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High-Temperature Exchange Third Virial Coefficient for Hard Spheres via an Asymptotic Method for Path Integrals

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The exchange part of the third cluster integral can be divided into two parts: b_3(exch-1), which arises from the exchange of two particles, and b_3(exch-2), which arises from the cyclic exchange of all three particles. The first few terms of b_3(exch-1) are calculated by arguing that $b_3\text{(exch-1)} = -[9\pi a^3/(4\lambda^3)]b_2\text{(exch)}[1 + O(\lambda/a)]$, where b_2(exch) is the exchange second cluster integral, λ is the thermal de Broglie wavelength, and a is the hard-sphere diameter. The first three terms of b_3(exch-2) are calculated by writing it in path integral form and expanding about the shortest path.

KEY WORDS: Third virial coefficient; asymptotic method for path integrals; three-body problem.

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1. INTRODUCTION AND RESULTS

Ever since the exchange second virial coefficient was shown to be exponentially suppressed at high temperatures,[2] the exchange parts of the higher virial coefficients have been believed to be similarly suppressed. This has been recently confirmed by Bruch for the leading term of each of the exchange parts of the third virial coefficient[(4)] and for the leading term of the cyclic exchange part of the fourth and higher virial coefficients.[(5)] Bruch's rigorous results were obtained by using a method closely related to the one introduced by Lieb[(2)] for the exchange second virial coefficient: He expressed the exchange parts in path integral form and constructed upper and lower bounds. The present paper extends Bruch's results for the exchange parts of the third virial coefficient by calculating the first four terms of the high-temperature expansion of b_3(exch-1) and the first three terms of the high-temperature expansion of b_3(exch-2).

The second and third virial coefficients B and C which appear in the expansion

$$\frac{PV}{NkT} = 1 + \frac{B}{V} + \frac{C}{V^2} + \cdots$$

of the equation of state are given by[3]

$$B = -Nb_2b_1^{-2} \tag{1a}$$

$$C = N^2(4b_2{}^2b_1^{-4} - 2b_3b_1^{-3}) \tag{1b}$$

where b_1, b_2, and b_3 are cluster integrals and N is the number of particles. For particles of spin S

$$b_1 = (2S + 1)\lambda^{-3} \tag{2}$$

where

$$\lambda = (2\pi\beta\hbar^2/m)^{1/2} \tag{3}$$

is the thermal de Broglie wavelength. Here $\hbar$ is Planck's constant h divided by 2π, m is the mass of the gas particles, and $\beta = (kT)^{-1}$, where k is Boltz-

[2] The exponential suppression of b_2(exch) was first demonstrated by Larsen *et al.*[(1)] The correct coefficient of the leading term was first obtained by Lieb.[(2)] Both of these papers obtained their results by expressing the exchange second virial coefficient in path integral form and constructing upper and lower bounds. Additional terms in the high-temperature expansion were obtained by Hill[(3)] by a method which Laplace-transformed the temperature variable and used the Sommerfeld–Watson transformation.

[3] Derivations of the virial expansion (with trivial differences in the definitions of the virial coefficients and cluster integrals) can be found in Refs. 6 and 7. An elementary derivation of the formulas for the second virial coefficient, which can be readily extended to the third virial coefficient, is given in Appendix A of Ref. 8.

mann's constant and T is the temperature. The cluster integrals b_2 and b_3 can be divided into direct and exchange parts:

$$b_2 = (2S + 1)^2 b_2(\text{direct}) \pm (2S + 1) b_2(\text{exch}) \tag{4a}$$

$$b_3 = (2S + 1)^3 b_3(\text{direct}) \pm (2S + 1)^2 b_3(\text{exch-1}) + (2S + 1) b_3(\text{exch-2}) \tag{4b}$$

The upper (plus) sign is for bosons and the lower (minus) sign is for fermions.

Only the hard-sphere potential

$$V(r) = \begin{cases} \infty, & r < a \\ 0, & r > a \end{cases} \tag{5}$$

(where r is the interparticle separation) will be treated here. The first few terms of high-temperature expansions for b_2(direct), b_2(exch), and b_3(direct) follows from results already in the literature.[(1-3),4] The present paper will show that at high temperatures

$$b_3(\text{exch-1}) = -9\pi^4 a^6 \lambda^{-9} \exp\left\{-\pi\left[\frac{1}{2}\left(\frac{\pi a}{\lambda}\right)^2 + \beta_1\left(\frac{\pi a}{\lambda}\right)^{2/3} + \frac{4}{45}\beta_1^2\left(\frac{\pi a}{\lambda}\right)^{-2/3}\right]\right\}\left[1 + O\left(\frac{\lambda}{a}\right)\right] \tag{6a}$$

and

$$b_3(\text{exch-2}) = \frac{16\pi^3 a^3}{3\lambda^6} \exp\left\{-\frac{2\pi}{9}\left[\frac{2\pi^2 a^2}{\lambda^2} + \left(\frac{2\pi^2 a^2}{\lambda^2}\right)^{1/3}\gamma_1\right]\right\} \times \left\{1 + O\left[\left(\frac{\lambda}{a}\right)^{2/3}\right]\right\} \tag{6b}$$

Here $\beta_1 \simeq 1.85576$ is related to the roots of Airy's function, and $\gamma_1 = 8.53 \pm 0.31$ is the lowest eigenvalue of an eigenvalue problem which must be solved numerically [see Eq. (73)]. The results (6a) and (6b) have been obtained via analogs of the steepest descent method whose rigorous validity for the leading term has been established by Bruch's work but which here is left unproven.

Section 2 lists certain basic formulas and outlines the basic idea, which is justified heuristically. Section 3 illustrates it in a simpler case by deriving

[4] The high-temperature expansion of b_2(direct) for hard spheres may be found in Ref. 8, which contains references to earlier work. Numerical results for both b_2(direct) and b_2(exch) for hard spheres are given by Boyd *et al.*[(9)] The high-temperature expansion of b_3(direct) for hard spheres has been investigated by Jancovici.[(10)]

known high-temperature results for b_2(exch). Section 4 presents the calculation of b_3(exch-1) and b_3(exch-2).

