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# ANALYTIC PROPERTIES OF THE QUANTUM CORRECTIONS TO THE SECOND VIRIAL COEFFICIENT


Hugh E. DeWitt


September 11, 1961






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# Analytic Properties of the Quantum Corrections to the Second Virial Coefficient*

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## ABSTRACT

The usefulness of the perturbation expansion and the Wigner-Kirkwood expansion of the quantum mechanical partition function is discussed for various interaction potentials. It is shown that, contrary to what is expected from the Wigner-Kirkwood expansion, quantum mechanical diffraction corrections at high temperature to the classical partition function may involve nonanalytic forms of $\hbar^2$. This occurs when the second-order perturbation term is finite in the classical limit, and the interaction potential has a cusp or singularity in any derivative. The second-order perturbation term is evaluated exactly for the exponential, screened Coulomb, and square barrier potentials, and the nonanalytic form $(\hbar^2)^{1/2}$ is found. For potentials more singular than $1/r$ at the origin, the diffraction corrections are analytic in $\hbar^2$.

A new method of deriving the Wigner-Kirkwood expansion from the perturbation expansion is given. The method allows one to subtract off any order of the perturbation expansion which may be evaluated separately, and is particularly useful for the screened Coulomb potential.

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The classical second virial coefficient and the $0(\hbar^2)$ and $0(\hbar^4)$ diffraction corrections are evaluated for the singular potential, $u(r) = (g_p/r^p)e^{-r/r_0}$, by using the Mellin transform of $e^{-\beta u}$.

# Analytic Properties of the Quantum Corrections to the Second Virial Coefficient

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## I. INTRODUCTION

The problem of calculating small quantum corrections at high temperature to classical thermodynamic quantities has been discussed extensively during the three decades since the classic papers of Wigner and Kirkwood.[1] In this paper the same problem is considered again, but with the purpose of establishing the analytic properties of the partition function with respect to Planck's constant for various interaction potentials. The quantum corrections to the classical partition function to be considered are those due to the operation of the uncertainty principle. Effects due to quantum statistics will not be treated here. Thus, we consider a gas of distinguishable particles interacting according to the laws of wave mechanics. Such quantum corrections will be referred to as diffraction effects.

The fundamental problem of quantum statistical mechanics is the evaluation of the partition function, $Z = \mathrm{Tr}\exp(-\beta H)$, where $H = \Sigma_i(-\hbar^2/2m_i)\nabla_i^2 + \Sigma_{i<j}u(r_{ij})$, and $\beta = 1/kT$ is the reciprocal temperature. Since the partition function may be evaluated directly for only a very limited set of interaction potentials, it is necessary in general to resort to some expansion procedure. One method is to expand in powers of the interaction potential. Such a perturbation expansion is appropriate when $u(r)$ is small in some sense compared

with the kinetic energy. When the terms of the perturbation expansion are evaluated, the diffraction corrections to the classical limit of the nth order appear as some function of $\hbar$ multiplying the nth power of the coupling constant of the interaction. A second method in common use involves expanding in powers of $\hbar^2\nabla^2$; thus the kinetic energy is considered small compared with the potential energy. This second method is appropriate when u(r) is very singular at r = 0. The expansion in powers of the kinetic energy is the well-known Wigner-Kirkwood expansion[1] (hereafter to be referred to as the WK expansion). Using the WK method, the partition function (written for one particle) is:

$$\mathrm{Tr}\, e^{-\beta H} = \left(\frac{2\pi mkT}{h^2}\right)^{3/2} \int d^3r\, e^{-u} \left\{1 - \frac{\lambda\!\!\!^{-2}}{12} (\nabla U)^2 + \frac{\lambda\!\!\!^{-4}}{1440} \left[((\nabla U)^2)^2 - 8(\nabla U)^2\nabla^2 U + 12(\nabla^2 U)^2\right] - \ldots\right\}, \quad (1)$$

where $U = \beta u(r)$, and $\lambda\!\!\!^{-} = \hbar/(2mkT)^{1/2}$ is the thermal de Broglie wavelength.[2] The $\lambda\!\!\!^{-4}$ term in Eq. (1) is the form obtained by Yaglom.[3] The evaluation of the terms of the WK expansion is quite lengthy and no terms beyond the $\lambda\!\!\!^{-4}$ term are known to exist in the literature. Equation (1) has had considerable practical application in the calculation of quantum corrections to the equation of state of nonideal gases.[4,5]

At first glance it would appear from the structure of Eq. (1) that the partition function is an analytic function of $\lambda\!\!\!^{-2}$, and in consequence there seems to be a common and erroneous belief among physicists that diffraction corrections necessarily involve only even powers of Planck's constant. The argument for the nonideal gas calculations is that any reasonable form of the intermolecular interaction potential is strongly repulsive near r = 0; usually $r^{-12}$ is assumed. Hence $e^{-U}$ goes to zero much faster as $r \to 0$ than the terms of the expansion go to $\infty$, so that the configuration space integrals are finite. Although little is known about the convergence of the resulting series, it seems reasonable that at high temperature the first couple of terms give the diffraction corrections accurately.

It is not true, however, that for all potential interactions the partition function is analytic in $\lambda^2$. A simple counter example is the exponential potential, $u(r) = g_0 e^{-r/r_0}$. Since this potential form is finite at $r = 0$, one cannot depend on the $e^{-U}$ factor for the existence of the coefficients of powers of $\lambda^2$. The $\underline{m}$th term of the WK expansion includes $(\nabla^2 U)^m$, and since $\nabla^2 e^{-r} = (1 - 2/r)e^{-r}$, one sees that the coefficient of $\lambda^{2m}$ includes at least one term of order $r^{-m}e^{-mr}$. Thus, after the integration over $\underset{\sim}{r}$ the coefficients of $\lambda^2$ and $\lambda^4$ are finite, but that of $\lambda^6$ is logarithmically divergent and all higher coefficients are more strongly divergent. The exponential potential is an example, albeit not very interesting for physical problems, for which the WK expansion may not be used. Instead, one must evaluate the terms of the perturbation expansion, and it will be found that the coefficient of each power of the coupling constant is a nonanalytic function of $\hbar^2$. It will be shown that the nonanalyticity takes the form of terms of order $(\hbar^2)^{m+1/2}$ in addition to the expected terms of order $\hbar^{2m}$. A more interesting, though less obvious example, is a potential with an $r^{-1}$ singularity at the origin. Evaluation of the second-order perturbation term for the screened Coulomb potential yields again a function with both even and odd powers of h in its expansion. In view of these examples it seems worthwhile to examine the question of when the partition function is analytic in $\hbar^2$ and when it is not.

Before taking up the analyticity of Z as a function of $\hbar^2$, its analyticity with respect to two other quantities should be considered, namely, the particle number density, $\rho$, and the coupling constant of the interaction, g. In this paper we will consider only potentials such that the cluster integrals of the Mayer cluster expansion exist.[6] With this restriction the pressure is an analytic function of $\rho$; i.e., it is given by a power series expansion in $\rho$, the usual virial expansion.[7] One is next interested in the analyticity of the virial coefficients as functions of g and $\hbar^2$. In this paper only the second virial coefficient will be studied since the methods used may be easily extended to the higher virial coefficients. The second virial coefficient is the sum of all two-body interactions, and is defined as:

$$B_2 = -\frac{(4\pi\lambda)^{3/2}}{2!}\left[\mathrm{Tr}\, e^{-\beta(H_0+u)} - \mathrm{Tr}\, e^{-\beta H_0}\right] \xrightarrow[\hbar \to 0]{} -\frac{1}{2!}\int d^3r\,(e^{-\beta u} - 1)\,, \quad (2)$$

where $H_0 = -(\hbar^2/2\mu)\nabla^2$ and $\mu$ is the reduced mass of the two interacting particles.

We will be primarily interested in the evaluation of $B_2$ for repulsive singular potentials of the form:

$$u(r) = (g_p/r^p)\, e^{-r/r_0}\,, \quad (3)$$

where the coupling constant $g_p$ has dimensions $EL^p$. The exponential screening function is chosen for mathematical convenience. Other screening functions such as the Gaussian form, $e^{-r^2/r_0^2}$, may also be used. The analyticity of the classical form of $B_2$ as a function of g is obvious for nonsingular potentials, say, of the form $r^m e^{-r/r_0}$. The first order singularity, p = 1 in Eq. (3), is the very interesting case of the screened Coulomb potential. For this potential the first two terms of the perturbation expansion are finite because of the three-dimensional volume element, $4\pi r^2 dr$. The third order is logarithmically divergent, and the higher orders more strongly divergent. The exact evaluation of $B_2$ for the screened Coulomb potential yields:

$$B_2 = -2\pi r_0^3\left\{-\beta g_1/r_0 + \frac{1}{4}(\beta g_1/r_0)^2 + \frac{1}{6}(\beta g_1/r_0)^3[\log(\beta g_1/r_0) + \text{const}] + \ldots\right\}. \quad (4)$$

Thus, the divergence of the third and higher orders of the perturbation expansion gives rise to the nonanalytic form $g_1^3 \log g_1$. For a second-order singularity, p = 2, the first term of the perturbation expansion is finite, and all higher orders are divergent. The exact result for $B_2$ contains the nonanalytic form $g_2^2 \log g_2$. Similarly, for p = 3 all orders of the perturbation expansion are infinite, and the exact result for $B_2$ begins with $g_3 \log g_3$. For $p > 3$, $B_2$ begins with $(g_p)^{3/p}$.

