^2)\mathcal{V}_2,$$
$$c_3'=-(\kappa^2/9M^2)\mathcal{V}_1+(\kappa^2/12M^2T)\mathcal{V}_2,$$
$$c_4'=(\kappa^2T/18M^2)\mathcal{V}_1-(\kappa^2/24M^2)\mathcal{V}_2,$$

and

$$\mathcal{V}_1=\int e^{-V(\mathbf{r})/T}\nabla^2V d\mathbf{r}, \quad \mathcal{V}_2=\int e^{-V(\mathbf{r})/T}(\nabla V)^2d\mathbf{r}.$$

As was shown in ZG, the exponential in (4.6) produces corrections to the cross section of relative order (m/M) and α^2, where

$$\alpha^2=mT/M\mathcal{E}_0.$$

Although their calculation involves no special difficulty, they are best omitted in a first estimate of intermolecular effects. Accordingly, we replace the exponential by unity.

Let us write $\sigma_{\mathrm{dir}}^{(1)}(\theta)$ for the part of the direct cross section under calculation. Then, by (2.19) and (ZG I, 4.7),

$$\begin{aligned}\sigma_{\mathrm{dir}}^{(1)}(\theta)&=B^2(N/V)\int\int(k/2\pi k_0)e^{-i\epsilon t}(D_1-\beta_1D_0)dtd\epsilon\\&=\frac{B^2(N/V)}{k_0}\textstyle\sum_n\left(\frac{m}{k}\frac{d}{dk}\right)^n(kc_n')\Big|_{k=k_0}, \quad (4.7)\end{aligned}$$

where B^2, apart from a factor of 4π, is the incoherent cross section for a gas particle. Consequently, we obtain

$$\sigma_{\mathrm{dir}}^{(1)}(\theta)$$
$$=B^2\alpha^2\frac{N}{V}\left(1-\frac{7}{8}\frac{T^2}{\mathcal{E}_0^2}\right)\left(\frac{\mathcal{V}_1}{18MT^2}-\frac{\mathcal{V}_2}{24MT^3}\right). \quad (4.8)$$

In order to estimate the magnitude of (4.8), we choose for V the Lennard-Jones potential

$$V(\mathbf{r})=V_0\left[\left(\frac{r_0}{r}\right)^{12}-\left(\frac{r_0}{r}\right)^{6}\right], \quad (4.9)$$

and suppose the scattering to be performed at room temperature. The values $r_0=(3.5)\times10^{-8}$ cm, $V_0=0.05$ ev are typical of the magnitudes assumed by the Lennard-Jones parameters. One may show, very approximately, that $\mathcal{V}_1\approx100V_0r_0$, $\mathcal{V}_2\approx40V_0^2r_0$. For $\mathcal{E}_0\approx T$, (4.8) becomes

$$\sigma_{\mathrm{dir}}^{(1)}(\theta)\approx B^2(N/V)(m/M)^2(10^{-23}\text{ cm}^3). \quad (4.10)$$

Equation (4.10) is to be compared with the leading term in the direct cross section which is of the order of B^2. Thus, the calculated correction is too small to be of importance at standard conditions of temperature and pressure where, for a gas, $N/V\approx3\times10^{19}$ cm^{-3}, but it may be of significance under other circumstances.

Our methods are not powerful enough to analyze in detail the convergence properties of either the density expansion or the time expansion. But it is probably safe to assert that for gas densities which are not too great and neutron energies which are not too small, the development presented here is valid. Equation (4.8) contains the largest imperfect gas corrections to the direct cross section in this development.

We turn now to a consideration of inelastic effects in the (N/V) part of the interference cross section. Again, only terms having fewer than three derivatives applied to the potential are to be retained, and quantum modifications of the classically computed thermal averages are included to this order. As in the previous section, we may drop all interference terms involving $I_n^{(1)}$ and $I_n^{(2)}$. The latter are identical to their time independent analogs and do not contribute noticeably to the cross section.