2. BASIC IDEA

The exchange contributions to the virial coefficients can be written in the form[4,7],[5]

$$b_2(\text{exch}) = \frac{1}{2V}\int G_6(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_2, \mathbf{r}_1; \beta)\, d^3\mathbf{r}_1\, d^3\mathbf{r}_2 \tag{7}$$

$$\begin{aligned} b_3(\text{exch-1}) = \frac{1}{2V}\int &[G_9(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3; \mathbf{r}_2, \mathbf{r}_1, \mathbf{r}_3; \beta) \\ &- G_6(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_2, \mathbf{r}_1; \beta) G_3(\mathbf{r}_3; \mathbf{r}_3; \beta)]\, d^3\mathbf{r}_1\, d^3\mathbf{r}_2\, d^3\mathbf{r}_3 \end{aligned} \tag{8}$$

$$b_3(\text{exch-2}) = \frac{1}{3V}\int G_9(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3; \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_1)\, d^3\mathbf{r}_1\, d^3\mathbf{r}_2\, d^3\mathbf{r}_3 \tag{9}$$

where the n-dimensional thermal Green's function $G_n(z_1, z_2,..., z_n; z_1', z_2',..., z_n'; \beta)$ is that solution of the n-dimensional Bloch equation $(H_n + \partial/\partial\beta)G_n = 0$ which satisfies the initial condition

$$G_n(z_1, z_2,..., z_n; z_1', z_2',..., z_n'; 0) = \delta(z_1 - z_1')\, \delta(z_2 - z_2') \cdots \delta(z_n - z_n')$$

and the boundary condition $G_n \to 0$ when the primed coordinates are far from the unprimed coordinates. Here the n-dimensional Hamiltonian H_n has the form

$$H_n = -\frac{\hbar^2}{2m} \sum_{i=1}^{n} \sum_{j=1}^{n} A_{ij} \frac{\partial^2}{\partial z_i\, \partial z_j} + U(z_1, z_2,..., z_n)$$

where the A_{ij} are elements of a real, symmetric, constant matrix all of whose eigenvalues are positive. The required Green's function G_n can be written in the path integral form[6]

$$\begin{aligned} &G_n(z_1, z_2,..., z_n; z_1', z_2',..., z_n'; \beta) \\ &\quad = \lim_{M\to\infty} (M\lambda^{-2})^{nM/2} (\det A_{ij})^{-M/2} \\ &\quad\times \int \cdots \int \prod_{k=1}^{M-1} \prod_{i=1}^{n} dz_i^{(k)} \exp\Bigg[-\frac{mM}{2\beta\hbar^2} \sum_{k=1}^{M} \sum_{i=1}^{n} \sum_{j=1}^{n} (A^{-1})_{ij} \\ &\quad\times (z_i^{(k)} - z_i^{(k-1)})(z_j^{(k)} - z_j^{(k-1)}) - \frac{\beta}{M} \sum_{k=1}^{M} U(z_1^{(k)}, z_2^{(k)},..., z_n^{(k)}) \Bigg] \end{aligned} \tag{10}$$

[5] Bruch's correction[4] of a misprint is incorporated in Eq. (9).

[6] The reader unfamiliar with path integrals may find the review articles of Refs. 12 and 13 useful. The book by Feynman and Hibbs[14] contains a chapter on path integrals in statistical mechanics. The path integral in (10) can be brought to the form considered in the above references by transforming the coordinates with a linear transformation which brings A_{ij} to diagonal form with diagonal elements 1.

Lieb's paper[(2)] contains a proof of (10) for the hard-core case with $n = 6$ and A_{ij} the Kronecker delta.

With the hard-core potential (5), the integrations in (10) are restricted to the regions where $U = \sum_{k<l} V(|\mathbf{r}_k - \mathbf{r}_l|)$ is zero. In such regions the $M \to \infty$ limit of the exponential in (10) is

$$\exp\left[-\pi\lambda^{-2}\int_0^1 \sum_{i=1}^{n}\sum_{j=1}^{n} A_{ij}(dz_i/dt)(dz_j/dt)\,dt\right]$$

where the discrete variable k has been replaced by the continuous variable t. In the high-temperature limit λ^{-2} is large and the dominant contribution to the integral in (10) comes from the neighborhood of the maximum of this exponent, i.e., from the neighborhood of the minimum of

$$\int_0^1 \sum_{ij} A_{ij}(dz_i/dt)(dz_j/dt)\,dt$$

The exchange parts b_2(exch) and b_3(exch-2) will be evaluated by substituting (10) into (7) and (9) and expanding about the maximum of the integral as in the ordinary saddle point method.[7] A rigorous demonstration that such a procedure leads to an asymptotic expansion of the path integral has been given by Schilder[(16)] for the case in which the maximum of the integrand occurs in the interior of the region so that the approximating path integrals are Gaussian in all variables. Unfortunately, Schilder's theorems do not apply to the present case because the maximum of the integrand occurs on the boundary of the region. However, because Lieb's[(2)] and Bruch's[(4)] upper and lower bounds make it clear that most of the contribution comes from the neighborhood of the maximum, there can be little doubt that expanding about the maximum to obtain additional terms in the high-temperature expansion is a correct procedure. The reasonableness of this approach is confirmed by the fact that it reproduces previously established results for the higher-order terms in the high-temperature expansion of b_2(exch). Nevertheless, it would be very useful to have extensions of Schilder's theorems to the case in which the maximum of the integrand of the path integral occurs on the boundary; such theorems are needed to make the present work completely rigorous.

Because the maximum of the integrand is on the boundary, the approximating path integrals are not Gaussian in all variables. This difficulty will be overcome by recognizing that the non-Gaussian parts are the path integral representations of the solutions of diffusion problems which can be adequately solved by eigenfunction expansion methods in the high-temperature limit.