A simple dimensional analysis gives quickly some information about the analyticity of $B_2$ as a function of $\hbar^2$. For the singular potentials defined by Eq. (3) the fundamental lengths which completely determine $B_2$ are: the classical interaction length, $\ell = (\beta g_p)^{1/p}$, the thermal wavelength, $\lambda\!\!\!^{-} = \hbar(\beta/2m)^{1/2}$, and the screening length, $r_0$. From these lengths we may form two independent dimensionless parameters which will be taken to be any two of the ratios:

$$\Lambda = \ell/r_0 \qquad \eta = \lambda\!\!\!^{-}/\ell \qquad \gamma = \lambda\!\!\!^{-}/r_0 .$$

By using Eqs. (1) and (2) the WK expansion of the second virial coefficient in terms of the parameters $\Lambda$ and $\eta$ is:

$$B_2 = -2\pi\ell^3 \left[C_0(\Lambda) - \eta^2 C_1(\Lambda) + \eta^4 C_2(\Lambda) - \ldots\right] , \tag{5}$$

where the expansion coefficients are:

$$\begin{aligned} C_0(\Lambda) &= \int_0^\infty x^2\, dx\, (e^{-U} - 1) , \\ C_1(\Lambda) &= \frac{1}{12} \int_0^\infty x^2\, dx\, e^{-U} (\nabla_x U)^2 , \end{aligned} \tag{6}$$

with $x = r/\ell$, and $U = x^{-p} e^{-\Lambda x}$. $C_0(\Lambda)$ gives the classical second virial coefficient. The coefficients of the diffraction corrections, $C_1(\Lambda) \ldots C_m(\Lambda)$, are finite for all $p \geq 1$ in the limit of no screening, $r_0 = \infty$ or $\Lambda = 0$. From

Eq. (5) we see that the parameter of smallness for the WK expansion is $\eta^2$. Since its dependence on the coupling constant is $g_p^{-2/p}$, it is clear that the WK expansion is a strong coupling expansion in contrast to the perturbation expansion. The temperature dependence of $\eta^2$ is $\beta^{1-2/p}$, and hence the diffraction corrections vanish at high temperature when $p \geq 3$. The radius of convergence of the power series in $\eta^2$ of Eq. (5) is not known, but it seems clear that a third-order singularity in the potential is sufficient to guarantee that diffraction corrections at high temperature involve only powers of $\eta^2$, and hence only even powers of $\hbar^2$.

The less singular cases, $p = 2$ and $p = 1$, must be considered separately from $p \geq 3$. For $p = 2$, $\eta^2$ has no temperature dependence, and hence the WK expansion would indicate that diffraction corrections do not depend on temperature. Finally, for $p = 1$, the screened Coulomb potential, the temperature dependence of $\eta^2$ is $\beta^{-1}$. Note that for $p \geq 3$ the thermal wavelength is small compared with the classical interaction length at high temperature, whereas for $p = 1$ the order is reversed, $\lambda \gg \ell$. Thus the terms of the WK expansion diverge in the high-temperature limit for $p = 1$. This behavior indicates that $B_2$ cannot be an analytic function of $\hbar^2$ for $p = 1$. The $r^{-1}$ singularity at first appears to be too weak to allow an expansion in which the kinetic energy is treated as small compared with $u(r)$. It will be shown in Sections III and V, however, that the nonanalyticity in $\hbar^2$ for $p = 1$ appears only in the second-order perturbation term. The diffraction corrections involve $\gamma = \eta\Lambda$, and in the second-order theory both odd and even powers of $\gamma$ appear. The diffraction corrections to the sum of all higher orders of the perturbation expansion involve only even powers of $\gamma$, and the coefficients may be calculated by a modification of the WK expansion.

In Section II the perturbation expansion is developed in some detail, and a method of deriving the WK expansion from the perturbation expansion is given. In Section III the second-order perturbation term is evaluated explicitly for a number of different potentials in order to illustrate the condition for which it is or is not analytic in $\gamma^2$. In Section IV some of the coefficients of the WK expansion are evaluated by a very convenient technique, the use of the Mellin transform. In Section V the special case of the screened Coulomb potential is considered in some detail.

## II. THE PERTURBATION EXPANSION AND ITS USE FOR DERIVING THE WK EXPANSION

The perturbation expansion of $B_2$ is most easily developed with the help of the resolvent operator. One uses:

$$e^{-\beta H} = \frac{1}{2\pi i} \int_C \frac{dz\, e^{-\beta H}}{z - H},$$

where the contour C goes from right to left in the upper half plane and left to right in the lower half. Thus, it encloses the simple poles on the real axis at the eigenvalues of H when the trace is taken. This method was used by Glassgold, Heckrotte, and Watson for the linked cluster expansion of the complete partition function.[8] If we put $H = (H - E_0) + E_0$ where $E_0 = p^2/2\mu$ is the unperturbed kinetic energy of relative motion, and use the resolvent of $e^{-\beta(H-E_0)}$ then the second virial coefficient is:

$$B_2 = -\frac{(4\pi\lambda^2)^{3/2}}{2!} \int \frac{d^3p\, e^{-\beta E_0}}{(2\pi\hbar)^3} \frac{1}{2\pi i} \int_C dz\, e^{-\beta z} \left\langle p \left| \frac{1}{z - (H_0 + u - E_0)} - \frac{1}{z - (H_0 - E_0)} \right| p \right\rangle. \tag{7}$$

Expanding in powers of u gives:

$$B_2 = -\frac{(4\pi\lambda^2)^{3/2}}{2!}\sum_{n=1}\int\frac{d^3p\, e^{-\beta E_0}}{(2\pi\hbar)^3}\,\frac{1}{2\pi i}\int_C \frac{dz\, e^{-\beta z}}{z}\left\langle p\left|\left(\frac{1}{z-(H_0-E_0)}u\right)^n\right|p\right\rangle$$

$$= \sum_{n=1} B_{2n}\,. \tag{8}$$

Since Boltzmann statistics have been assumed, the individual particle momenta may be transformed to center-of-mass and relative momenta, and the center-of-mass momentum integrated out. Thus, $H_0$ is the free-particle Hamiltonian for relative motion. $H_0 = -(\hbar^2/2\mu)\nabla^2$, and $|p\rangle$ indicates its eigenfunctions.

The operator product in Eq. (8) is written out in momentum space to give the nth order of $B_2$ as:

$$B_{2n} = -\frac{(4\pi\lambda^2)^{3/2}}{2!}\int\frac{d^3p\, e^{-p^2/2\mu kT}}{(2\pi\hbar)^3}\int\frac{V^n d^3k_1\ldots d^3k_n}{(2\pi)^{3(n-1)}}\,\delta(\underset{\sim}{k}_n-\underset{\sim}{k}_1-\ldots-\underset{\sim}{k}_{n-1})$$

$$\times\, u(k_1)\ldots u(k_n)\,\frac{1}{2\pi i}\int_C\frac{dz\, e^{-\beta z}}{z}\,\frac{1}{z-(p_{n-1}^2-p^2)/2\mu}\cdots\frac{1}{z-(p_1^2-p^2)/2\mu}\,, \tag{9}$$

where $\underset{\sim}{p}_1 = \underset{\sim}{p}+\hbar\underset{\sim}{k}_1,\ \ldots,\ \underset{\sim}{p}_{n-1} = \underset{\sim}{p}+\hbar(\underset{\sim}{k}_1+\ldots+\underset{\sim}{k}_{n-1})$, and $u(k) = V^{-1}\int d^3r\, e^{i\underset{\sim}{k}\cdot\underset{\sim}{r}}u(r)$ is the Fourier transform of the potential. The quantities $\hbar\underset{\sim}{k}_1,\ \ldots,\ \hbar\underset{\sim}{k}_n$ are the momentum transfers at the respective n interactions. The $\delta$ function insures momentum conservation in the final interaction. The contour integration in Eq. (9) may be performed and the result represented as:

$$\frac{1}{2\pi i}\int_C\frac{dz\, e^{-\beta z}}{z}\cdots$$

$$= \int_0^{\beta} d\beta_n\int_0^{\beta_n} d\beta_{n-1}\cdots\int_0^{\beta_2} d\beta_1\,\exp -\Big[(\beta_n-\beta_{n-1})(p_{n-1}^2-p^2)/2\mu + \ldots (\beta_2-\beta_1)(p_1^2-p^2)/2\mu\Big] \tag{10}$$

The multiple integral form [ Eq. (10)] is the nth term of the familiar ordered exponential expansion commonly used in field theory calculations and in recent years also in quantum statistical mechanics.[9] Equation (10) shows the equivalence of the linked cluster expansion of the partition function in the resolvent operator formalism[8] and the work of Bloch and de Dominicis.[10]

The relative momentum integration may be readily performed when Eq. (10) is used in Eq. (9). The result is:

$$B_{2n} = -\frac{(-\beta)^n}{2!}\int \frac{V^n d^3k_1 \ldots d^3k_n}{(2\pi)^{3(n-1)}}\,\delta(\underset{\sim}{k}_n - \underset{\sim}{k}_1 - \ldots - \underset{\sim}{k}_{n-1}) \\ \times u(k_1)\ldots u(k_n)F_n(\lambda\underset{\sim}{k}_1, \ldots, \lambda\underset{\sim}{k}_{n-1}) , \tag{11}$$

where

$$F_n(\lambda\underset{\sim}{k}_1, \ldots, \lambda\underset{\sim}{k}_{n-1}) = \int_0^1 dv_n \ldots \int_0^{v_2} dv_1 \exp - \lambda^2\Big\{\big[(v_2 - v_1)k_1{}^2 + \ldots \\ + (v_n - v_{n-1})(\underset{\sim}{k}_1 + \ldots + \underset{\sim}{k}_{n-1})^2\big] - \big[(v_2 - v_1)\underset{\sim}{k}_1 + \ldots + (v_n - v_{n-1})(\underset{\sim}{k}_1 + \ldots \\ + \underset{\sim}{k}_{n-1})\big]^2\Big\} . \tag{12}$$

All quantum mechanical diffraction effects are contained in the functions $F_n$. The $F_n$ are entire functions of $\lambda^2$. The first term of $F_n$ when expanded in powers of $\lambda^2$ is $1/n!$ , and consequently in the classical limit, $\lambda \to 0$, Eq. (11) reduces to:

$$B_{2n\ \text{classical}} = -\frac{(-\beta)^n}{2n!}\int d^3r\, u(r)^n . \tag{13}$$

Also since $F_1 \equiv 1$ the first-order perturbation term has no diffraction effects.