We observe that

$$\begin{aligned} e^{iHt}\exp(i\boldsymbol{\kappa}\cdot\mathbf{r}_1)e^{-iHt}\exp(-i\boldsymbol{\kappa}\cdot\mathbf{r}_2) &= e^{iHt}e^{-iH_{(1)}'t}\exp(i\boldsymbol{\kappa}\cdot\mathbf{r}_{12}) \\ &= \chi_1(t)\exp(i\boldsymbol{\kappa}\cdot\mathbf{r}_{12}). \end{aligned}$$

Proceeding as before, we obtain for the cross section $\sigma_{\text{int}}(\theta)$, including presently calculated corrections,

$$\sigma_{\text{int}}(\theta)=A^2(N/V)\int\int(k/2\pi k_0)e^{-i\epsilon t}I_0\,dt\,d\epsilon,$$

where

$$\begin{aligned} I_0=\left(\frac{1}{V}\right)\left(\frac{2\pi}{MT}\right)^3\int\{\sum_i\psi_i^*(\mathbf{r}_1,\mathbf{r}_2) &\times[\chi_1(t)\exp(i\boldsymbol{\kappa}\cdot\mathbf{r}_{12})e^{-H/T} \\ &-\exp(i\boldsymbol{\kappa}\cdot\mathbf{r}_{12})e^{-H_0/T}]\psi_i(\mathbf{r}_1,\mathbf{r}_2)\}d\mathbf{r}_1d\mathbf{r}_2. \qquad (4.11) \end{aligned}$$

The reduction of (4.11) will yield a single spatial integral whose integrand contains the factor $e^{-V/T}\times\exp(i\boldsymbol{\kappa}\cdot\mathbf{r})$. Since

$$\nabla[e^{-V/T}\exp(i\boldsymbol{\kappa}\cdot\mathbf{r})]=[-(\nabla V)/T+i\boldsymbol{\kappa}]e^{-V/T}\exp(i\boldsymbol{\kappa}\cdot\mathbf{r}),$$

it follows that by an integration by parts, factors of $\boldsymbol{\kappa}$ can be replaced by derivatives of V inside the integral. Accordingly, such factors of κ are to be counted equivalent to derivatives for the purpose of determining which terms in the expansion are to be retained or rejected. Hence, from (4.11), we derive

$$\begin{aligned} I_0=\int(e^{-V(\mathbf{r})/T}-1)\exp(i\boldsymbol{\kappa}\cdot\mathbf{r})d\mathbf{r} \\ +\int e^{-V(\mathbf{r})/T}\exp(i\boldsymbol{\kappa}\cdot\mathbf{r})[d_0+d_1t+d_2t^2]d\mathbf{r}, \qquad (4.12) \end{aligned}$$

with

$$\begin{aligned} d_0&=(\nabla V)^2/12MT^3-(\nabla^2V)/6MT^2, \\ d_1&=(\boldsymbol{\kappa}\cdot\nabla V)/2MT-i\kappa^2/2M, \\ d_2&=-i(\boldsymbol{\kappa}\cdot\nabla V)/2M-T\kappa^2/2M. \end{aligned}$$

But when the suggested integrations by parts are performed in (4.12) the t and t^2 terms disappear. All that remains is the term representing the quantum correction to the classically evaluated $\sigma_{\text{int}}^{(0)}(\theta)$:

$$\sigma_{\text{int}}(\theta)=\sigma_{\text{int}}^{(0)}(\theta)+A^2\left(\frac{N}{V}\right)\int e^{-V/T}\times\exp(i\boldsymbol{\kappa}\cdot\mathbf{r})\left\{\frac{(\nabla V)^2}{12MT^3}-\frac{\nabla^2V}{6MT^2}\right\}dr.$$

Nothing remains of the inelastic corrections, to the order considered. Thus, in neutron diffraction by imperfect gases as in diffraction by free molecules, inelastic effects are much less prominent in the interference terms than in the direct scattering.

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APPENDIX

For a given integer N, consider the proposition $P(N)$ that for all $n<N$, each U_n defined by Eq. (2.5) is a cluster function if and only if each W_n is separable. The truth of $P(N)$ for the smallest values of N is inferred directly from (2.7). Assuming $P(N)$, we shall prove $P(N+1)$ and so establish, by mathematical induction, the fundamental relation between U and W functions for clusters of arbitrary size.

