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WKB for coupled equations and virial coefficients^{a)}

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Using semiclassical expressions for eigenphase shifts and bound state energies arising from WKB approximations to the solutions of coupled equations, we show that quantum mechanical formulas for the third virial coefficient (restricted to positive potentials) and for the second virial coefficient (with anisotropic interactions) lead to the known classical results when \hbar goes to zero. The procedure can be extended to the case of higher virials.

INTRODUCTION

In this article we propose to follow in some of the footsteps of Kahn and Uhlenbeck.¹ Some time ago Uhlenbeck and Beth² and independently, Gropper³ obtained fully quantum mechanical (QM) formulas for the second virial coefficient of gases subject to spherical potentials. As part of his doctoral thesis, Kahn¹ then showed that, using WKB or semiclassical approximations for two-body phase shifts and bound state energies, one could recover from these QM formulas the well-known classical expression for the second virial, in the limit in which $\hbar \rightarrow 0$. Since, in the same limit, we expect the QM partition function to take the form of its (properly normalized) classical counterpart, this is a satisfactory result. The derivation of additional asymptotic terms (\hbar^2 and higher) and numerical evaluations of the basic formula then complemented the QM theory in a useful and desirable way.

Our aim in this paper is to show that generalizations of the formula of Uhlenbeck and Beth expressions for the third virial coefficient⁴ and for the second virial with anisotropic interactions⁵ reduce to the classical expressions, in the limit $\hbar \rightarrow 0$.

The formulations for the virials, from which we start, involve eigenphase shifts and eigenvalues which arise from the characterization of the solutions of coupled equations. These in turn are the results of expansions of the wave functions in terms of hyperspherical harmonics for the third virial or of products of spherical harmonics for the second virial. WKB expressions for phases and eigenvalues must then, perforce, involve a semiclassical treatment of the coupled equations.

We think that the results that we obtain are of some interest. To take the third virial, the formula from

which we start must clearly involve a three-body problem with its attendant difficulties. Buslaev and Merkuriev⁶ have stated that in the formulas for the cluster in terms of S matrices,⁷ additional terms should appear to "counter" singularities appearing in selected plane wave matrix elements of the S matrices which are involved. Dashen and Ma,⁷ in an analysis of the singularities, show that those appearing in the cluster expressions cancel out and that, further, they never appear if an angular momentum decomposition is carried out.

The fact that in our limit we recover the classical result does not, obviously, provide a proof of the primary QM formula. It does, however, meet a necessary requirement and increases our confidence in its correctness and usefulness.

Since numerical work involving the use of the basic formula is forthcoming, and, through other methods, QM corrections useful at high temperatures have been obtained, the paths of the 30's are perhaps being retraced for the higher virials.

SECOND VIRIAL: SPHERICAL POTENTIAL

To begin with, we state and modify the arguments of Kahn,¹ to simplify and generalize his reasoning. As is usual in the application of the semiclassical method one writes the solution of the time independent radial Schrödinger equation:

$$\frac{d^2\Psi}{dr^2} + \frac{2\mu}{\hbar^2} \left\{ E - \left[V(r) + \frac{\hbar^2}{2\mu} \frac{l(l+1)}{r^2} \right] \right\} \Psi = 0 \quad (1)$$

as

$$\Psi = \exp[(i/\hbar)S(r)],$$

where

$$S(r) = S_0 + \frac{\hbar}{i} S_1 + \left(\frac{\hbar}{i} \right)^2 S_2 + \dots \quad (2)$$

Taking into account terms up to S_1 only, using the connection formulas, and assuming that there is a left turning point, we obtain the semiclassical expression for the phase shifts:

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$$\eta_l(k) = \frac{1}{2}\pi(l + \frac{1}{2}) - kr_0 + \int_{r_0}^{\infty} [\sqrt{k^2 - f(r)} - k] dr, \quad (3)$$

where $f(r) = (2\mu/\hbar^2)V(r) + [(l + \frac{1}{2})^2/r^2]$, $k^2 = (2\mu/\hbar^2)E$, μ = reduced mass.

Equation (3) is slightly different from Kahn's in that we use Langer's modification which leads to $(l + \frac{1}{2})$ instead of $\sqrt{l(l+1)}$. The expression must also be generalized to the case of more turning points. This is not trivial and requires comment.

Let us first observe that Kahn, and Curtiss and Powers⁸ (using their formalism exploiting the behavior of the density matrix and its relationship to the derivative of the phase shifts), extend the integration in Eq. (3) wherever the wave function oscillates, i. e., wherever the argument of the square root is positive. Thus given three turning points, with a positive region in $[f(r) - k^2]$ between r_2 and r_3 , Eq. (3) becomes

$$\eta_l(k) = \frac{\pi}{2}(l + \frac{1}{2}) - kr_3 + \int_{r_3}^{\infty} dr + \int_{r_1}^{r_2} dr. \quad (4)$$

Actually Curtiss and Powers give their result for a reduced phase shift (essentially $\hbar\eta$) as a sum of functions of classical observables, energy and angular momentum, multiplied in higher order terms by powers of \hbar^2 or of the de Boer parameter squared. Their first order result, restated for any \hbar not equal to zero, leads immediately to Eq. (4).