The actual evaluation of Eq. (11) for any given potential is tractable only in second order since for n = 2 there is only one integration variable. This integration for a few examples is discussed in the next section. For higher order terms the evaluation of Eq. (11) is very difficult because it requires integration over the n - 1 wave vectors, $\underset{\sim}{k}_1 \ldots \underset{\sim}{k}_{n-1}$. Because of this complexity it may be wondered whether or not the integration is simpler in configuration space rather than in wave-number space. Two different forms may be obtained directly from Eq. (11). One of these is:

$$B_{2n} = -\frac{1}{2}(4\pi\lambda^2)^{3/2}(-\beta)^n \int \ldots \int d^3r_1 \ldots d^3r_n\, u(r_1) \ldots u(r_n) \int_0^1 dv_n \ldots \int_0^{v_2} dv_1$$

$$\frac{\exp\left[-(\underset{\sim}{r}_1 - \underset{\sim}{r}_n)^2/4\lambda^2(1 - v_n + v_1)\right]}{\left[4\pi\lambda^2(1 - v_n + v_1)\right]^{3/2}} \; \frac{\exp\left[-(\underset{\sim}{r}_2 - \underset{\sim}{r}_1)^2/4\lambda^2(v_2 - v_1)\right]}{\left[4\pi\lambda^2(v_2 - v_1)\right]^{3/2}} \ldots \tag{14}$$

$$\frac{\exp\left[-(\underset{\sim}{r}_n - \underset{\sim}{r}_{n-1})^2/4\lambda^2(v_n - v_{n-1})\right]}{\left[4\pi\lambda^2(v_n - v_{n-1})\right]^{3/2}} \,.$$

The details required to turn Eq. (11) into Eq. (14) are not given here since this form and its derivation are adequately discussed by Goldberger and Adams[9] and also by Green.[11] Unfortunately, the evaluation of $B_{2n}$ in the form of Eq. (14) appears to be even harder than in the form of Eq. (11) since one must still integrate over the n vectors $\underset{\sim}{r}_1 \ldots \underset{\sim}{r}_n$ which represent the separation of the two particles at the "times" $v_1 \ldots v_n$.

The second form of $B_{2n}$ as a configuration space integral is obtained by using the familiar representation of the three-dimensional delta function:

$$\delta(\underset{\sim}{k}) = \frac{1}{(2\pi)^3}\int d^3r\, e^{i\underset{\sim}{k}\cdot\underset{\sim}{r}}$$

and noting that in the power series expansion of $F_n$ the wave numbers $\underset{\sim}{k}_1 \ldots \underset{\sim}{k}_{n-1}$ become the differential operators, $i\underset{\sim}{\nabla}_1 \ldots i\underset{\sim}{\nabla}_{n-1}$. Thus, one obtains:

$$B_{2n} = -\frac{1}{2}(-\beta)^n \int d^3r\, u_n(r) F_n(i\lambda\underset{\sim}{\nabla}_1, \ldots, i\lambda\underset{\sim}{\nabla}_{n-1}) u_1(r) \ldots u_{n-1}(r) \,. \tag{15}$$

The subscripts 1 through n in Eq. (15) are for bookkeeping purposes. They may be erased after the differential operators $\underset{\sim}{\nabla}_1 \ldots \underset{\sim}{\nabla}_{n-1}$ in the expansion of $F_n$ are applied, respectively, on $u_1 \ldots u_{n-1}$.

$B_{2n}$ in the form (15) is not particularly useful for explicit evaluation, but it is useful as a means of obtaining the WK expansion from the perturbation expansion. For this derivation the expansion of $F_n$ as defined by Eq. (12) in powers of $\lambda^2$ is needed. The exponent of the integrand of Eq. (12) may be written as:

$$\left\{\left[(v_2 - v_1)k_1^2 + \ldots + (v_n - v_{n-1})(\underset{\sim}{k}_1 + \ldots + \underset{\sim}{k}_{n-1})^2\right] - \left[(v_2 - v_1)\underset{\sim}{k}_1 + \ldots + (v_n - v_{n-1}) \times (\underset{\sim}{k}_1 + \ldots + \underset{\sim}{k}_{n-1})\right]^2\right\} = \sum_{r=1}^{n-1} a_{nrr}\, k_r^2 + 2 \sum_{r_2 > r_1}^{n-1} a_{nr_2r_1}\, \underset{\sim}{k}_{r_2} \cdot \underset{\sim}{k}_{r_1} ,$$

where

$$a_{nr_2r_1} = (v_n - v_{r_2})\left[1 - (v_n - v_{r_1})\right] .$$

The differences, $v_n - v_r$, are a measure of the "times" from the interactions with momentum transfer $\hbar\, \underset{\sim}{k}_r$ to the final interaction. The multiple v integrations in Eq. (12) represent an average over the duration of these excitations. It may be shown that:

$$\langle a_{nr_2r_1}\rangle_{av} \equiv \int_0^1 dv_n \ldots \int_0^{v_2} dv_1\, a_{nr_2r_1} = \frac{(r_1 + 1)(n - r_2)}{(n+2)!} . \quad (16)$$

The expansion of $F_n(\lambda \underset{\sim}{k}_1, \ldots, \lambda \underset{\sim}{k}_{n-1})$ is:

$$\begin{aligned} F_n &= \int_0^1 dv_n \ldots \int_0^{v_2} dv_1 \left\{1 - \lambda^2\left[\sum_{r=1}^{n-1} a_{nrr}\, k_r^2 + 2\sum_{r_2>r_1}^{n-1} a_{nr_2r_1}\, \underset{\sim}{k}_{r_2} \cdot \underset{\sim}{k}_{r_1}\right] + 0(\lambda^4) \ldots\right\} \\ &= \frac{1}{n!} - \lambda^2\left[\sum_{r=1}^{n-1} \langle a_{nrr}\rangle_{av}\, k_r^2 + 2\sum_{r_2>r_1}^{n-1} \langle a_{nr_2r_1}\rangle_{av}\, \underset{\sim}{k}_{r_2} \cdot \underset{\sim}{k}_{r_1}\right] + \ldots . \end{aligned} \quad (17)$$

When Eq. (17) is put into $B_{2n}$ in the form of Eq. (15) and the summations over $r_1$ and $r_2$ carried out, one obtains:

$$B_{2n} = \sum_{m=0}^{\infty} B_{2n}^{(m)}$$

$$= -\frac{1}{2}\int d^3r \left\{ \frac{(-U)^n}{n!} - \frac{\lambda^2}{(n+2)!}\left[ \frac{(n-1)n(n+4)}{6} \nabla^2 U(-U)^{n-1} - \frac{(n-2)(n-1)n(n+5)}{12} (\nabla U)^2 (-U)^{n-2} \right] + \ldots \right\} . \quad (18)$$

The $0(\lambda^{2m})$ term of the WK expansion is obtained by summing $B_{2n}^{(m)}$ for all orders of perturbation theory. Clearly $B_{2n}^{(0)}$ summed from n = 1 to ∞ gives the classical second virial coefficient. The method will be carried out explicitly only for the $0(\lambda^2)$ term. In order to obtain the usual form of the $0(\lambda^2)$ term it is necessary to integrate the $\nabla^2 U(-U)^{n-1}$ portion of Eq. (19) by parts. Since we are interested primarily in potentials which are singular at the origin, the integration by parts is done by excluding a sphere of radius $\delta$ about the origin. The result for $B_{2n}^{(1)}$ in Eq. (19) including a surface term from the integration by parts is:

$$B_{2n}^{(1)} = -\frac{\lambda^2}{2} \lim_{\delta \to 0} \left\{ \int \frac{d^3r (\nabla U)^2 (-U)^{n-2}}{12(n-2)!} - \frac{(n-1)n(n+4)}{6(n+2)!} 4\pi\delta^2 U'(\delta)(-U(\delta))^{n-1} \right\} . \quad (19)$$

When Eq. (19) is summed over n the surface term gives no contribution, and one obtains:

$$B_2 = -\frac{1}{2}\int d^3r \left\{ (e^{-U} - 1) - \frac{\lambda^2}{12} (\nabla U)^2 e^{-U} + \ldots \right\} \quad (20)$$

in agreement with Eq. (1). In order to obtain higher-order terms in the WK expansion, one needs formulae analogous to Eq. (16) for powers and products of the $a_{nr_1r_2}$. These may be calculated readily but laboriously.