[7] See Ref. 15, Vol. I, pp. 437–443. The saddle point method for path integrals is discussed on pp. 88–89 of Brush's review article.[(13)]

3. EXCHANGE SECOND VIRIAL COEFFICIENT

This section will derive the known result[1-3]

$$b_2(\text{exch}) = 4\pi^3 a^3 \lambda^{-6} \exp\{-\tfrac{1}{2}\pi(\pi a/\lambda)^2 - \pi\beta_1(\pi a/\lambda)^{2/3} + O[(a/\lambda)^{-2/3}]\} \tag{11}$$

where $\beta_1 = 1.85576$. An understanding of the approximations which are adequate to obtain (11) will be very useful for the calculation of $b_3(\text{exch-2})$ to the same order in the next section.

The use of (10) in (7) yields

$$b_2(\text{exch}) = \frac{1}{2V} \lim_{M\to\infty} \left(\frac{M}{\lambda^2}\right)^{3M} \int \cdots \int \prod_{k=1}^{M} d^3\mathbf{z}_1^{(k)}\, d^3\mathbf{z}_2^{(k)} \times \exp\left\{-\pi M\lambda^{-2} \sum_{k=1}^{M} [(\mathbf{z}_1^{(k)} - \mathbf{z}_1^{(k-1)})^2 + (\mathbf{z}_2^{(k)} - \mathbf{z}_2^{(k-1)})^2]\right\} \tag{12}$$

where $\mathbf{z}_1^{(0)} \equiv \mathbf{z}_2^{(M)}$, $\mathbf{z}_2^{(0)} \equiv \mathbf{z}_1^{(M)}$, and the integration region is restricted by $|\mathbf{z}_1^{(k)} - \mathbf{z}_2^{(k)}| \geqslant a$. The transformation $\mathbf{z}_1^{(k)} = \mathbf{Z}_k + \frac{1}{2}\mathbf{z}_k$ and $\mathbf{z}_2^{(k)} = \mathbf{Z}_k - \frac{1}{2}\mathbf{z}_k$ to relative and center-of-mass variables produces

$$b_2(\text{exch}) = \frac{1}{2V} \lim_{M\to\infty} \left(\frac{M}{\lambda^2}\right)^{3M} \int \cdots \int \prod_{k=1}^{M} d^3\mathbf{Z}_k\, d^3\mathbf{z}_k \times \exp\left[-2\pi M\lambda^{-2} \sum_{k=1}^{M} (\mathbf{Z}_k - \mathbf{Z}_{k-1})^2 - \tfrac{1}{2}\pi M\lambda^{-2} \sum_{k=1}^{M} (\mathbf{z}_k - \mathbf{z}_{k-1})^2\right] \tag{13}$$

where $\mathbf{Z}_0 = \mathbf{Z}_M$, $\mathbf{z}_0 = -\mathbf{z}_M$, and the integration region is restricted by $|\mathbf{z}_k| \geqslant a$. The convolution theorem for the Fourier transform can be used (see Appendix A) to evaluate the integrals over $\mathbf{Z}_1, \mathbf{Z}_2, \ldots, \mathbf{Z}_{M-1}$; the remaining integral over $\mathbf{Z}_M$ just yields a factor of the volume V. This reduces (13) to

$$b_2(\text{exch}) = 2^{1/2}\lambda^{-3} \lim_{M\to\infty} \left(\frac{M}{2\lambda^2}\right)^{3M/2} \int \cdots \int \prod_{k=1}^{M} d^3\mathbf{z}_k \times \exp\left[-\tfrac{1}{2}\pi M\lambda^{-2} \sum_{k=1}^{M} (\mathbf{z}_k - \mathbf{z}_{k-1})^2\right] \tag{14}$$

The path integral (14) is most easily handled in polar coordinates, where $\mathbf{z}_k$ is characterized by z_k, θ_k, ϕ_k. With $\mathbf{z}_0 = -\mathbf{z}_M$ fixed, orient the coordinate systems for $\mathbf{z}_1, \mathbf{z}_2, \ldots, \mathbf{z}_{M-1}$ so that the initial point $\mathbf{z}_0$ and final point $\mathbf{z}_M$ lie on the z axis at $\theta = 0$ and $\theta = \pi$, respectively. It is easily shown that in these coordinates

$$(\mathbf{z}_k - \mathbf{z}_{k-1})^2 = (z_k - z_{k-1})^2 + 2z_k z_{k-1}\{1 - \cos(\theta_k - \theta_{k-1}) + (\sin\theta_k \sin\theta_{k-1})[1 - \cos(\phi_k - \phi_{k-1})]\} \tag{15}$$

Approximations to the M-fold integral in (14) will be based on the facts that a/λ and M are large. Because $a \gg \lambda$, most of the contribution to the integral comes from the neighborhood of the shortest paths from $\mathbf{z}_0$ to $\mathbf{z}_M$. These paths occur for $|\mathbf{z}_0| = |\mathbf{z}_M| = a$, and are characterized by $z_k = a$, $\theta_k = \pi k/M$, and $\phi_2 = \phi$, where different choices of ϕ specify different great-circle routes from $\theta = 0$ to $\theta = \pi$. Because M is large, it is tempting to argue that $1 - \cos(\theta_k - \theta_{k-1})$ can be replaced by $(\theta_k - \theta_{k-1})^2/2$ and $1 - \cos(\phi_k - \phi_{k-1})$ by $(\phi_k - \phi_{k-1})^2/2$ with the approximation becoming exact in the limit as $M \to \infty$. However, as was pointed out by Edwards and Gulyaev,[17] such an approximation does not become exact as $M \to \infty$. The individual integrations must be evaluated to order M^{-1} [which, for example, requires approximating $1 - \cos(\theta_k - \theta_{k-1})$ by $(\theta_k - \theta_{k-1})^2/2 - (\theta_k - \theta_{k-1})^4/24$] if the $M \to \infty$ limit is to be calculated correctly. This is a consequence of the curvature of the coordinate surfaces, and can be understood by noting that something of the form $\prod_{k=1}^{M} [1 + M^{-1}f(k/M)]$ becomes $\exp[\int_0^1 f(x)\,dx]$ in the $M \to \infty$ limit. Furthermore, $1 - \cos(\phi_k - \phi_{k-1})$ cannot be expanded at all when θ_k is near either 0 or π and $\sin\theta_k \sin\theta_{k-1}$ is small; this is a consequence of the coordinate singularities at $\theta = 0$ and at $\theta = \pi$.