Within the range of energy and angular momentum for which multiple turning points occur, the wave functions at any fixed value of the energy will pass through multiple resonances, as \hbar is made small, and the phase will increase by π at each resonance.

This must be taken into account. Curtiss' formula, which includes a contribution from the inner region does precisely that. It must be looked at, either as giving for a particular phase shift the result of the semiclassical limit as $\hbar \rightarrow 0$, or as giving (for small \hbar) the result of the average of the phase shift over a small range of the energy—large enough, however, to include many resonances.

From Eqs. (3) and (4) we can now proceed to calculate the continuum part of the Boltzmann second virial coefficient which is given by the following formulas^{1,2,9}:

$$B = \sum_{l=0}^{\infty} (2l+1)B_l$$

$$B_l = -\frac{\sqrt{2}}{\pi} N\lambda_T^3 \int_0^{\infty} dk \left[\frac{d}{dk} \eta_l(k) \right] \times \exp[-(\lambda_T^2/2\pi)k^2], \quad (5)$$

where the thermal wavelength λ_T is given by $\lambda_T^2 = \hbar^2/2\pi m\kappa T$; κ is Boltzmann's constant, T is the temperature.

We follow a more direct method than that used by Kahn, in order to obtain the classical limit of Eq. (5). First we perform an integration by parts and, using Levinson's theorem to evaluate the surface terms, obtain an additional bound state contribution:

$$B_l = -\frac{\sqrt{2}}{\pi} N\lambda_T^5 \int_0^{\infty} \left\{ \frac{\pi}{2}(l + \frac{1}{2}) - kr_0 + \int_{r_0}^{\infty} [\sqrt{k^2 - f(r)} - k] dr \right\} k \exp[-(\lambda_T^2/2\pi)k^2] dk \quad (6)$$

+ an additional bound state expression.

As we shall see, the case of more turning points will not cause problems. Assume for the moment that the potential is never negative and interchange the order of the integrations. We obtain:

$$\int_0^{\infty} dr \left[\int_{\sqrt{f(r)}}^{\infty} dk \sqrt{k^2 - f(r)} k \exp[-(\lambda_T^2/2\pi)k^2] - \int_0^{\infty} dk k^2 \exp[-(\lambda_T^2/2\pi)k^2] \right]. \quad (7)$$

The last integral can, of course, be evaluated on sight and, after a minor change of variables, so can the one on the left. We obtain for the continuum

$$B_l = -\frac{\sqrt{2}}{\pi} N\lambda_T^5 \left\{ \frac{\pi}{2}(l + \frac{1}{2}) \frac{\pi}{\lambda_T^2} + \frac{\pi^2}{\sqrt{2}} \frac{1}{\lambda_T^3} \times \int_0^{\infty} dr [\exp\{-\beta V(r) - (\lambda_T^2/2\pi)[(l + \frac{1}{2})^2/r^2]\} - 1] \right\}. \quad (8)$$

In this procedure (as contrasted with Kahn's) there is no need to divide the integration plane into several regions. If there is more than one turning point, the change in the order of integration works beautifully. The lower boundary on k (again given by $\sqrt{f(r)}$) simply picks up the contribution of the classically allowed regions in the $r-k$ plane.

If the potential has a part which is negative, $f(r)$ will also at times be negative for some r 's. For those values of r it is clear that the lower limit of the left-hand k integral in expression (7) will be zero. In order to obtain Eq. (8) we must add the contribution of the l th partial wave to the bound state part, which reads

$$B_l^{bd} = -\frac{\sqrt{2}}{\pi} N\lambda_T^5 \frac{1}{\lambda_T^2} \sum_n [\exp(-\beta E_{n,l}) - 1]. \quad (9)$$

As $\hbar \rightarrow 0$, the well will become filled with bound states and we can surely pass from the discrete index n to a continuous variable:

$$B_l^{bd} = -\frac{\sqrt{2}}{\pi} N\lambda_T^5 \frac{1}{\lambda_T^2} \int_{v_{\min}^{\text{eff}}}^0 dE \frac{dn}{dE} (e^{-\beta E} - 1). \quad (10)$$

Effectuating a partial integration and setting the surface terms to zero we find

$$B_l = -\frac{\sqrt{2}}{\pi} N\lambda_T^5 \left[\frac{\beta}{\lambda_T^2} \int_{v_{\min}^{\text{eff}}}^0 dE n(E) e^{-\beta E} \right]. \quad (11)$$

Using the WKB quantization condition

$$\int \sqrt{k^2 - f(r)} dr = (n + \frac{1}{2})\pi, \quad (12)$$

where the integral is taken between the two turning points of the classical motion in the well for negative k^2 , and neglecting the $\frac{1}{2}$ as we approach $\hbar = 0$, we can write

$$B_i^{bd} = -\frac{\sqrt{2}}{\pi^2} N \lambda_T^5 \frac{1}{2} \int_{f(r)_{\min}}^0 d(k^2) \times \left(\int_{\sqrt{k^2 - f(r)}} dr \right) \exp[-(\lambda_T^2/2\pi)k^2]. \quad (13)$$