The usual method for the derivation of the WK expansion described in textbooks[12] follows the procedure used by Kirkwood[1] in which the Bloch equation, $\partial f/\partial\beta = -Hf$, is solved by iteration in powers of $h\nabla$ subject to the condition that $f = \exp -\beta(p^2/2m + u(r))$ at $\hbar = 0$. This method is very analogous to the WKB method for solving the Schröedinger equation. It is straightforward but very tedious. Other methods have been given by Goldberger and Adams,[9] Oppenheim and Ross,[13] Chester,[14] Siegert,[15] and Yaglom.[3] All these methods require considerable effort even to obtain the $0(\hbar^4)$ term. The very elegant method of Yaglom is probably the most useful as judged by the ease in which the $0(\hbar^4)$ term is obtained. In this method the solution of the Bloch equation is expressed as a Wiener functional integral which is expanded in a Taylor series in powers of $\hbar$.

The derivation given in the preceding paragraphs in which a given power of $\hbar^2$ in the perturbation expansion is summed has been described in some detail, not as an addition to the list of methods of obtaining the WK expansion, but because of an important advantage that it has. With this method one may subtract out any number of lower orders of the perturbation expansion which have a finite classical limit and make a WK expansion on the remainder. This procedure must be used for potentials with $r^{-2}$ and $r^{-1}$ singularities at the origin.

## III. ANALYTICITY OF SECOND-ORDER PERTURBATION THEORY AS A FUNCTION OF $\hbar^2$

In the previous section three different forms were given for the $\underline{n}$th-order perturbation term, $B_{2n}$. The explicit evaluation of $B_{2n}$ when $n > 2$ for any potential is in general a formidable task. The second-order term, however, is sufficiently simple that the evaluation may often be accomplished.

In this section $B_{22}$ will be evaluated for a few potentials in order to exhibit the diffraction corrections, and to indicate the analyticity as a function of $\lambda^2$, hence also of $\hbar^2$. For the evaluation of $B_{22}$ the momentum space form (11) is the easiest to use.

The unpleasant function $F_n(\lambda \underset{\sim}{k}_1, \ldots, \lambda \underset{\sim}{k}_{n-1})$ defined by Eq. (12) may be expressed in terms of known functions for n = 2. It is:

$$F_2(\lambda \underset{\sim}{k}) = \frac{1}{2}\int_0^1 dv\ e^{-\kappa^2 v(1-v)} ,$$

$$= \frac{1}{2}(2/\kappa)\ e^{-\kappa^2/4}\ \mathrm{Erfi}(\kappa/2) , \tag{21}$$

$$= \frac{1}{2}\sum_{s=1} \frac{(-1)^s \kappa^{2s}}{2^s(2s+1)!!} ,$$

where $\kappa = \lambda k$, and $\mathrm{Erfi}(a) = \int_0^a dt e^{t^2}$ is the imaginary error function. $F_2$ has the following asymptotic expansion for large real $\kappa$:

$$F_2 = \frac{1}{2}\left[\frac{2}{\kappa^2} + \frac{2^2}{\kappa^4} + \ldots + \frac{2^n(2n-3)!!}{\kappa^{2n}}\right] . \tag{22}$$

The expression (11) for the second-order term may also be found in the work of Montroll and Ward.[16] They develop their results for certain terms in the perturbation expansion of the partition function of a many-body system by using the pair interaction propagator. For Boltzmann statistics the pair propagator is $G(\lambda \underset{\sim}{k}, \beta' - \beta'') = N\beta \exp[-\lambda^2 k^2 v(1 - v)]$ where N is the number of particles of the system and $v = (\beta' - \beta'')/\beta$. Because of the symmetry property of the propagator, $G(\underset{\sim}{k}, \beta - (\beta' - \beta'')) = G(\underset{\sim}{k}, \beta' - \beta'')$, it may be expanded in Fourier series, $G = N\beta\Sigma_t L_t(\kappa^2) \exp(2\pi i t v)$. The Fourier components are:

$$L_t(\kappa^2) = \int_0^1 dv \exp[2\pi i t v - \kappa^2 v(1 - v)] . \tag{23}$$

Thus, $F_2(\underline{k})$ is the $\underline{0}$th component of the pair propagator, $F_2 \equiv 1/2\, L_0(\kappa^2)$.

The second-order perturbation term to be evaluated is:

$$B_{22} = -\frac{\beta^2}{4}\int_0^\infty \frac{4\pi k^2\, dk}{(2\pi)^3}\,(Vu(k))^2 L_0(\lambda\!\!\!^-{}^2 k^2)\;. \tag{24}$$

Note from the series expansion (21) of $L_0$ that the integrand of Eq. (24) is an analytic function of $\lambda\!\!\!^-{}^2$. The resulting function of $\lambda\!\!\!^-$ after the integration is not necessarily analytic in $\lambda\!\!\!^-{}^2$.

As the first example we consider $B_{22}$ for the exponential potential, $u(r) = g_0\, e^{-r/r_0}$. Its Fourier transform is $Vu(k) = 8\pi r_0{}^3 g_0/(1 + k^2 r_0{}^2)^2$. After changing the integration variable to $x = kr_0$, $B_{22}$ becomes:

$$B_{22} = -\frac{r_0{}^3(8\pi\,\beta g_0)^2}{8\pi^2}\int_0^\infty \frac{x^2\, dx\, L_0(\gamma^2 x^2)}{(x^2+1)^4} \tag{25}$$

with $\gamma = \lambda\!\!\!^-/r_0$. The diffraction effects may not be obtained by integrating term by term the expansion of $L_0(\gamma^2x^2)$ since all terms beyond $0(\gamma^4)$ are divergent. Integrals of this type may be evaluated in the following manner:

$$\begin{aligned} H_r(\gamma) &= \int_0^\infty \frac{x^2\, dx\, L_0(\gamma^2 x^2)}{(x^2+1)^r}\;, \\ &= \int_0^\infty x^2\, dx\, L_0(\gamma^2x^2)\,\frac{(-1)^{r+1}}{(r-1)!}\,\frac{d^{r-1}}{da^{r-1}}\,\frac{1}{(x^2+a)}\bigg|_{a=1}\;, \\ &= \frac{(-1)^{r+1}}{(r-1)!}\,\frac{d^{r-1}}{da^{r-1}}\,aH(\gamma,a)\bigg|_{a=1}\;, \end{aligned} \tag{26}$$

with

$$\begin{aligned} H(\gamma,a) &= \int_0^\infty \frac{dx\, L_0(\gamma^2x^2)}{x^2+a} = \int_0^1 dv \int_0^\infty \frac{dx\, \exp[-\gamma^2x^2 v(1-v)]}{x^2+a}\;, \\ &= \int_0^1 dv\, \theta\left\{\frac{\pi}{2}\,\frac{e^{a\theta^2}}{a^{1/2}\theta} - \sqrt{\pi}\, e^{a\theta^2}\,\frac{\mathrm{Erf}(a^{1/2}\theta)}{a^{1/2}\theta}\right\}, \end{aligned} \tag{27}$$

where $\theta^2 = \gamma^2 v(1 - v)$.[17] After carrying out the differentiations indicated in Eq. (26) one obtains for Eq. (25):

$$B_{22} = -\frac{2\pi}{3} r_0{}^3(\beta g_0)^2 \left\{ \sum_{m=0} \frac{(m + 1/2)(m - 1/2)(m - 3/2)\gamma^{2m}}{2^m(2m + 1)!!} - \frac{\sqrt{\pi}\gamma^5 e^{\gamma^2/4}}{64} \right\} . \quad (28)$$

This result (28) consists of an expected analytic function of $\gamma^2$ plus another analytic function multiplied by the nonanalytic form $(\gamma^2)^{1/2}$. The summation in Eq. (28) is the expansion of

$$\frac{3}{8} - \frac{\gamma^2}{16} + \frac{\gamma^4}{32} + \frac{\gamma^6}{64} L_0(-\gamma^2) ,$$

where $L_0(-\gamma^2)$ as defined by Eq. (23) for imaginary argument is $(2/\gamma)e^{\gamma^2/4}\mathrm{Erf}(\gamma/2)$. Consequently, the odd and even powers of $\gamma$ in the braces of Eq. (28) may be combined into one function:

$$\left\{ \quad \right\} = \frac{3}{8} - \frac{\gamma^2}{16} + \frac{\gamma^4}{32} - \frac{\gamma^5}{32} e^{\gamma^2/4}\mathrm{Erfc}(\gamma/2) . \quad (29)$$

As a contrast to the exponential potential we next consider the Gaussian potential, $u(r) = g_0 e^{-r^2/r_0{}^2}$, which has the Fourier transform, $Vu(k) = \pi^{3/2} r_0{}^3 g_0 \exp - (kr_0)^2/4$. Since u(k) is also Gaussian, $B_{22}$ may be evaluated by expanding $L_0(\gamma^2 x^2)$ and integrating term by term. One obtains:

$$\begin{aligned} B_{22} &= -\frac{(\beta g_0)^2 r_0{}^3}{8\pi^2} \int_0^\infty dx\, x^2(\pi^{3/2} e^{-x^2/4})^2 L_0(\gamma^2 x^2) , \\ &= -\frac{\pi}{8}(\beta g_0)^2 r_0{}^3 \sum_{m=0} \frac{(-1)^m \gamma^{2m}}{2^m(2m + 1)!!} \int_0^\infty dx\, x^{2m+2} e^{-x^2/2} , \quad (30) \\ &= -\frac{(2\pi)^{3/2}}{32} \frac{(\beta g_0)^2 r_0{}^3}{1 + \gamma^2/2} , \end{aligned}$$

which is an analytic function of $\gamma^2$.