An approximate treatment of the angular integrations will be given first. The curvature effects can be ignored to the order of interest here: $1 - \cos(\theta_k - \theta_{k-1})$ will be approximated by $(\theta_k - \theta_{k-1})^2/2$. The problems near $\theta = 0$ and $\theta = \pi$ are most easily avoided by using a different coordinate system near 0 and near π. On the shortest path from 0 to π, $\theta_k = \pi k/M$. Furthermore, most of the contribution to the path integral comes when θ_k is near its value on the shortest path. Therefore the range $0 \leqslant k \leqslant M$ of the index k will be split into three pieces: $0 \leqslant k \leqslant k_0$, $k_0 \leqslant k \leqslant M - k_0$, and $M - k_0 \leqslant k \leqslant M$, where k_0 is $O(M^{2/3})$. The following approximations are then made: for $0 \leqslant k \leqslant k_0$, $\sin\theta_k \simeq \theta_k$; for $k_0 \leqslant k \leqslant M - k_0$, $1 - \cos(\phi_k - \phi_{k-1}) \simeq (\phi_k - \phi_{k-1})^2/2$; for $M - k_0 \leqslant k \leqslant M$, $\sin\theta_k \simeq \pi - \theta_k$. Introduction of new coordinates x_k, y_k via $x_k = \theta_k \cos\phi_k$ and $y_k = \theta_k \sin\phi_k$ for $0 \leqslant k \leqslant k_0$ and $x_k = (\pi - \theta_k)\cos\phi_k$ and $y_k = (\pi - \theta_k)\sin\phi_k$ for $M - k_0 \leqslant k \leqslant M$ then eliminates the coordinate singularity problem and brings (14) to the form

$$
\begin{aligned}
b_2(\text{exch}) \simeq{}& 2^{1/2}\lambda^{-3} \lim_{M\to\infty} \left(\frac{M}{2\lambda^2}\right)^{3M/2} \int\cdots\int \left(\prod_{k=1}^{M} z_k^2\,dz_k\right) \prod_{k=1}^{k_0-1} dx_k\,dy_k \\
&\times \prod_{k=k_0}^{M-k_0} \sin\theta_k\,d\theta_k\,d\phi_k \prod_{k=M-k_0+1}^{M-1} dx_k\,dy_k\,d\Omega_M \\
&\times \exp\left(-\frac{1}{2}\pi M\lambda^{-2}\left\{\sum_{k=1}^{M} (z_k - z_{k-1})^2\right.\right. \\
&+ \sum_{k=1}^{k_0} z_k z_{k-1}[(x_k - x_{k-1})^2 + (y_k - y_{k-1})^2]
\end{aligned}
$$

$$+\sum_{k=k_0+1}^{M-k_0} z_k z_{k-1}[(\theta_k-\theta_{k-1})^2+(\sin\theta_k\sin\theta_{k-1})(\phi_k-\phi_{k-1})^2]$$
$$+\sum_{k=M-k_0+1}^{M} z_k z_{k-1}[(x_k-x_{k-1})^2+(y_k-y_{k-1})^2]\Big\}\Big) \tag{16}$$

When evaluating (16) it must be remembered that $\theta_{k_0}^2 = x_{k_0}^2 + y_{k_0}^2$ and $(\pi-\theta_{M-k_0})^2 = x_{M-k_0}^2 + y_{M-k_0}^2$. The further approximation of extending the ranges of integration for x_k, y_k, θ_k, and $\phi_k - \phi_{k-1}$ from $-\infty$ to ∞ makes it possible to evaluate (16) via the methods of Appendix A. The result of integrating over x_k, y_k, ϕ_k, and $d\Omega_M$ is

$$b_2(\text{exch}) \simeq 2^{1/2}\lambda^{-3}8\pi^2 \lim_{M\to\infty}\left(\frac{M}{2\lambda^2}\right)^{M-k_0}\int\cdots\int\prod_{k=1}^{M} dz_k$$
$$\times \prod_{k=k_0+1}^{M-k_0}(z_k z_{k-1})^{1/2}(\sin\theta_{k_0}\sin\theta_{M-k_0})^{1/2}\prod_{k=k_0}^{M-k_0} d\theta_k$$
$$\times\left[\sum_{k=1}^{k_0}(z_k z_{k-1})^{-1}\right]^{-1}\left[\sum_{k=M-k_0+1}^{M}(z_k z_{k-1})^{-1}\right]^{-1}$$
$$\times\exp\left(-\tfrac{1}{2}\pi M\lambda^{-2}\left\{\left[\sum_{k=1}^{k_0}(z_k z_{k-1})^{-1}\right]^{-1}\theta_{k_0}^2\right.\right.$$
$$+\sum_{k=k_0+1}^{M-k_0} z_k z_{k-1}(\theta_k-\theta_{k-1})^2$$
$$\left.\left.+\left[\sum_{k=M-k_0+1}^{M}(z_k z_{k-1})^{-1}\right]^{-1}(\pi-\theta_{M-k_0})^2\right\}\right) \tag{17}$$

As a function of the θ_k, the integrand in (17) peaks sharply about

$$\theta_k = \pi\sum_{l=1}^{k}(z_l z_{l-1})^{-1}\Big/\sum_{l=1}^{M}(z_l z_{l-1})^{-1}$$