Let $\mathbf{r}^N$ be composed of two clusters $\mathbf{r}^{N'}$ and $\mathbf{r}^{N''}$, $N'+N''=N$, with the coordinates of $\mathbf{r}^{N''}$ labeled $\mathbf{r}_{N'+1},\cdots,\mathbf{r}_N$. Then

$$\frac{\delta}{\delta a(\mathbf{r}_1)}\cdots\frac{\delta}{\delta a(\mathbf{r}_{N'})}e^{GU(a)}=e^{GU(a)}\left[W_{N'}(\mathbf{r}^{N'})+\frac{1}{(N'')!}\int a(\boldsymbol{\varrho}^{N''})U_N(\mathbf{r}^{N'},\boldsymbol{\varrho}^{N''})d\boldsymbol{\varrho}^{N''}+\text{other terms}\right]. \qquad (A.1)$$

We note that the right side of (A.1) reduces to $W_{N'}(\mathbf{r}^{N'})$ when $a=0$.

Let (A.1) be differentiated with respect to each of the functional variables $a(\mathbf{r}_i)$ with $N'+1\leqslant i\leqslant N$, and the parametric function then set equal to zero. We find that

$$W_N(\mathbf{r}^N)=W_{N'}(\mathbf{r}^{N'})W_{N''}(\mathbf{r}^{N''})+U_N(\mathbf{r}^N)+\text{other terms}, \quad \text{(A.2)}$$

where the "other terms" in (A.2) consist of certain products containing functions U_n with $n<N$. At least one U_n in each product has arguments drawn from both the groups $\mathbf{r}^{N'}$ and $\mathbf{r}^{N''}$. If $\mathbf{r}^{N'}$ and $\mathbf{r}^{N''}$ are now isolated from each other and the inductive hypothesis $P(N)$ is invoked, the "other terms" vanish. The validity of $P(N+1)$ follows immediately.

The extension of this proof to cases of lower symmetry requires only notational changes.

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Microwave Spectra of the Tl, In, and Ga Monohalides*

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A high-temperature spectrometer has been used to study the rotational spectra of the gallium, indium, and thallium monohalides. The molecular constants are

	B_e (Mc/sec)	α_e (Mc/sec)	r_e (A)
$Tl^{205}F$	6689.97 ±0.06	44.97 ±0.08	2.0844±0.0001
$Tl^{205}Cl^{35}$	2740.05 ±0.02	11.90 ±0.01	2.4848±0.0001
$Tl^{205}Br^{79}$	1293.89 ±0.01	3.927±0.005	2.6181±0.0001
$Tl^{205}I^{127}$	814.479±0.015	1.985±0.005	2.8135±0.0001
$In^{115}Cl^{35}$	3269.47 ±0.14	15.35 ±0.15	2.4011±0.0001
$In^{115}Br^{79}$	1670.14 ±0.02	5.706±0.01	2.5432±0.0001
$In^{115}I^{127}$	1104.95 ±0.45	3.117±0.015	2.7539±0.0009
$Ga^{69}Cl^{35}$	4493.73 ±0.19	23.27 ±0.12	2.2017±0.0001
$Ga^{69}Br^{79}$	2481.99 ±0.04	9.74 ±0.03	2.3525±0.0001
$Ga^{69}I^{127}$	1706.86 ±0.04	5.67 ±0.15	2.5747±0.0001

The quadrupole coupling constants determined in the present experiment are related to the molecular bond and the role of *s-p* hybridization in the molecular bond is discussed.

INTRODUCTION

MICROWAVE spectroscopy of molecules in the gaseous state has provided a large amount of accurate information about molecular structure.[1,2] Of all the molecules studied, the diatomic one is the easiest to interpret in terms of a theoretical model. The number of diatomic molecules which can be studied by conventional microwave spectroscopy is severely limited by the small fraction of such molecules in the gaseous state at room temperature. The development of the high-temperature spectrometer[3,4] made it possible to observe the pure rotation spectra of most of the alkali halides[5] and its use has been extended to the molecules reported here.

Diatomic molecules in the gaseous state have been investigated by the techniques of electron diffraction,[6,7] molecular-beam magnetic and electric resonance,[8–10] and microwave spectroscopy. Electron diffraction experiments yielded internuclear distances but with an accuracy far below present standards. Early magnetic-resonance experiments gave information concerning the nuclear magnetic moments and the interaction of the electric quadrupole moment with the rotating molecule. Electric-resonance experiments have been of two kinds. In the first of these, $\Delta m_J=\pm1$ transitions are observed; these yield, in addition to the molecular hyperfine structure, information concerning the electric dipole moment and moment of inertia of the molecule. However, the last two quantities are not determined with

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