The reason for the different analyticity properties of the two forms (28) and (30), for the two potentials lies in the behavior as $r \to 0$. The

Gaussian form and all of its derivatives are smooth as $r \to 0$, whereas the exponential form has a cusp at $r = 0$. As functions of a complex variable $z$, one notes that $e^{-z^2}$ is analytic at $z = 0$, while $e^{-|z|}$ is nonanalytic since its first derivative is discontinuous at $z = 0$. In the Fourier transform the cusp of $e^{-r/r_0}$ is manifested by the second-order pole of $u(k) \propto (k^2 + 1/r_0{}^2)^{-2}$ at $i/r_0$.

In general, the second-order perturbation term will be an analytic function $h^2$ for any potential that is smooth at $r = 0$, for example, $r^m e^{-r^2/r_0{}^2}$, while some nonanalytic form of $h^2$ will appear for any potential that has a cusp in any derivative. For example, $r^m e^{-r/r_0}$ has a cusp in the mth derivative at $r = 0$. (Its Fourier transform has a pole of order $m + 2$ at $i/r_0$.) $B_{22}$ can be evaluated for $u(r) \propto r^m e^{-r/r_0}$ for any integer m using Eq. (26); the first nonanalytic form to appear is of order $\gamma^{4m+5}$.

An interesting example of a potential with a cusp not at $r = 0$ is the square barrier:

$$u(r) = g_0 \qquad r < r_0$$
$$\quad = 0 \qquad r > r_0$$

which has the Fourier transform $Vu(k) = 4\pi g_0 r_0{}^3 (kr_0)^{-1} j_1(kr_0)$ where $j_1(x)$ is a spherical Bessel function. The second-order perturbation term for this potential is:

$$\begin{aligned} B_{22} &= -\frac{r_0{}^3(4\pi\beta g_0)^2}{8\pi^2} \int_0^\infty dx\, j_1{}^2(x)\, L_0(\gamma^2 x^2) \\ &= -\pi r_0{}^3(\beta g_0)^2 \left[ \frac{1}{3} - \frac{\gamma}{4}\,\mathrm{Erf}(2/\gamma) + \frac{\gamma^3}{32}\,\mathrm{Erf}(2/\gamma) - \frac{\gamma^2}{16}\, e^{-4/\gamma^2} \right] . \end{aligned} \tag{31}$$

Some details of the integration required to obtain Eq. (31) are given in an appendix. For small $\gamma$ the expression in brackets in Eq. (31) becomes

[ ] $= 1/3 - \sqrt{\pi}\,\gamma/8 + \sqrt{\pi}\,\gamma^3/64$. Again the diffraction corrections to the classical result are nonanalytic in $\gamma^2$.

Next we consider the screened Coulomb potential, $u(r) = (g_1/r)\, e^{-r/r_0}$, which has the Fourier transform $Vu(k) = 4\pi g_1 r_0^{\,2}/(k^2 + 1/r_0^{\,2})$. This potential has not just a cusp but an infinite spike at $r = 0$. According to the rule discussed in a previous paragraph a result nonanalytic in $\gamma^2$ is to be expected; the first nonanalytic diffraction correction should be of $O(\gamma)$. Also, as was discussed in the Introduction, nonanalytic behavior for the $1/r$ singularity is indicated even by the WK expansion parameter $\eta^2$ which increases linearly with temperature. The integration of $B_{22}$ for this potential is easily worked out by using Eq. (26). The result is:

$$
\begin{aligned}
B_{22} &= -\frac{r_0^{\,3}(4\pi\beta g_1/r_0)^2}{8\pi^2}\int_0^\infty \frac{x^2\, dx\, L_0(\gamma^2 x^2)}{(x^2+1)^2} \\
&= -\frac{1}{2}\pi r_0^{\,3}(\beta g_1/r_0)^2\left\{\left[1 + (\gamma^2/2)L_0(-\gamma^2)\right] - \sqrt{\pi}(\gamma/2)e^{\gamma^2/4}\right\}.
\end{aligned}
\tag{32}
$$

Equation (32) has the expected form similar to the result for the exponential potential, i.e., the power series expansion of the function in braces contains both even and odd powers of $\gamma$. By using the definition of $L_0(-\gamma^2)$ in terms of the error function, the expression in braces of Eq. (32) may be written as:

$$
\{\quad\} = 1 - \gamma e^{\gamma^2/4}\,\mathrm{Erfc}(\gamma/2)\,. \tag{33}
$$

The second form (33) is convenient for obtaining an asymptotic expansion for large $\gamma$; it begins with $2/\gamma^2$. This limit means $\lambda\!\!\!^{-} \gg r_0$ and is not interesting physically since quantum statistics have not been considered.

Some remarks about the electron gas at finite temperature are in order at this point. In the electron gas the interaction potential is the unscreened Coulomb potential, $e^2/r$. Electrical neutrality is maintained by the assumption of a continuous background of positive charge equal to the charge of N electrons in a volume V. Since every term of the perturbation expansion of the partition function in powers of $e^2/r$ is divergent (because of the infinite range of the interaction) finite results for the free energy are obtained by selective summation of terms in perturbation expansion. It is well known that the sum of the most divergent part of each cluster integral, the sum of the ring diagrams, gives the Debye-Huckel free energy. The fundamental lengths of the electron gas are $\ell = \beta e^2$, the Debye screening length $\lambda_D = (4\pi\beta e^2\rho)^{-1/2}$ which replaces $r_0$, and the thermal wavelength. The free energy of the classical gas is a function of the ratio of the two classical lengths, $\Lambda = \beta e^2/\lambda_D = 2\pi^{1/2}\beta^{3/2}\rho^{1/2}e^3$. The Debye-Huckel contribution to $\beta F = -\log Z$ is $-2/3\, N\Lambda$. It is the leading interaction term when $\Lambda \ll 1$; note that it is nonanalytic in $\rho$ and $e^2$, i.e., $\Lambda$ involves $\rho^{1/2}$ and $(e^2)^{3/2}$. Diffraction corrections will be in a function of the ratio $\gamma = \lambda/\lambda_D$ multiplying the classical Debye term. The WK expansion cannot be used to find the diffraction corrections since the WK expansion parameter, $\eta^2 = (\lambda/\beta e^2)^2$, diverges as $\beta^{-1}$ at high temperature. Instead, the diffraction corrections must be found by an evaluation of the quantum mechanical ring sum.[16,18] There is an analogy between the quantum ring sum for the electron gas and the second-order perturbation term for the static screened Coulomb potential. However, the mathematical expression for the ring sum is far more complicated than $B_{22}$, and important additional physical effects due to plasma oscillations are described by it. Since the Coulomb potential has a spike at $r = 0$ (and its Fourier transform, $Vu(k) = 4\pi e^2/k^2$, has a double pole at $k = 0$), it is to be expected that the function of $\gamma^2$ multiplying the classical Debye term will be nonanalytic in $\gamma^2$ in exactly the same manner as Eq. (32) is nonanalytic. This nonanalyticity, the appearance of both even and odd powers of $\gamma$ in the diffraction corrections to the Debye term, has already been reported.[19] The explicit evaluation will be given in a forthcoming publication. Because of the complexity of the mathematical expressions in the quantum ring sum, it is not possible to obtain the diffraction corrections in closed form as in Eqs. (32) or (33), but instead only as two convergent series, one involving $\gamma^{2m}$ and the other $(\gamma^2)^{m+1/2}$.

## IV. EVALUATION OF TERMS IN THE WK EXPANSION

In this section the evaluation of a few terms of the WK expansion will be described for the singular potential $\beta u(r) = (\beta g_p/r^p)e^{-r/r_0} = x^{-p}e^{-\Lambda x}$ with $x = r/\ell$. Specifically, we need the coefficients $C_m(\Lambda)$ of $\eta^{2m}$ in Eq. (5). The coefficients $C_0$, $C_1$, and $C_2$ have been evaluated for the Lennard-Jones potential in the form of infinite series of gamma functions, and for other more complicated potentials used in the theory of nonideal gases they have been evaluated numerically.[4] The usefulness of these results is somewhat limited by the fact that little is known about the convergence of the WK expansion. The simple singular potential to be discussed here does not correspond well to any physical problem, but the results do show the dependence of the coefficients $C_m(\Lambda)$ on the order of the singularity and thus give a little more information about the convergence of the expansion.

The coefficients in Eq. (5) may be evaluated readily by the use of the Mellin transform, an elegant and useful method in statistical mechanics recently pointed out by Iwata.[20] The Mellin transformation of the exponential series is:

$$\sum_{n=r} \frac{(-U)^n}{n!} = \frac{1}{2\pi i}\int_{\sigma-i\infty}^{\sigma+i\infty} ds\,\Gamma(s)U^{-s} \qquad -r < \sigma < -(r-1)\,. \tag{34}$$

In our use of this transform, the contour of integration is deformed to enclose the entire negative real axis to the left of $-(r - 1)$. For the evaluation of the $C_m(\Lambda)$, the exponential $e^{-U}$ in the integrand is expanded with Eq. (34) and the order of x and s integration inverted.