If the factor $(\sin\theta_{k_0}\sin\theta_{M-k_0})^{1/2} \simeq [\theta_{k_0}(\pi-\theta_{M-k_0})]^{1/2}$ is evaluated at this peak, the θ_k integrations can be performed via the methods of Appendix A. The result yields

$$b_2(\text{exch}) \simeq 4\pi^3\lambda^{-6}\lim_{M\to\infty}\left(\frac{M}{2\lambda^2}\right)^{M/2}\int\cdots\int\prod_{k=1}^{M} dz_k$$
$$\times\left[M^{-1}\sum_{k=1}^{M}(z_k z_{k-1})^{-1}\right]^{-3/2}\exp\left(-\tfrac{1}{2}\pi M\lambda^{-2}\left\{\sum_{k=1}^{M}(z_k-z_{k-1})^2\right.\right.$$
$$\left.\left.+\pi^2\left[\sum_{k=1}^{M}(z_k z_{k-1})^{-1}\right]^{-1}\right\}\right) \tag{18}$$

The accuracy of the approximate result (18) is most easily assessed by comparing it with the exact result

$$b_2(\text{exch}) = 4\pi^3\lambda^{-6} \lim_{M\to\infty} \left(\frac{M}{2\lambda^2}\right)^{M/2} \int \cdots \int \prod_{k=1}^{M} dz_k$$
$$\times \left[M^{-1} \sum_{k=1}^{M} (z_k z_{k-1})^{-1}\right]^{-3/2} \sum_{l=0}^{\infty} (-1)^l (2l+1)$$
$$\times \exp\left\{\frac{\lambda^2}{8\pi M} \sum_{k=1}^{M} (z_k z_{k-1})^{-1}\right.$$
$$\left. - \frac{2\pi^3}{\lambda^2}\left(l+\frac{1}{2}\right)^2 \left[M^{-1} \sum_{k=1}^{M} (z_k z_{k-1})^{-1}\right]^{-1}\right\} \tag{19}$$

which is derived in Appendix B. Clearly (18) is an adequate approximation to (19) for the calculation of b_2(exch) to the order indicated in (11). Unfortunately, the exact methods which produced (19) do not generalize readily to the third virial coefficient; fortunately, the methods which produced (18) do generalize.

The radial integrations will now be handled. Expand about the shortest path by setting $z_k = a + \xi_k$ and expanding in powers of ξ_k. The result to lowest order is

$$b_2(\text{exch}) \simeq 4\pi^3 a^3 \lambda^{-6} \lim_{M\to\infty} \left(\frac{M}{2\lambda^2}\right)^{M/2} \int_0^\infty \cdots \int_0^\infty \prod_{k=1}^{M} d\xi_k$$
$$\times \exp\left[-\frac{\pi^3 a^2}{2\lambda^2} - \frac{\pi M}{2\lambda^2} \sum_{k=1}^{M} (\xi_k - \xi_{k-1})^2 - \frac{\pi^3 a}{M\lambda^2} \sum_{k=1}^{M} \xi_k\right] \tag{20}$$

The path integral in (20) can be evaluated by comparing it with (10), which shows that (20) is equivalent to

$$b_2(\text{exch}) \simeq 4\pi^3 a^3 \lambda^{-6} \exp\left(-\frac{\pi^3 a^2}{2\lambda^2}\right) \int_0^\infty G_1(\xi;\, \xi;\, \beta)\, d\xi \tag{21}$$

where $G_1(\xi;\, \xi';\, t)$ is the solution of

$$\left(-\frac{\hbar^2}{m}\frac{\partial^2}{\partial \xi^2} + \frac{2\pi^4\hbar^2 a}{m\lambda^4}\xi + \frac{\partial}{\partial t}\right) G_1(\xi;\, \xi';\, t) = 0 \tag{22}$$

which reduces to $\delta(\xi - \xi')$ at $t = 0$ and satisfies the boundary conditions $G_1 = 0$ at $\xi = 0$ and $G_1 \to 0$ as $\xi \to \infty$. Separation of variables produces the solution

$$G_1(\xi;\, \xi';\, t) = \sum_{n=1}^{\infty} \psi_n(\xi)\bar{\psi}_n(\xi') e^{-\kappa_n t} \tag{23}$$

where κ_n and ψ_n are the eigenvalue and normalized eigenfunctions of

$$\left(-\frac{\hbar^2}{m}\frac{d^2}{d\xi^2}+\frac{2\pi^4\hbar^2 a}{m\lambda^4}\,\xi\right)\psi_n(\xi)=\kappa_n\psi_n(\xi) \tag{24}$$

Introduction of the new variable

$$\eta = 2^{1/3}(\pi a/\lambda)^{4/3}\xi/a - 2^{-2/3}(\pi a/\lambda)^{-8/3}ma^2\kappa_n/\hbar^2 \tag{25}$$

brings (24) to the form of Airy's equation:

$$(d^2\psi_n/d\eta^2) - \eta\psi_n = 0 \tag{26}$$

The Airy function $Ai(\eta)$ is the solution of (26) that tends to zero as η tends to infinity. Imposing the boundary condition $\psi_n = 0$ at $\xi = 0$ then yields the eigenvalue condition

$$Ai[-2^{-2/3}(\pi a/\lambda)^{-8/3}ma^2\kappa_n/\hbar^2] = 0$$

Hence if the numbers β_n are the roots of

$$Ai(-2^{1/3}\beta_n) = 0$$

ordered so that $\beta_{n+1} > \beta_n$, the eigenvalues κ_n are

$$\kappa_n = 2\left(\frac{\pi a}{\lambda}\right)^{8/3}\frac{\hbar^2}{ma^2} = \pi\left(\frac{\pi a}{\lambda}\right)^{2/3}\beta^{-1}\beta_n \tag{27}$$

The tabulation of the roots of the Airy function given by Abramowitz and Stegun[18] yields $\beta_1 = 1.85576$ and $\beta_2 = 3.24460$.