Interchanging the integrations we obtain

$$B_i^{bd} = -\frac{\sqrt{2}}{\pi^2} N \lambda_T^5 \frac{1}{2} \int dr \times \int_{f(r)}^0 d(k^2) \sqrt{k^2 - f(r)} \exp[-(\lambda_T^2/2\pi)k^2], \quad (14)$$

where the limits on the r integration are the values of r for which $f(r)=0$, i. e., where the effective potential crosses the zero energy axis. Since for these values of r the energy integration of the left-hand integral in Eq. (7) stops at k or $k^2=0$, we see that the above integral complements exactly that integral. Thus, with or without additional turning points, the sum of the continuum contribution lead us to rewrite Eq. (7) as

$$\int_0^\infty dr \left[\frac{1}{2} \int_{f(r)}^\infty d(k^2) \sqrt{k^2 - f(r)} \exp[-(\lambda_T^2/2\pi)k^2] - \int_0^\infty dk k^2 \exp[-(\lambda_T^2/2\pi)k^2] \right], \quad (15)$$

which then gives Eq. (8) as the total contribution to the l th partial wave of the virial.

In order to bring the term $(\pi/2)(1 + \frac{1}{2})$ into the integrals, Kahn now uses the identity

$$\int_0^\infty dx [1 - \exp(-\alpha^2/x^2)] = \sqrt{\pi} \alpha \quad (16)$$

to obtain

$$B_i = -\frac{\sqrt{2}}{\pi^2} N \lambda_T^5 \left(\frac{\pi^2}{\sqrt{2} \lambda_T^3} \right) \int_0^\infty dr \left\{ \exp \left[-\beta V(r) - \frac{\lambda_T^2}{2\pi} \frac{(l + \frac{1}{2})^2}{r^2} \right] - \exp \left[-\frac{\lambda_T^2}{2\pi} \frac{(l + \frac{1}{2})^2}{r^2} \right] \right\}, \quad (17)$$

where $\beta = 1/(\kappa T)$. Following Kahn we evaluate $\sum (2l+1) \times \exp[-\beta l(l+1)/r^2]$ using an asymptotic expansion and obtain r^2/β as the leading term. Since $V(r)$ is spherically symmetric the answer is

$$B_{\text{class}} = -\frac{N}{2} \int d\mathbf{r} (e^{-\beta V(r)} - 1). \quad (18)$$

For a more general treatment, it is convenient to rewrite the sums over l as traces. For example, (letting $\hbar^2/2\mu = 1$)

$$\sum_{l=0}^\infty (2l+1) \exp \left[-\beta \frac{l(l+1)}{r^2} - \beta V(r) \right] = \text{Tr}^A \left(\exp \left\{ -\beta \left[\frac{L^2}{r^2} + V(r) \right] \right\} \right). \quad (19)$$

We write the angular trace as

$$\int d\omega \left\langle \omega \left| \exp \left\{ -\beta \left[\frac{L^2}{r^2} + V(r) \right] \right\} \right| \omega \right\rangle = \int d\omega \left\langle \omega \left| \exp \left(-\beta \frac{L^2}{r^2} \right) \right| \omega \right\rangle \exp[-\beta V(r)] \quad (20)$$

since in this case $V(r)$ commutes with L^2 , and ω repre-

sents the angles θ, ϕ . We then have

$$\left\langle \omega \left| \exp \left(-\beta \frac{L^2}{r^2} \right) \right| \omega \right\rangle = \sum_{l,m} \langle \omega | l, m \rangle \exp \left[-\beta \frac{l(l+1)}{r^2} \right] \langle l, m | \omega \rangle = \sum_{l,m} Y_{l,m}^*(\theta, \phi) Y_{l,m}(\theta, \phi) \exp \left[-\beta \frac{l(l+1)}{r^2} \right]. \quad (21)$$

The sum over m gives $[(2l+1)/4\pi] P_l[\cos(0)] = (2l+1)/4\pi$ and thus we obtain

$$\text{Tr}^A \left(\exp \left\{ -\beta \left[\frac{L^2}{r^2} + V(r) \right] \right\} \right) = \int \frac{d\omega}{4\pi} \sum_{l=0}^\infty (2l+1) \exp \left[-\beta \frac{l(l+1)}{r^2} - \beta V(r) \right] \quad (22)$$

which yields the desired result if we appeal once more to the fact that $V(r)$ is spherically symmetric.

In the work that follows the *traces* are the expressions that appear naturally and they lead to formulas involving angular integrations. We also note that in so far as the asymptotic expansion is concerned, it does not matter if $(l + \frac{1}{2})^2$ or $l(l+1)$ appears in the exponential. The leading result is the same.

THIRD VIRIAL COEFFICIENT

To apply the method of the preceding section to the semiclassical calculation of the third virial coefficient, we will start with an expression for the third cluster (i. e., for the third coefficient in the fugacity expansion for the pressure) in terms of three-body shifts. Derived by Larsen and Mascheroni,⁴ and based on a hyperspherical harmonic expansion, it reads:

$$b_3^{\text{Boltz}} = \frac{(2S+1)^3 \sqrt{3}}{(2\pi)^2} \frac{1}{\lambda_T} \sum_\lambda \int_0^\infty dk k [\eta_\lambda^{(123)}(k) - 3\eta_\lambda^{(12/3)}(k)] \exp \left(-\frac{\lambda_T^2}{4\pi} k^2 \right). \quad (23)$$

Here $\eta^{(123)}$ is a three-body phase shift associated with the comparison of the wave function of three interacting particles with that of three free particles. $\eta^{(12/3)}$ is again a three-body phase shift, but one for which only particles 1 and 2 are allowed to interact, particle 3 acting as a spectator, and a comparison is made with three free particles. The λ is put here only as a reminder that we have to provide indices to enumerate the phase shifts, and differently for $\eta^{(123)}$ and for $\eta^{(12/3)}$, and systematically sum over them.