The classical second virial coefficient, $C_0(\Lambda)$ from Eq. (6) is:

$$C_0(\Lambda) = \frac{1}{2\pi i}\int_C ds\,\Gamma(s)\int_0^\infty x^2\,dx\,(x^{-p}e^{-\Lambda x})^{-s} \tag{35}$$

subject to $-1 < \mathrm{Re}(s) < 0$ since $e^{-U} - 1$ is being expanded. With the change of variable $y = -\Lambda sx$, the x integral in Eq. (35) becomes a gamma function, and the result is:

$$C_0(\Lambda) = \frac{1}{2\pi i}\int_C ds\,\Gamma(s)\Gamma(ps + 3)(-s\Lambda)^{-(ps+3)}\,. \tag{36}$$

The result is obtained by summing the residues of all poles to the left of $s = 0$. The integrand has first-order poles when $ps + 3 = 0, -1, -2, \ldots, -t$ but s is not an integer; it has second-order poles when $s = -1, -2, \ldots$ . The residues of the first-order poles are $0(\Lambda^t)$ while the residues of the second-order poles are nonanalytic in $\Lambda$. The complete result is:

$$C_0(\Lambda) = \frac{\pi}{p}\sum_{\gamma_p=0}^{p-1}{}' \frac{(-1)^{\gamma_p+1}}{\sin\pi(\gamma_p+3)/p}\sum_{t=0}^{\infty}\frac{(-1)^{t(p+1)}\{[t+(\gamma_p+3)/p]\Lambda\}^{pt+\gamma_p}}{\Gamma[t+1+(\gamma_p+3)/p]\Gamma(1+pt+\gamma_p)}$$

$$+\sum_{t=0}\frac{(-1)^{(p+1)t+p-1}[(t+1)\Lambda]^{pt+p-3}}{\Gamma(t+2)\Gamma(pt+1+p-3)}\left\{\log(t+1)\Lambda + 1 - 3/p(t+1) - \frac{\Gamma'(t+2)}{p\Gamma(t+2)} - \frac{\Gamma'(pt+p-2)}{\Gamma(pt+p-2)}\right\}, \tag{37}$$

where $\gamma_p = 0, 1, 2, \ldots, p-4, p-2, p-1$. The prime on the summation indicates that the value $\gamma_p = p - 3$ is to be excluded; for this value the integrand has double poles, and the second summation in Eq. (37) gives these residues. This expression (37) is general for $p \geq 3$. For $p = 2$, however, in addition to Eq. (37) there is a residue from the simple pole at $s = -1$ which is $-\Lambda^{-1}$. This additional term is the first-order perturbation term, i. e.,

$\int_0^\infty x^2\, dx(-x^{-2}e^{-\Lambda x}) = -\Lambda^{-1}$. Similarly, for the screened Coulomb potential, $p = 1$, the first two orders of perturbation theory are finite and are given by the residues of the simple poles at $s = -1$ and $-2$.

The coefficient of the first diffraction correction, $C_1(\Lambda)$, is evaluated by the same method. It is:

$$C_1(\Lambda) = \frac{1}{12}\int_0^\infty x^2\, dx \exp(-x^{-p}e^{-\Lambda x})\left(\frac{d}{dx}x^{-p}e^{-\Lambda x}\right)^2 ,$$

$$= \frac{1}{12}\int_C \frac{ds}{2\pi i}\Gamma(s)\int_0^\infty x^2\, ds(x^{-p}e^{-\Lambda x})^{-s}[p^2x^{-(2p+2)} + 2p\Lambda x^{-(2p+1)} + \Lambda^2 x^{-2p}] . \tag{38}$$

The contour for Eq. (38) crosses the real s axis to the right of $s = 0$. With the change of variable $y = -(s - 2)\Lambda x$, Eq. (38) becomes:

$$C_1(\Lambda) = \frac{1}{12}\int_C \frac{ds}{2\pi i}\Gamma(s)\Big\{p^2[-(s-2)\Lambda]^{-(ps-2p+1)}\Gamma(ps-2p+1)$$
$$+ 2p\Lambda[-(s-2)\Lambda]^{-(ps-2p+2)}\Gamma(ps-2p+2) + \Lambda^2[-(s-2)\Lambda]^{-(ps-2p+3)}$$
$$\Gamma(ps-2p+3)\Big\} . \tag{39}$$

The first few terms in $\Lambda$ are:

$$C_1(\Lambda) = \frac{1}{12}\Big\{[p\Gamma(2-1/p) - (\Lambda^2/2p)\Gamma(2-3/p) + \ldots] + \frac{(-1)^{3(p+1)}(3\Lambda)^{3p-1}}{\Gamma(3p)\Gamma(2)}$$
$$\times\left[\log 3\Lambda + 1 - 1/3p - \frac{\Gamma'(2)}{p\Gamma(2)} - \frac{\Gamma'(3p)}{\Gamma(3p)}\right] + \ldots\Big\} . \tag{40}$$

The complete result for Eq. (39) is easily obtained by summing all residues from the first- and second-order poles of the integrand. It is a lengthy result and is not written down since it is not needed.

The coefficient of $\eta^4$ as defined by Eq. (1) is:

$$C_2(\Lambda) = \frac{1}{1440}\int_0^\infty x^2\, dx\, e^{-U}\left[((\nabla_x U)^2)^2 - 8(\nabla_x U)^2\nabla_x{}^2U + 12(\nabla_x{}^2U)^2\right] . \tag{41}$$

A more convenient form for computational purposes is obtained by using

$\nabla_x^2 U = U'' + (2/x)U'$, and then integrating by parts the terms $U'^2U''$ and $U'U''/x$. The result is:

$$C_2(\Lambda) = \frac{1}{120}\int_0^\infty x^2\, dx\, e^{-U}\left[-\frac{5}{36}U'^4 + \frac{10}{3}\frac{U'^3}{x} + \frac{2U'^2}{x^2} + U''^2\right]. \tag{42}$$

With $U = x^{-p}e^{-\Lambda x}$, the same procedure used for $C_1(\Lambda)$ gives, after some algebra:

$$\begin{aligned}C_2(\Lambda) = \frac{1}{1440}\int_C \frac{ds}{2\pi i}\Gamma(s)\Big\{&-\frac{5}{3}\Big[p^4\Gamma(ps-4p-1)[-(s-4)\Lambda]^{-(ps-4p-1)}\\
&+4p^3\Lambda\Gamma(ps-4p)[-(s-4)\Lambda]^{-(ps-4p)} + 6p^2\Lambda^2\Gamma(ps-4p+1)[-(s-4)\Lambda]^{-(ps-4p+3)}\\
&+4p\Lambda^3\Gamma(ps-4p+2)[-(s-4)\Lambda]^{-(ps-4p+2)} + \Lambda^4\Gamma(ps-4p+3)[-(s-4)\Lambda]^{-(ps-4p+3)}\Big]\\
&-\frac{40}{3}\Big[p^3\Gamma(ps-3p-1)[-(s-3)\Lambda]^{-(ps-3p-1)} + 3p^2\Lambda\Gamma(ps-3p)[-(s-3)\Lambda]^{-(ps-3p)}\\
&+3p\Lambda^2\Gamma(ps-3p+1)[-(s-3)\Lambda]^{-(ps-3p+1)} + \Lambda^3\Gamma(ps-3p+2)[-(s-3)\Lambda]^{-(ps-3p+2)}\Big]\\
&+12\Big[p^2((p+1)^2+2)\Gamma(ps-2p-1)[-(s-2)\Lambda]^{-(ps-2p-1)} + (4p^2(p+1)+4p)\\
&\times\Lambda\Gamma(ps-2p)[-(s-2)\Lambda]^{-(ps-2p)} + (2p(p+1)+4p^2+2)\Lambda^2\Gamma(ps-2p+1)\\
&\times[-(s-2)\Lambda]^{-(ps-2p+1)} + 4p^2\Lambda^3\Gamma(ps-2p+2)[-(s-2)\Lambda]^{-(ps-2p+2)}\\
&+\Lambda^4\Gamma(ps-2p+3)[-(s-2)\Lambda]^{-(ps-2p+3)}\Big]\Big\}.\end{aligned} \tag{43}$$

Each term in this lengthy expression may be evaluated by summing the residues of first- and second-order poles. We give only the value of the leading term:

$$C_2(\Lambda) = \frac{p(2p^2 - 11p + 21)}{1440}\Gamma(2 + 1/p) + \dots . \tag{44}$$

Collecting the previous results gives the second virial coefficient for $U = x^{-p}$ valid for $p > 3$ as:

$$B_2 = -2\pi \ell^3 \left\{ -\frac{\pi}{p \sin 3\pi/p} \frac{1}{\Gamma(1+3/p)} - \frac{p\eta^2}{12}\Gamma(2-1/p) + \frac{(2p^3 - 11p^2 + 21p)\eta^4}{1440} \times \Gamma(2+1/p) + \ldots \right\} . \quad (45)$$

Although it has not been possible to obtain a general term for this expansion, it is clear that the form of the general term for large p is $p^{2m-1}\eta^{2m}$. Thus the convergence of the WK expansion for any given value of $\eta^2$ depends strongly on the order of the singularity of the repulsive core of the potential.

The limit of large p is interesting because the potential $g_p r^{-p}$ becomes equivalent to a hard sphere with radius $r_0 = \lim (\beta g_p)^{1/p}$ as $p \to \infty$. The first term in Eq. (45) reduces to $(2/3)\pi r_0^3$, the classical hard sphere second virial coefficient. Thus, WK expansion when fully evaluated could give the diffraction corrections to the hard sphere second virial coefficient at high temperature. For large p Eq. (45) becomes:

$$B_2 = -2\pi r_0^3 \left\{ -1/3 - \eta \left[ \frac{p\eta}{12} - \frac{(p\eta)^3}{720} + \ldots \right] \right\} , \quad (46)$$

where $\eta = ƛ/r_0$. It appears from the numerical values of the first two diffraction terms in Eqs. (45) and (46) that the WK expansion is a convergent series in powers of $p\eta$, although nothing can be said about the radius of convergence. It is possible that the limit of the square bracket in Eq. (46) as $p \to \infty$ is finite and nonzero, in which case the diffraction corrections to the hard sphere virial coefficient are nonanalytic in $\eta^2$. This result seems very probable in view of the nonanalytic result (31) for $B_{22}$ with a barrier potential of finite height. It should be noted that most recent work on the quantum mechanical hard sphere gas has been at low temperature so that $ƛ$ is much greater than the hard sphere radius. Thus, in the work of Yang and Lee[21] the expansion parameter is $r_0/ƛ$, rather than $ƛ/r_0$. We hope to study the hard sphere gas at high temperature, $ƛ << r_0$, in more detail in a later publication.