It now follows from (23), (27), and the fact that the eigenfunctions $\psi_n(\xi)$ are normalized that

$$\int_0^\infty G_1(\xi;\xi;\beta)\,d\xi = \sum_{n=1}^{\infty}\exp[-\pi(\pi a/\lambda)^{2/3}\beta_n] \tag{28}$$

For $a \gg \lambda$ the first term of (28) dominates the expansion. Inserting (28) in (21) and taking only the first term of the sum over n yields (11). The error estimate in (11) follows when one notes that the change of variables (25), together with the fact that expectation values of η are of order unity, implies that ξ/a is to be treated as being of order $(\lambda/a)^{4/3}$ when carrying out the expansion in powers of ξ_k which led from (18) to (20).

4. EXCHANGE THIRD VIRIAL COEFFICIENT

4.1. The Coordinate System

Let $\mathbf{r}_1$, $\mathbf{r}_2$, and $\mathbf{r}_3$ be the positions of the three particles. It is convenient to use as coordinates the center of mass

$$\mathbf{R} = \tfrac{1}{3}(\mathbf{r}_1 + \mathbf{r}_2 + \mathbf{r}_3) \tag{29}$$

the interparticle separations

$$s_1 = |\mathbf{r}_3 - \mathbf{r}_2|, \qquad s_2 = |\mathbf{r}_1 - \mathbf{r}_3|, \qquad s_3 = |\mathbf{r}_2 - \mathbf{r}_1| \tag{30}$$

and a set of Euler angles α, β, γ describing the orientation of the triangle whose vertices are at $\mathbf{r}_1$, $\mathbf{r}_2$, $\mathbf{r}_3$. Edmond's conventions[19] will be used to define the Euler angles: A rotation through α about the z axis of the space-fixed system is followed by a rotation through β about the new y axis and in turn by a rotation through γ about the new z axis (in the body system). If x_i, y_i, z_i are Cartesian coordinates of $\mathbf{r}_i$ in a right-handed space-fixed system and ξ_i, η_i, ζ_i are the Cartesian coordinates of $\mathbf{r}_i$ in the body system, then

$$\begin{aligned} x_i &= (\cos\alpha\cos\beta\cos\gamma - \sin\alpha\sin\gamma)\xi_i \\ &\quad - (\cos\alpha\cos\beta\sin\gamma + \sin\alpha\cos\gamma)\eta_i + (\cos\alpha\sin\beta)\zeta_i \\ y_i &= (\sin\alpha\cos\beta\cos\gamma + \cos\alpha\sin\gamma)\xi_i \\ &\quad - (\sin\alpha\cos\beta\sin\gamma - \cos\alpha\cos\gamma)\eta_i + (\sin\alpha\sin\beta)\zeta_i \\ z_i &= -(\sin\beta\cos\gamma)\xi_i + (\sin\beta\sin\gamma)\eta_i + (\cos\beta)\zeta_i \end{aligned} \tag{31}$$

Nine conditions are needed to specify the coordinates ξ_i, η_i, ζ_i ($i = 1, 2, 3$) in the body system. Three are provided by the (rotationally invariant) equations (30), three more by the conditions

$$\zeta_1 = \zeta_2 = \zeta_3 = 0 \tag{32}$$

which state that the $\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3$ triangle lies in the ξ–η plane, and two more by the conditions

$$\xi_1 + \xi_2 + \xi_3 = \eta_1 + \eta_2 + \eta_3 = 0 \tag{33}$$

which state that the center of mass lies at the origin of the ξ–η–ζ system. The positive direction on the ζ axis is specified by requiring that a circuit from $\mathbf{r}_1$ to $\mathbf{r}_2$ to $\mathbf{r}_3$ back to $\mathbf{r}_1$ encircles the origin of the ξ–η plane in a counterclockwise direction.

This statement plus the conditions (30), (32), and (33) fixes the orientation of the $\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3$ triangle in the ξ–η–ζ system up to a rotation about the ζ axis. If polar coordinates ρ, ϕ are introduced in the ξ–η plane via

$$\xi_i = \rho_i \cos\phi_i, \qquad \eta_i = \rho_i \sin\phi_i \tag{34}$$

it follows from (30) and (32)–(34) that ρ_1, ρ_2, ρ_3 are given by

$$\rho_1 = \tfrac{1}{3}(-s_1^2 + 2s_2^2 + 2s_3^2)^{1/2} \tag{35a}$$

$$\rho_2 = \tfrac{1}{3}(2s_1^2 - s_2^2 + 2s_3^2)^{1/2} \tag{35b}$$

$$\rho_3 = \tfrac{1}{3}(2s_1^2 + 2s_2^2 - s_3^2)^{1/2} \tag{35c}$$

and that the angles ϕ_{21}, ϕ_{32}, ϕ_{13} defined by

$$\phi_{21} = \phi_2 - \phi_1, \qquad \phi_{32} = \phi_3 - \phi_2, \qquad \phi_{13} = \phi_1 - \phi_3 \tag{36}$$

are given by

$$\sin\phi_{21} = (I_1 I_2)^{1/2}/(3^{1/2}\rho_1\rho_2) \tag{37a}$$

$$\cos\phi_{21} = (s_1^2 + s_2^2 - 5s_3^2)/(18\rho_1\rho_2) \tag{37b}$$

$$\sin\phi_{32} = (I_1 I_2)^{1/2}/(3^{1/2}\rho_2\rho_3) \tag{37c}$$

$$\cos\phi_{32} = (-5s_1^2 + s_2^2 + s_3^2)/(18\rho_2\rho_3) \tag{37d}$$

$$\sin\phi_{13} = (I_1 I_2)^{1/2}/(3^{1/2}\rho_3\rho_1) \tag{37e}$$

$$\cos\phi_{13} = (s_1^2 - 5s_2^2 + s_3^2)/(18\rho_3\rho_1) \tag{37f}$$

where I_1 and I_2 are the principal axis values of the moments of inertia in the ξ–η plane divided by the particle mass. Explicitly,