The formula above was derived for the case of no two- or three-body bound states (e. g., for 3 He³ atoms) though the potential can have an attractive part. For the purposes of this article, however, we impose a further requirement: that the potential have no negative part. This implies that as \hbar becomes small, no bound state can appear.

We also note that we can rewrite the bracket in Eq. (23) as

$$[\eta_\lambda^{(123)}(k) - \eta_\lambda^{(12/3)}(k) - \eta_\lambda^{(13/2)}(k) - \eta_\lambda^{(23/1)}(k)], \quad (24)$$

which is a form which arises naturally when using an Ursell expansion in the derivation of the phase shift formula. We shall use it later to obtain an explicitly

convergent integral for the cluster. See Eq. (41).

The phase shifts appearing in Eq. (23) are obtained from the solutions of coupled equations such as

$$\phi_K''(\rho) + k^2 \phi_K(\rho) - \sum_{K'} M_{KK'} \phi_{K'}(\rho) = 0, \quad (25)$$

where

$$M_{KK'} = \left[\frac{(N+2)^2 - \frac{1}{4}}{\rho^2} \right] \delta_{KK'} + \frac{2m}{\hbar^2} V_{KK'}.$$

These arise from expanding the internal wave function of the three particles in hyperspherical harmonics, inserting the wave function in the Schrödinger equation, and taking inner products with the hyperspherical (surface) harmonics. Thus,

$$\Psi^{\text{rel}}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = \sum_K \rho^{-5/2} \phi_K(\rho) \mathcal{Y}_K(\Omega). \quad (26)$$

The hyper radius ρ is the magnitude of a six-dimensional vector formed from the two Jacobi vectors:

$$\rho = \begin{pmatrix} \xi \\ \eta \end{pmatrix} \quad \begin{cases} \xi = (\frac{2}{3})^{1/2} [\frac{1}{2}(\mathbf{r}_1 + \mathbf{r}_2) - \mathbf{r}_3], \\ \eta = 2^{-1/2}(\mathbf{r}_1 - \mathbf{r}_2). \end{cases} \quad (27)$$

The \mathcal{Y} 's are the harmonics and the angles Ω describe the orientation of ρ in the six-dimensional space; K represents a set of indices enumerating the harmonics. N in Eq. (25) is the order of the harmonic (and a subset of K). $V_{KK'}$ is a matrix element formed by integrating over the angles a binary potential (or a sum of binary potentials) with two normalized harmonics. In any calculation one limits oneself to a finite number of harmonics, which can then be increased to demonstrate convergence.

From the solution of Eq. (25) one then obtains an R matrix, which when diagonalized provides us with the required eigenphase shifts.

The idea behind the WKB treatment of this problem consists in arguing that when the matrix M changes slowly within oscillations of the solutions, then one can diagonalize the set of equations, i. e., obtain a set of uncoupled equations with effective potentials.

The uncoupled equations, in turn, can be treated in a more or less conventional WKB fashion.

Since M is symmetric and can be chosen real we can diagonalize M for any particular ρ . If M changes slowly enough so that we can neglect all terms containing derivatives of the matrix U which diagonalizes M we will obtain

$$\tilde{\phi}'' + [k^2 I - \Lambda(\rho)] \tilde{\phi}(\rho) = 0, \quad (28)$$

where $\phi = U \tilde{\phi}$ and $\Lambda = U^T M U$ and $\Lambda(\rho)$ is a diagonal matrix.

The set of second-order equations displayed above is equivalent to the set of first order equations proposed by Eu¹⁰ (see his equations II.18). We note that while he keeps the diagonal part of $[U_2^T(d/dx)U_2]$ where U_2 plays the same role as our U , our U is orthogonal and the diagonal elements of $[U^T(d/d\rho)U]$ are equal to zero. Eu's solutions (II.19) are precisely the ones that we ob-

tain from Eq. (28). Eu also argues that corrections to these solutions, stemming from the neglected terms involving the derivative of U_2 , are of order at least $\hbar^{1/2}$ higher than those kept.

Fulling¹¹ in a more recent work, writes a systematic WKB (adiabatic) solution for Eq. (25) valid away from turning points and crossings of the elements (eigenvalues) λ_ν , of Λ . He also assumes what we call ($k^2 I - M$) to be a positive definite matrix.

The leading term in his expansion reproduces precisely the leading two terms (the square root normalization and the phase) of our WKB solution: ϕ . The other terms are of higher (integral) order in \hbar . He emphasizes also, that the eigenvectors must be chosen with care so that, e. g., "capricious" phases are not introduced in the eigenvectors upon changing the value of ρ . Since we can choose our vectors to be real, we need only require continuity as a function of ρ to essentially determine our function ϕ .