## V. THE SCREENED COULOMB POTENTIAL

The screened Coulomb potential must be considered separately from the more singular potentials treated in the previous section since the WK expansion parameter, $\eta^2$, is large at high temperature. The diffraction corrections to the classical limit of the second virial coefficient for this potential must be expressed in powers of $\gamma = \eta\Lambda = \kappa/r_0$, which goes to zero as $\beta^{1/2}$ at high temperature. The classical value of $B_2$ is obtained from Eq. (37) with p = 1 and with the additional residues of the two simple poles at s = -1 and -2. It is:

$$B_2 \text{ classical} = -2\pi(\beta g_1)^3 C_0(\Lambda)$$

$$= -2\pi r_0^3 \left\{ -\Lambda + \frac{1}{4}\Lambda^2 + \sum_{r=1} \frac{\Lambda^{r+2}(r+2)^{r-1}}{\Gamma(r+3)\Gamma(r)} \left[ \log (r+2)\Lambda + 2C - 2h_r + \frac{r^3+2}{r(r+1)(r+2)} - \frac{1}{r+2} \right] \right\}. \tag{47}$$

In obtaining Eq. (47) from Eq. (37) the relation $\Gamma'(r+1)/\Gamma(r+1) = -C + h_r$ with $h_r = 1 + 1/2 + \ldots + 1/r$ has been used. The first two terms of Eq. (47) are the first and second orders of the perturbation expansion (from the residues of the simple poles at s = -1 and -2). The higher orders of the perturbation expansion are individually infinite, but their sum gives the nonanalytic form $\Lambda^{r+2} \log \Lambda$. The summation in Eq. (47) is identical with Iwata's[20] result, the $S_2$ integral of Abe's[22] modified cluster expansion for the classical electron gas.

This section is devoted to obtaining diffraction corrections to Eq. (47). The first-order perturbation term is always classical. The diffraction corrections to the second-order term were obtained in closed form in Section III, Eqs. (32) and (33) and found to be nonanalytic in $\gamma^2$, i.e., they involve both even and odd powers of $\gamma$. Our problem then is to find diffraction corrections to the $\Lambda^{r+2}\log\Lambda$ terms in Eq. (47). One conceivable approach is to evaluate every order of the quantum perturbation expansion and sum them. (The third order begins with $\Lambda^3 \log\gamma$ and the higher orders with $\Lambda^n/\gamma^{n-3}$.) Such an approach is approximately as difficult as solving a quantum mechanical scattering problem by calculating the nth order Born approximation and summing the Born series. Instead, it will be shown how the WK expansion may be used, even though at first glance the $1/r$ singularity appears to be too weak to allow the WK expansion.

Let us first consider what happens when the screened Coulomb potential is used blindly in the evaluation of the WK expansion coefficients $C_m(\Lambda)$. The general form may be shown to be:

$$C_m(\Lambda) = \sum_{s=0}^{2m-1} a_{ms}\Lambda^s + \Lambda^{2m-1}\sum_{r=1}^{\infty} \Lambda^r(b_{mr}\log\Lambda + c_{mr}) . \qquad (48)$$

The calculation of the coefficients $a_{ms}$, $b_{mr}$, and $c_{mr}$ in Eq. (48) is feasible in any order with such expressions as Eq. (39) and (43), but is very tedious even for m = 2. For example, the complete result for $C_1(\Lambda)$ obtained from Eq. (39) with p = 1 is:

$$C_1(\Lambda) = \frac{1}{12}(1 - \Lambda/2) - \frac{1}{12}\sum_{r=1}^{\infty}\frac{\Lambda^{r+1}(r+2)^{r-1}}{\Gamma(r+2)\Gamma(r)}\left[\log(r+2)\Lambda + 2C - 2h_r - \frac{r^3+2}{r(r+1)(r+2)}\right] . \qquad (49)$$

The series in Eq. (49) closely resembles the series in the classical expression (47). Both series are rapidly convergent. The limit of $C_1(\Lambda)$ as $\Lambda \to 0$ is 1/12.

The infinite sum in Eq. (48) comes from the residues of second-order poles, and the finite sum comes from the 2m simple poles all lying to the right of the second-order poles on the real s axis. The diffraction corrections from the finite sum are of order $\eta^{2m}\Lambda^{s}$ and have temperature dependence of $\beta^{-m+s}$; thus they become large at high temperature for $s < m$. The diffraction corrections from the infinite sum, however, are of order $\eta^{2m}\Lambda^{2m-1+r} = \gamma^{2m}\Lambda^{r-1}$ and are small at high temperature. In fact, the finite sum in Eq. (48) contributes only to the second-order perturbation term, $B_{22}$, and the divergence at high temperature of $\eta^{2m}\Lambda^{s}$ is just what is needed to give the nonanalytic form $(\gamma^2)^{1/2}$ which appears in $B_{22}$. The infinite sum gives the quantum corrections to the third and higher orders of the perturbation expansion, i. e., the desired diffraction corrections to the $\Lambda^{r+2}\log\Lambda$ terms in Eq. (47). These diffraction corrections are analytic in $\gamma^2$.

There is no point in giving a direct proof that $\Sigma_m \eta^{2m} C_m(\Lambda)$ with only the finite sum part of Eq. (48) does indeed reproduce $B_{22}$. Instead, the proper procedure is to subtract out of the second virial coefficient the first and second orders of the perturbation expansion, and make a WK expansion of the remainder. Thus we define:

$$B_2' = \sum_{n=3} B_{2n} = -2\pi(\beta g_1)^3 \sum_{m=0} \eta^{2m} C_m'(\Lambda) , \tag{50}$$

and use Eq. (18) for $B_{2n}$. The coefficients $C_m'(\Lambda)$ where the prime indicates the removal of first- and second-order perturbation theory are defined as:

$$-2\pi(\beta g_1)^3 \eta^{2m} C_m'(\Lambda) = \sum_{n=3} B_{2n}^{(m)} .$$

In Section II only $B_{2n}^{(0)}$ and $B_{2n}^{(1)}$ were explicitly evaluated. By summing Eq. (18), and (19) from n = 3 one obtains for the modified second virial coefficient:

$$B_2' = -\frac{1}{2}\left\{\int d^3r \left[\left(e^{-U} - 1 + U - \frac{U^2}{2}\right) - \frac{\lambda\!\!\!^{-2}}{12}(\nabla U)^2(e^{-U} - 1) + 0(\lambda\!\!\!^{-4})\right]\right.$$
$$\left. + \frac{\lambda\!\!\!^{-2}}{12}\lim_{\delta\to 0} 4\pi\delta U'(\delta)U(\delta)\right\} , \tag{51}$$

instead of Eq. (20). The surface term in Eq. (19) must be retained in order that the $0(\lambda^2)$ term in Eq. (51) be finite. The singularity in the integral coefficient of $\lambda^2$ is cancelled by the surface term for the $1/r$ potential. The terms of the WK expansion of $B_2'$ are calculated as described in the previous section with the help of the Mellin transform of the exponential series. Thus $C_0'(\Lambda)$ is defined as in Eq. (35), but the condition on the contour of the s integration is $-3 < \mathrm{Re}(s) < -2$ where the contour crosses the real axis. Thus the simple poles at $s = -1$ and $-2$ are not included and the result for $C_0'(\Lambda)$ is the infinite sum in Eq. (47). Similarly, $C_1'(\Lambda)$ is given by Eq. (39), but with the restriction that $-1 < \mathrm{Re}(s) < 0$ where the contour crosses the real axis. Again this restriction eliminates the simple poles and leaves only the second-order poles within the contour. Thus $C_1'(\Lambda)$ is equal to the infinite sum in Eq. (49). Similarly, for arbitrary m the subtraction of second-order perturbation theory leaves only the second-order poles within the contour, and $C_m'(\Lambda)$ is equal to the infinite sum indicated in Eq. (48).