$$I_1 I_2 = (-s_1^4 - s_2^4 - s_3^4 + 2s_1^2 s_2^2 + 2s_2^2 s_3^2 + 2s_3^2 s_1^2)/12 \tag{38}$$

and

$$I_1 + I_2 = (s_1^2 + s_2^2 + s_3^2)/3 \tag{39}$$

One more condition is needed to finish specifying the orientation of the $\mathbf{r}_1$, $\mathbf{r}_2$, $\mathbf{r}_3$ triangle in the ξ–η–ζ plane. The usual condition

$$\xi_1\eta_1 + \xi_2\eta_2 + \xi_3\eta_3 = 0 \tag{40}$$

(vanishing of the products of inertia) aligns the ξ–η–ζ axes with the principal axes of the moment of inertia tensor, and implies that

$$\phi_1 = \frac{1}{2}\tan^{-1}\left[\frac{6(s_3^2 - s_2^2)(3I_1 I_2)^{1/2}}{2s_1^4 + 5s_2^4 + 5s_3^4 - 5s_1^2 s_2^2 - 2s_2^2 s_3^2 - 5s_3^2 s_1^2}\right] \tag{41}$$

The traditional condition (40) has the disadvantage of introducing a coordinate singularity at the equilateral triangle configuration $s_1 = s_2 = s_3$, where $I_1 = I_2$ and the right-hand side of (41) is undefined. One circuit around the line $s_1 = s_2 = s_3$ in the s_1–s_2–s_3 spaces changes the right-hand side of (41) by π. Furthermore, infinitesimal changes in s_1, s_2, and s_3 in the neighborhood of $s_1 = s_2 = s_3$ can result in finite changes in the right-hand side of (41); this makes it difficult to expand about $s_1 = s_2 = s_3$.[8]

The aforementioned difficulties can be avoided by replacing the traditional condition (40) by the condition

$$\phi_1 = \tfrac{1}{3}(-\phi_{21} + \phi_{13}) \tag{42}$$

When using (41), we adopt the convention that ϕ_{21}, ϕ_{32}, and ϕ_{13}, all of which can be calculated from (36), lie between zero and π, so that $\phi_{21} + \phi_{32} +$

[8] This coordinate singularity caused difficulties in the theory of the nonlinear triatomic molecule.[20] The behavior of wave functions in the neighborhood of this coordinate singularity is discussed by Derrick.[21]

$\phi_{13} = 2\pi$. Then ϕ_1 lies between $-\pi/3$ and $\pi/3$; furthermore, (36) and (42) imply that

$$\phi_2 = \phi_{21} + \phi_1 = \tfrac{2}{3}\pi + \tfrac{1}{3}(-\phi_{32} + \phi_{21}) \tag{43}$$

$$\phi_3 = \phi_{32} + \phi_2 = \tfrac{4}{3}\pi + \tfrac{1}{3}(-\phi_{13} + \phi_{32}) \tag{44}$$

The choice (42) treats the particles symmetrically, since the expressions for ϕ_1, ϕ_2, ϕ_3 go into one another under cyclic permutation of the indices 1, 2, 3 plus a $2\pi/3$ rotation. Furthermore, the right-hand sides of (42)–(44) remain well defined at the equilateral triangle configuration $s_1 = s_2 = s_3$. With the choice (42), permutation of particles is accomplished by performing the rotation which permutes the particles when they are in the equilateral triangle configuration, and then making the corresponding permutation of s_1, s_2, s_3.

The volume element in the coordinate system described above is

$$\prod_{i=1}^{3} d^3\mathbf{r}_i = d^3\mathbf{R} \prod_{i=1}^{3} s_i\, ds_i\, d\alpha \sin\beta\, d\beta\, d\gamma \tag{45}$$

The ranges of the internal coordinates are $|s_2 - s_3| < s_1 < s_2 + s_3$, $0 \leqslant s_2 \leqslant \infty$, $0 \leqslant s_3 \leqslant \infty$, $0 \leqslant \alpha \leqslant 2\pi$, $0 \leqslant \beta \leqslant \pi$, and $0 \leqslant \gamma \leqslant 2\pi$. The finite distance between two points is

$$\sum_{i=1}^{3} (\mathbf{r}_i - \mathbf{r}_i')^2 = 3(\mathbf{R} - \mathbf{R}')^2 + F_0(s_1, s_2, s_3; s_1', s_2', s_3') + \sum_{j=1}^{4} F_j(s_1, s_2, s_3; s_1', s_2', s_3') S_j(\alpha, \beta, \gamma; \alpha', \beta', \gamma') \tag{46}$$

where

$$F_0 \equiv \sum_{i=1}^{3} [(\xi_i - \xi_i')^2 + (\eta_i - \eta_i')^2] \tag{47a}$$

$$F_1 \equiv 2 \sum_{i=1}^{3} (\xi_i\xi_i' + \eta_i\eta_i') \tag{47b}$$

$$F_2 \equiv 2 \sum_{i=1}^{3} (\xi_i\eta_i' - \eta_i\xi_i') \tag{47c}$$

$$F_3 \equiv 2 \sum_{i=1}^{3} (\xi_i\xi_i' - \eta_i\eta_i') \tag{47d}$$

$$F_4 \equiv 2 \sum_{i=1}^{3} (\xi_i\eta_i' + \eta_i\xi_i') \tag{47e}$$

and

$$\begin{aligned} S_1 \equiv{} & \sin^2[\tfrac{1}{2}(\beta - \beta')] \\ & + 2\cos^2(\tfrac{1}{2}\beta)\cos^2(\tfrac{1}{2}\beta')\sin^2[\tfrac{1}{2}(\alpha - \alpha' + \gamma - \gamma')] \\ & + \sin\beta \sin\beta' \sin^2[\tfrac{1}{2}(\alpha - \alpha')] \\ & + 2\sin^2(\tfrac{1}{2}\beta)\sin^2(\tfrac{1}{2}\beta')\sin^2[\tfrac{1}{2}(\alpha - \alpha' - \gamma + \gamma')] \end{aligned} \tag{48a}$$