The phases of ϕ can now be obtained by considering simplified forms of asymptotic solutions for the $\tilde{\phi}$ which appears in Eq. (28). The square root normalization does not affect the phase shift. Thus, we write

$$\begin{aligned} \tilde{\phi}_\nu &\sim \cos\left(k\rho - k\rho_0 - \frac{\pi}{4}\right) + \int_{\rho_0}^{\infty} \left[\sqrt{k^2 - \lambda_\nu(\rho) - \frac{1}{4\rho^2}} - k \right] d\rho, \\ \tilde{\phi}_\nu^{\text{trree}} &\sim \cos\left[k\rho - (N+2)\frac{\pi}{2} - \frac{\pi}{4}\right]. \end{aligned} \quad (29)$$

The lower limit of the integral is written here as ρ_0 . The situation involving multiple turning points has to be treated, again, by replacing the single integral by a sum of such integrals, each one evaluated over a physically allowed region. For the case of a single turning point, we find

$$\eta_\nu \sim (N+2)\frac{\pi}{2} - k\rho_0 + \int_{\rho_0}^{\infty} \left[\sqrt{k^2 - \lambda_\nu - \frac{1}{4\rho^2}} - k \right] d\rho \quad (30)$$

with the obvious extensions for multiple turning points.

Let us, to be definite, consider one of the phase shifts: $\eta^{(123)}$. According to Eq. (23) we have to integrate the phase shifts over the wave number:

$$\int_0^\infty dk k \eta^{(123)}(k) \exp\left(-\frac{\lambda_T^2 k^2}{4\pi}\right).$$

Inserting the expression for the phase shift, Eq. (30) and interchanging the order of integration as was done for the case of the second virial, we obtain

$$\begin{aligned} (N+2)\frac{\pi^2}{\lambda_T^2} + 2\frac{(\pi^2)}{\lambda_T^3} \\ \times \int_0^\infty d\rho \left\{ \exp\left[-\frac{\lambda_T^2}{4\pi}\left(\lambda_\nu + \frac{1}{4\rho^2}\right)\right] - 1 \right\}, \end{aligned} \quad (31)$$

which may be written as

$$\frac{2(\pi^2)}{\lambda_T^3} \int_0^\infty d\rho \left\{ \exp\left[-\frac{\lambda_T^2}{4\pi}\left(\lambda_\nu + \frac{1}{4\rho^2}\right)\right] - \exp\left[-\frac{\lambda_T^2}{4\pi}\frac{(N+2)^2}{\rho^2}\right] \right\}. \quad (32)$$

Our virial formula involves a summation over ν and therefore we can rewrite the exponentials in terms of traces:

$$\sum_{\nu} \left\{ \exp \left[-\frac{\lambda_T^2}{4\pi} \left(\lambda_{\nu} + \frac{1}{4\rho^2} \right) \right] - \exp \left[-\frac{\lambda_T^2}{4\pi} \frac{(N+2)^2}{\rho^2} \right] \right\} \\ = \text{Tr}^{\mathbf{R}} \left\{ \exp \left[-\frac{\lambda_T^2}{4\pi} \Lambda(\rho) \right] - \exp \left[-\frac{\lambda_T^2}{4\pi} \frac{\mathfrak{M}^2 + \frac{1}{4}}{\rho^2} \right] \right\}, \quad (33)$$

where the trace is restricted so as not to involve ρ (which may be considered a parameter of the matrix elements, and $\hbar^2 \mathfrak{M}^2$ is the grand angular momentum operator whose values are diagonal in the hyperspherical basis. Since

$$\exp \left[-\frac{\lambda_T^2}{4\pi} \Lambda(\rho) \right] = \exp \left(-\frac{\lambda_T^2}{4\pi} U^T M U \right) \\ = U^T \exp \left(-\frac{\lambda_T^2}{4\pi} M \right) U, \quad (34)$$

the trace becomes

$$\text{Tr}^{\mathbf{R}} \left\{ \exp \left[-\frac{\lambda_T^2}{4\pi} M(\rho) \right] - \exp \left(-\frac{\lambda_T^2}{4\pi} \frac{\mathfrak{M}^2 + \frac{1}{4}}{\rho^2} \right) \right\} \\ = \text{Tr}^{\mathbf{R}} \left[\exp \left(-\beta V - \frac{\lambda_T^2}{4\pi} \frac{\mathfrak{M}^2 + \frac{1}{4}}{\rho^2} \right) - \exp \left(-\frac{\lambda_T^2}{4\pi} \frac{\mathfrak{M}^2 + \frac{1}{4}}{\rho^2} \right) \right]. \quad (35)$$

Here V is the potential $V(12) + V(13) + V(23)$, associated with η which appears in our original basis as $V_{KK'}$.