In this paper only the $0(\lambda^2)$ corrections to $B_2'$ have been evaluated explicitly. The $0(\lambda^4)$ corrections may be obtained as the residues of the second-order poles of Eq. (43) with $p = 1$. Higher-order corrections must await the evaluation of more terms of the WK expansion. Our complete result for $B_2$ for the screened Coulomb potential including the second-order term is:

$$
\begin{aligned}
B_2 &= B_{21} + B_{22} + B_2' , \\
&= -2\pi r_0^3 \left\{ -\Lambda + \frac{1}{4}\Lambda^2 \left[ 1 + \frac{1}{2}\gamma^2 L_0(-\gamma^2) - \frac{1}{2}\sqrt{\pi}\,\gamma\, e^{\gamma^2/4} \right] + \sum_{r=1} \frac{\Lambda^{r+2}(r+2)^{r-1}}{(r+2)!(r-1)!} \right. \\
&\times \left[ \log(r+2)\Lambda + 2C - 2h_r + \frac{r^2+2}{r(r+1)(r+2)} - \frac{1}{r+2} \right] + \gamma^2 \sum_{r=1} \frac{\Lambda^{r+2}(r+2)^r}{(r+2)!(r-1)!} \\
&\left. \times \left[ \log(r+2)\Lambda + 2C - 2h_r + \frac{r^2+2}{r(r+1)(r+2)} \right] + 0(\gamma^4) \right\} .
\end{aligned}
\tag{52}
$$

In Section III it was pointed out that the quantum mechanical ring sum for the electron gas and $B_{22}$ for the screened Coulomb potential were rather similar. Diffraction corrections to both are nonanalytic in $\gamma^2$. In the same way there is a considerable similarity between $B_2'$ for the screened Coulomb potential and the quantum mechanical generalization of the Abe $S_2(\Lambda)$ contribution to the electron gas free energy.[22] The $S_2$ term is the next step in the rearrangement of the perturbation expansion of the partition function after the ring terms have been grouped together. It is the sum of three and more effective interactions between two electrons in the plasma. Each effective interaction is the sum of all possible chains of Coulomb interactions; the result is a screened Coulomb interaction with $r_0 = \lambda_D$ in the classical limit. Thus the classical form of $S_2$, Abe's result, is identical in form to $B_2'$ for the screened Coulomb potential.

The quantum theory of $S_2$ has not been completely developed yet, although it is implicit in the article by Montroll.[16] It seems clear, however, that diffraction corrections to $S_2$ must be calculated in the same manner that $B_2'$ in Eq. (52) was obtained, that is, by a WK expansion of $S_2$. This calculation is being carried out now.

## VI. CONCLUDING REMARKS

The main point of this article has been to show with specific examples that nonanalytic forms of $\hbar^2$ may appear in the diffraction corrections to the classical partition function of an interacting gas for some potentials. The analysis here has been limited for simplicity to the second virial coefficient, although some of our conclusions will apply also to the higher virial coefficients. No attempt has been made to give an exhaustive specification of what nonanalytic forms of $\hbar^2$ may appear. The following statements seem to be valid conclusions from the examples worked out. If the second-order perturbation term $B_{22}$ has a finite classical limit for a given potential, then the diffraction corrections to that classical limit include nonanalytic forms of $\hbar^2$ when the potential has a cusp or singularity in any derivative. For the examples of the square wall potential and the form $r^m e^{-r/r_0}$ this nonanalytic form is $(\hbar^2)^{1/2}$. This statement applies also to the Coulomb potential for a gas in three dimensions, since in three dimensions the spatial volume element, $4\pi r^2\, dr$, assures the finiteness of $B_{22}$ for the screened Coulomb potential and of the ring sum for the electron gas.

For potentials more singular at the origin than $1/r$, $B_{22}$ is infinite, and one must evaluate the entire second virial coefficient. The virial coefficient is nonanalytic in the coupling constant of the interaction, but the diffraction corrections are analytic in $\hbar^2$ and may be obtained as the first few terms of the WK expansion. Hence, the WK expansion is quite justified for calculating diffraction corrections to the virial coefficients of nonideal gases. The convergence of the expansion, however, depends strongly on the order of the singularity assumed in the intermolecular potential.

Any sharp corners in the potential will result in diffraction corrections that are nonanalytic in $\hbar^2$. The reason is that the WK expansion fails since its coefficients are integrals over derivatives of the potential and thus are delta functions and derivatives of delta functions. Thus the second virial coefficient for the square barrier potential has nonanalytic diffraction corrections, and so also does the hard sphere potential (a special case of the square barrier with the height of the barrier put to $\infty$) give rise to nonanalytic form $(\hbar^2)^{1/2}$.

The screened Coulomb interaction in three dimensions is particularly interesting since its second virial coefficient has two parts with different types of diffraction corrections. $B_{22}$ is finite classically, but because of the $1/r$ singularity its diffraction corrections involve both $\hbar^2$ and $(\hbar^2)^{1/2}$. The remainder of $B_2$, i. e., all higher orders of the perturbation expansion, is nonanalytic in the coupling constant ($g_1{}^3 \log g_1$), but the diffraction corrections are analytic in $\hbar^2$ since they may be calculated with the WK expansion. In one and two dimensions, however, all diffraction corrections to $B_2$ are analytic in $\hbar^2$ since $B_{22}$ is infinite. With this mathematical structure in mind, it is easy to make the extension to the electron gas for which $u(r) = e^2/r$. The ring sum which is analogous to $B_{22}$ must have nonanalytic diffraction corrections, while the diffraction corrections to the remaining orders of the perturbation expansion when appropriately grouped together (the Abe expansion) involve only powers of $\hbar^2$. It is believed that the method described in this article for using the WK expansion will have considerable utility in evaluating the theory of the quantum mechanical electron gas.

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## APPENDIX

The integral required for the second-order perturbation term (31) for the square wall potential is:

$$I = \int_0^\infty dx\ j_1(x)^2 L_0(\gamma^2 x^2) . \tag{A1}$$

In order to evaluate it, the square of the spherical Bessel function is written in terms of trigonometric functions,

$$j_1(x)^2 = x^{-4}\left[\frac{1}{2}(1 - \cos 2x) - x \sin 2x + \frac{1}{2} x^2 (1 + \cos 2x)\right] ,$$

and expanded in powers of x. Also the integral representation (23) of $L_0(\gamma^2 x^2)$ is used. Equation (A1) becomes:

$$I = \int_0^\infty dx\ 2^3 \sum_{n=3} \frac{(-1)^n (2x)^{2n-4}}{(2n-4)!}\left(\frac{1}{2n} - \frac{1}{4}\right)\int_0^1 dv\ e^{-\gamma^2 x^2 v(1-v)} , \tag{A2}$$

$$= \sqrt{\pi} \sum_{n=3} \frac{(-1)^n 2^{2n-3}}{(2n-3)}\left(\frac{1}{n!} - \frac{1}{2(n-1)!}\right)\int_0^{\pi/2} d\,(\sin\theta)(\gamma \cos\theta)^{-2n+3} .$$

The second line of Eq. (A2) is obtained by doing the x integration over the Guassian function first, and with the change of variable, $v = (1 + \sin\theta)/2$.

For each value of n, the $\theta$ integral in Eq. (A2) is divergent. This trouble is avoided by using the Mellin transform of the series in Eq. (A2); it becomes:

$$I = -\sqrt{\pi}\int_C \frac{ds}{2\pi i}\frac{2^{-2s+3}}{2s+3}\left[\Gamma(s) + \frac{1}{2}\Gamma(s+1)\right]\int_0^{\pi/2} d\,(\sin\theta)(\gamma\cos\theta)^{2s+3} , \tag{A3}$$

where the contour C encloses the entire real axis to the left of the point -3. The $\theta$ integration for arbitrary s is:

$$\int_0^{\pi/2} d\,(\sin\theta)\cos\theta^{2s+3} = \frac{\sqrt{\pi}}{2}\frac{\Gamma(s+5/2)}{\Gamma(s+3)} ,$$

so that Eq. (A3) becomes:

$$I = -\frac{\pi}{2}\int_C \frac{ds}{2\pi i}\,\frac{\gamma^{2s+3}}{2^{2s+3}}\,\frac{\Gamma(s+5/2)}{(s+2)(s+1)(2s+3)}\left(\frac{1}{s}+\frac{1}{2}\right) . \tag{A4}$$

The integrand of Eq. (A4) has only simple poles. After calculating the residues one obtains:

$$I = \frac{\pi}{2}\sum_{r=0} \frac{(-1)^r (2/\gamma)^{2r+2}}{(2r+3)(2r+5)(r+1)!} . \tag{A5}$$

Equation (A5) is the expansion of

$$\frac{\pi}{2}\left[\frac{1}{3} - \frac{1}{2a}\int_0^a dt\, e^{-t^2} + \frac{1}{2a^3}\int_0^a dt\, t^2 e^{-t^2}\right] , \tag{A6}$$

with $a = 2/\gamma$. Integrating the last terms of Eq. (A6) by parts gives the form recorded in Eq. (31).

## FOOTNOTES

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[6]For the unscreened Coulomb potential, the cluster integrals are all divergent because of the infinite range of $e^2/r$. The correct pressure expression includes the nonanalytic forms $\rho^{3/2}$ (the Debye-Huckel term) and $\rho^2 \log \rho$.

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$$e^{-a} \sum_{n=0} (-1)^n \int_0^1 dv_n \ldots \int_0^{v_2} dv_1 \, e^{av_n} b \, e^{-a(v_n - v_{n-1})} b \ldots b \, e^{-a(v_2 - v_1)} b \, e^{-av_1} .$$

When b is chosen to be the kinetic energy operator and a the potential energy, the WK expansion is obtained. Conversely, when b is the potential energy, the perturbation expansion is obtained.

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between their form and Eq. (21) of this paper. The factor of 2 in $L_0(2x^2)$ represents the change to the reduced mass of the two interacting particles, i.e., $2\beta\hbar^2k^2/2m = \beta\hbar^2k^2/2\mu = \lambda^2k^2$.

[17]The x integral in Eq. (27) after the change of variable $y = x^2$, is the Laplace transform of $y^{-1/2}(y + a)^{-1} \exp(-\theta^2 y)$ and is $(\pi/2)\, e^{1/2}\, e^{a\theta^2}\, \mathrm{Erfc}(a^{1/2}\theta)$. See Bateman Project Tables (McGraw-Hill Book Co., New York, 1953) Vol. I, p. 136, No. 24. In Eq. (27) we have used $\mathrm{Erfc}(y) = \sqrt{\pi}/2 - \mathrm{Erf}(y)$.

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