Since we are interested in recovering the classical expressions, we can make use of the commutator expansion and write the exponential as the product of two exponentials, discarding the terms of higher order in \hbar . Introducing, then eigenkets and eigenbras which depend on the hyperspherical angles, conjugate to the discrete variables, we can write the trace as

$$\int d\Omega \left\langle \Omega \left| \exp \left(-\frac{\lambda_T^2}{4\pi} \frac{\mathfrak{M}^2 + \frac{1}{4}}{\rho^2} \right) \right| \Omega \right\rangle \{ \exp[-\beta V(\rho)] - 1 \}. \quad (36)$$

The matrix element above can now be evaluated and to leading order equals $(\rho/\lambda_T)^5$, as we show:

$$\left\langle \Omega \left| \exp \left(-\frac{\lambda_T^2}{4\pi} \frac{\mathfrak{M}^2 + \frac{1}{4}}{\rho^2} \right) \right| \Omega \right\rangle \\ = \sum_{N,\nu} \mathcal{Y}_{N,\nu}(\Omega) \mathcal{Y}_{N,\nu}^*(\Omega) \exp \left[-\frac{\lambda_T^2}{4\pi} \frac{(N+2)^2}{\rho^2} \right] \quad (37)$$

understanding that the sum enumerates the order of the polynomials N and the lineary independent polynomials of degree N . The sum over ν of the product of polynomials, keeping N fixed, yields¹²:

$$\sum_{\nu} \mathcal{Y}_{\nu}(\Omega) \mathcal{Y}_{\nu}^*(\Omega) = \frac{1}{\pi^3} \sum_N \frac{(N+3)!(N+2)}{12N!}. \quad (38)$$

An Euler McLaurin expansion¹³ yields easily the first term of an asymptotic expansion for the remaining sum in the expression for the matrix element:

$$\frac{1}{\pi^3} \sum_N \frac{(N+3)!(N+2)}{12N!} \exp \left[-\frac{\lambda_T^2}{4\pi} \frac{(N+2)^2}{\rho^2} \right] \\ = \frac{1}{12(\pi^3)} \sum_N [(N+2)^4 - (N+2)^2] \\ \times \exp \left[-\frac{\lambda_T^2}{4\pi} \frac{(N+2)^2}{\rho^2} \right] - \frac{\rho^5}{\lambda_T^5} + \dots \quad (39)$$

Apart from a factor $[(2S+1)^3 \sqrt{3}]/[(2\pi)^2 \lambda_T]$, we see that the contribution of $\eta^{(423)}$ is then

$$\frac{2(\pi^2)}{\lambda_T^3} \frac{1}{\lambda_T^5} \int_0^{\infty} d\rho \rho^5 \int d\Omega \{ \exp[-\beta V(\rho)] - 1 \} \\ = \frac{2(\pi^2)}{\lambda_T^8} \int d\xi d\eta \{ \exp[-\beta[V(12) + V(13) + V(23)]] - 1 \}. \quad (40)$$

The expression above, derived solely from the contribution of $\eta^{(423)}$, diverges for the infinite volume. However, including the terms in $\eta^{(42/3)}$, $\eta^{(23/1)}$, $\eta^{(43/2)}$ in the bracket (24), we obtain a convergent answer. The complete result is

$$b_3^{\text{Boltz}} = \frac{(2S+1)}{2} \frac{\sqrt{3}}{\lambda_T^3} \int d\xi d\eta \{ \exp[-\beta[V(12) + V(13) + V(23)]] \\ - \exp[-\beta V(12)] - \exp[-\beta V(13)] - \exp[-\beta V(23)] + 2 \}. \quad (41)$$

Integrating over \mathbf{R} the center-of-mass coordinate, dividing by the volume V and changing coordinates to \mathbf{r}_1 , \mathbf{r}_2 , \mathbf{r}_3 we obtain

$$b_3^{\text{Boltz}} = \frac{(2S+1)^3}{3!} \frac{1}{V \lambda_T^3} \int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 \dots, \quad (42)$$

since the Jacobian of the transformation from \mathbf{R} , ξ , η to \mathbf{r}_1 , \mathbf{r}_2 , \mathbf{r}_3 is $3^{-3/2}$.

Finally, the contribution of the third cluster to the third virial equals $-2N^2 b_3/b_1^3$, where $b_1 = (2S+1)/\lambda_T$, and thus

$$\frac{b_3^{\text{Boltz}}}{b_1^3} = \frac{1}{3! V} \int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 \\ \times \{ \exp[-\beta[V(12) + V(13) + V(23)]] - \dots \}, \quad (43)$$

which is the classical expression with all the correct factors. We recall that the factor of λ_T^{-3} which appears in the l th cluster is sometimes absorbed in the fugacity.

SECOND VIRIAL WITH ANISOTROPIC INTERACTIONS

We consider a specific case: a hydrogen molecule interacting with a helium atom. In this case, again, the quantum mechanical formulation involves sets of coupled equations and a generalized Uhlenbeck and Beth-eigenphase shift formula⁵ and we wish to obtain semi-classical expressions for the eigenphase shifts.

We write the eigenfunction of the system as linear combinations of products of wave functions representing the internal states of the molecules together with amplitudes describing the relative motion of the two centers of mass.

The radial part of the amplitudes satisfy the differential equations:

$$D_l f_l(r) = \sum_{l'} V_{ll'}(r) f_{l'}(r), \quad (44)$$

where

$$D_l \equiv \frac{d^2}{dr^2} + \left(k^2 - \frac{2\mu}{\hbar^2} \epsilon_{\nu J}^0 \right) - \frac{L(L+1)}{r^2},$$

$$V_{ll'} \equiv \frac{2\mu}{\hbar^2} \sum_J \langle \chi_{\nu J} | V_j(Rr) | \chi_{\nu J} \rangle \langle Y_{KM}^{JL} | P_j(\cos \gamma) | Y_{KM}^{J'L'} \rangle,$$

$$V(\mathbf{R}, \mathbf{r}) = \sum_j V_j(R, r) P_j(\cos \gamma).$$

The $\chi_{vJ}(R)$ denotes the radial part of the wave functions of the isolated molecule for the vibrational-rotational state v, J . The ϵ_{vJ}^0 are the energies of the molecule corresponding to that state.

The \mathcal{Y}_{KM}^{JL} form a complete orthonormal set of functions, simultaneous eigenfunctions of the total angular momentum, i. e., of K^2 , of its projection on the z axis K_z , of J^2 and L^2 , where J is the angular momentum of the molecular rotation and L the angular momentum of the relative motion of the two particles. We abbreviate vJL by 1.

To pursue the treatment which is now familiar we absorb the $(2\mu/\hbar^2)\epsilon_{vJ}^0$ into the M and the Λ . I. e.,

$$M_{11'} = \frac{2\mu}{\hbar^2}\epsilon_{vJ}^0 + \frac{(L + \frac{1}{2})^2 - \frac{1}{4}}{r^2} + V_{11'} . \quad (45)$$

After the system is uncoupled the solutions to the equations will at large distances have oscillations characterized by $k_{vJ}^2 = k^2 - (2\mu/\hbar^2)\epsilon_{vJ}^0$ and we form $\bar{\lambda}_v = \lambda_v - (2\mu/\hbar^2)\epsilon_{vJ}^0$, for each λ_v subtracting the appropriate energy of excitation of the molecule. The phase shifts are then given by:

$$\eta_{\nu}(k) \sim (L + \frac{1}{2})\frac{\pi}{2} - k_{vJ}r_0 + \int_{r_0}^{\infty} \left(\sqrt{k_{vJ}^2 - \bar{\lambda}_v - \frac{1}{4r^2}} - k_{vJ} \right) dr , \quad (46)$$

where, for simplicity, we consider one turning point r_0 where $k_{vJ}^2 = \bar{\lambda}_v$.

In terms of these phase shifts the continuum part of the mixed virial is given by

$$B_{He, H_2}^{\text{cont}} = -\frac{N\lambda_T^5}{4(\pi^2)} \frac{1}{Q^{\text{rot+vib}}} \int dk k \times \left[\sum_{K, \nu} (2K+1)\eta_{\nu}^K(k) \right] \exp\left(-\frac{\lambda_{\mu}^2}{4\pi} k^2\right) , \quad (47)$$

where $Q^{\text{rot+vib}}$ is the partition function of the isolated molecule, $\lambda_{\mu}^2 = [\hbar^2/(2\pi\mu\kappa T)]$, and μ is the relative mass of He and H_2 .

An important point, now, is that we must integrate the phase shift from its threshold which is no longer necessarily zero. Thus,

$$\int_{(2\mu/\hbar^2)\epsilon_{vJ}^0}^{\infty} dk k \eta(k) \exp\left(-\frac{\lambda_{\mu}^2}{4\pi} k^2\right) = \exp(-\beta\epsilon_{vJ}^0) \int_0^{\infty} dk_{vJ} k_{vJ} \eta(k) \exp\left(-\frac{\lambda_{\mu}^2}{4\pi} k_{vJ}^2\right) . \quad (48)$$

Continuing in the same vein as before we obtain:

$$\frac{2(\pi^2)}{\lambda_{\mu}^3} \exp(-\beta\epsilon_{vJ}^0) \int_0^{\infty} dr \times \left\{ \exp\left[-\frac{\lambda_{\mu}^2}{4\pi} \left(\bar{\lambda}_v + \frac{1}{4r^2}\right)\right] - \exp\left[-\frac{\lambda_{\mu}^2}{4\pi} \frac{(L + \frac{1}{2})^2}{r^2}\right] \right\} . \quad (49)$$

Reabsorbing the ϵ_{vJ}^0 into λ_v and summing over all ν , K , and M we recover an expression involving Λ :

$$\frac{2(\pi^2)}{\lambda_{\mu}^3} \int dr \text{Tr}^R \left\{ \exp\left[-\frac{\lambda_{\mu}^2}{4\pi} \Lambda(r)\right] - \exp\left[-\frac{\lambda_{\mu}^2}{4\pi} \frac{(\mathcal{L}^2 + \frac{1}{4})}{r^2} - \beta H_0\right] \right\} , \quad (50)$$

where H_0 is the Hamiltonian for the isolated molecule, \mathcal{L}^2 the square of the angular momentum operator, and the trace does not involve r . Changing basis for the first term we obtain our matrix M , and further

$$\frac{2(\pi^2)}{\lambda_{\mu}^3} \int dr \text{Tr}^R \left\{ \exp\left[-\beta V(R\mathbf{r}) - \frac{\lambda_{\mu}^2}{4\pi} \frac{(\mathcal{L}^2 + \frac{1}{4})}{r^2} - \beta H_0\right] - \exp\left[-\frac{\lambda_{\mu}^2}{4\pi} \frac{(\mathcal{L}^2 + \frac{1}{4})}{r^2} - \beta H_0\right] \right\} . \quad (51)$$

To demonstrate that in the semiclassical limit we obtain the classical expressions we need to make contact with the formulas obtained classically by others. Typically, the molecules are replaced by rigid dumbbels¹⁴ and the potential $V(Rr\gamma)$ is then, no longer, a function of R .

Dropping the R dependence is sufficient to allow us to factor the trace. We obtain [apart from $2(\pi^2)/\lambda_{\mu}^3$]:

$$\text{Tr}[\exp(-\beta H_0)] \int dr \text{Tr}^R \left\{ \exp\left[-\beta V(\mathbf{r}) - \frac{\lambda_{\mu}^2}{4\pi} \frac{(\mathcal{L}^2 + \frac{1}{4})}{r^2}\right] - \exp\left[-\frac{\lambda_{\mu}^2}{4\pi} \frac{(\mathcal{L}^2 + \frac{1}{4})}{r^2}\right] \right\} = Q^{\text{rot}} \int dr \int d\omega \sum_{L=0}^{\infty} \frac{2L+1}{4\pi} \times \exp\left[-\frac{\lambda_{\mu}^2}{4\pi} \frac{(L + \frac{1}{2})^2}{r^2}\right] \{\exp[-\beta V(\mathbf{r})] - 1\} , \quad (52)$$

where ω is the set of angles associated with \mathbf{r} .

The sum over the angular momentum gives $4\pi r^2/\lambda_{\mu}^2$ and Q^{rot} appears also in the denominator of the virial formula because the mixed virial involves the ratio of the second cluster with the isolated first clusters and thus the Q^{rot} cancels out in the final formula. The result is

$$B_{He, H_2} = -\frac{N}{2} \int d\mathbf{r} \{\exp[-\beta V(\mathbf{r})] - 1\} . \quad (53)$$

The inclusion of bound states is straightforward, follows the path outlined earlier when discussing spherical potentials, and leads to the above result.

If we want to allow for a nonrigid molecule in a classical way we will obtain from our trace (using the first term in a Bloch equation expansion of the matrix elements of $e^{-\beta H_0}$):

$$\int d\mathbf{R} \int d\mathbf{r} \exp[-\beta V_0(\mathbf{R})] \{\exp[-\beta V(\mathbf{R}, \mathbf{r})] - 1\} , \quad (54)$$

which, to obtain the virial, will have to be divided by the nonkinetic part of the rotational-vibrational partition function, i. e., divided by $\int d\mathbf{R} \exp[-\beta V_0(\mathbf{R})]$. $V_0(\mathbf{R})$ is the potential appearing in H_0 .

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- ¹B. Kahn, *Studies in Statistical Mechanics*, edited by J. de Boer and G. E. Uhlenbeck (North Holland, Amsterdam 1965) Vol III, p. 339.
- ²G. E. Uhlenbeck and E. Beth, *Physica* **3**, 729 (1936); E. Beth and G. E. Uhlenbeck, *ibid.* **4**, 915 (1937).
- ³L. Gropper, *Phys. Rev.* **50**, 963 (1936); **51**, 1108 (1937).
- ⁴S. Y. Larsen and P. L. Mascheroni, *Phys. Rev. A* **2**, 1018 (1970).
- ⁵S. Y. Larsen and J. D. Poil, *Can. J. Phys.* **52**, 1914 (1974).
- ⁶V. S. Buslaev and S. P. Merkuriev, *Izv. Akad. Nauk. SSSR Teoret. Mat. Phys.* **5**, 372 (1970). See also comments by T. A. Osborn and T. Y. Tsang, *Ann. Phys.* **101**, 119 (1976), p. 146.
- ⁷R. Dashen, S.-k. Ma, and H. Bernstein, *Phys. Rev.* **187**, 345 (1969); D. Bedeaux, *Physica* **45**, 469 (1970); V. S. Buslaev and S. P. Merkuriev, *Izv. Akad. Nauk. SSSR Teoret. Mat. Phys.* **5**, 372 (1970); *Izv. Akad. Nauk. SSSR Trudi Mat.* **110**, 29 (1970); also in translation *Proc. Steklov. Inst. Math.* **110**, 28 (1970).
- ⁸C. F. Curtiss and R. S. Powers, *J. Chem. Phys.* **40**, 2145 (1964).
- ⁹M. E. Boyd, S. Y. Larsen, and J. E. Kilpatrick, *J. Chem. Phys.* **45**, 499 (1966).
- ¹⁰B. C. Eu, *J. Chem. Phys.* **52**, 1882 (1970).
- ¹¹S. A. Fulling, *J. Math. Phys.* **16**, 875 (1975).
- ¹²A. Erdelyi, W. Magnus, F. Oberhettinger, and F. G. Tricomi, *Higher Transcendental Functions* (McGraw Hill, New York, 1955), Vol. II, Sec. 11.4, p. 243, Eq. (2). We note a typographical error in that $C_p^{(1/2)p}(1)$ should read $C_n^{(1/2)p}(1)$.
- ¹³E. T. Whittaker and G. N. Watson, *Modern Analysis*, 4th ed. (Cambridge, Oxford, 1927), p. 127.
- ¹⁴J. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1954), p. 435.