$$S_2 \equiv -\cos^2(\tfrac{1}{2}\beta)\cos^2(\tfrac{1}{2}\beta')\sin(\alpha-\alpha'+\gamma-\gamma') - \tfrac{1}{2}\sin\beta\sin\beta'\sin(\alpha-\alpha') - \sin^2(\tfrac{1}{2}\beta)\sin^2(\tfrac{1}{2}\beta')\sin(\alpha-\alpha'-\gamma+\gamma') \quad (48b)$$

$$S_3 \equiv \sin^2(\tfrac{1}{2}\beta)\cos^2(\tfrac{1}{2}\beta')\cos(\alpha+\alpha'-\gamma+\gamma') - \tfrac{1}{2}\sin\beta\sin\beta'\cos(\alpha+\alpha') + \cos^2(\tfrac{1}{2}\beta)\sin^2(\tfrac{1}{2}\beta')\cos(\alpha+\alpha'+\gamma-\gamma') \quad (48c)$$

$$S_4 \equiv -\sin^2(\tfrac{1}{2}\beta)\cos^2(\tfrac{1}{2}\beta')\sin(\alpha+\alpha'-\gamma+\gamma') + \tfrac{1}{2}\sin\beta\sin\beta'\sin(\alpha+\alpha') - \cos^2(\tfrac{1}{2}\beta)\sin^2(\tfrac{1}{2}\beta')\sin(\alpha+\alpha'+\gamma-\gamma') \quad (48d)$$

The formulas (46)–(48) follow from (29) and (31)–(33). The explicit dependence of the F_i on s_1, s_2, s_3, s_1', s_2', and s_3' can be calculated from (30), (33)–(39), and (42)–(44). We record only the expansions of the F_i to second order about $s_1 = s_2 = s_3 = s_1' = s_2' = s_3' = a$ that will be needed later. Let $s_i = a(1+\epsilon\sigma_i)$, $s_i' = a(1+\epsilon\sigma_i')$. Then

$$F_0 = a^2\epsilon^2\{\tfrac{5}{9}[(\sigma_1-\sigma_1')^2+(\sigma_2-\sigma_2')^2+(\sigma_3-\sigma_3')^2] - \tfrac{2}{9}[(\sigma_1-\sigma_1')(\sigma_2-\sigma_2')+(\sigma_2-\sigma_2')(\sigma_3-\sigma_3') + (\sigma_3-\sigma_3')(\sigma_1-\sigma_1')] + O(\epsilon)\} \quad (49a)$$

$$F_1 = 2a^2\{1+\tfrac{1}{3}\epsilon(\sigma_1+\sigma_1'+\sigma_2+\sigma_2'+\sigma_3+\sigma_3') + \tfrac{1}{12}\epsilon^2[(\sigma_1+\sigma_1')^2 + (\sigma_2+\sigma_2')^2+(\sigma_3+\sigma_3')^2] - \tfrac{7}{36}\epsilon^2[(\sigma_1-\sigma_1')^2 + (\sigma_2-\sigma_2')^2+(\sigma_3-\sigma_3')^2] + \tfrac{1}{9}\epsilon^2[(\sigma_1-\sigma_1')(\sigma_2-\sigma_2')+(\sigma_2-\sigma_2')(\sigma_3-\sigma_3') + (\sigma_3-\sigma_3')(\sigma_1-\sigma_1')] + O(\epsilon^3)\} \quad (49b)$$

$$F_2 = \tfrac{4}{9}\sqrt{3}a^2\epsilon^2[(-\sigma_1\sigma_2'+\sigma_2\sigma_1'-\sigma_2\sigma_3'+\sigma_3\sigma_2'-\sigma_3\sigma_1'+\sigma_1\sigma_3')+O(\epsilon)] \quad (49c)$$

$$F_3 = a^2\epsilon\{-\tfrac{4}{3}(\sigma_1+\sigma_1')+\tfrac{2}{3}(\sigma_2+\sigma_2'+\sigma_3+\sigma_3')+\epsilon[-\tfrac{1}{3}(\sigma_1+\sigma_1')^2 + \tfrac{1}{6}(\sigma_2+\sigma_2')^2+\tfrac{1}{6}(\sigma_3+\sigma_3')^2+\tfrac{1}{9}(\sigma_1-\sigma_1')^2-\tfrac{1}{18}(\sigma_2-\sigma_2')^2 - \tfrac{1}{18}(\sigma_3-\sigma_3')^2+\tfrac{2}{9}(\sigma_1-\sigma_1')(\sigma_2-\sigma_2'+\sigma_3-\sigma_3') - \tfrac{4}{9}(\sigma_2-\sigma_2')(\sigma_3-\sigma_3')]+O(\epsilon^2)\} \quad (49d)$$

$$F_4 = \sqrt{3}a^2\epsilon\{\tfrac{2}{3}(\sigma_2+\sigma_2'-\sigma_3-\sigma_3')+\epsilon[\tfrac{1}{6}(\sigma_2+\sigma_2')^2-\tfrac{1}{6}(\sigma_3+\sigma_3')^2 - \tfrac{1}{18}(\sigma_2-\sigma_2')^2+\tfrac{1}{18}(\sigma_3-\sigma_3')^2 - \tfrac{2}{9}(\sigma_1-\sigma_1')(\sigma_2-\sigma_2'-\sigma_3+\sigma_3')]+O(\epsilon^2)\} \quad (49e)$$

4.2. Calculation of b_3(exch-1)

This section will derive the results (6a) for b_3(exch-1) by showing that

$$b_3(\text{exch-1}) = -[9\pi a^3/(4\lambda^3)]b_2(\text{exch})[1+O(\lambda/a)] \quad (50)$$

Divide the region of integration in Eq. (8) into two regions, I and II. In I at least one member of the pair s_1, s_2 is less than a; in II both s_1 and s_2 are greater than a. In region I the integrand $G_9 - G_6G_3$ of (8) reduces to $-G_6G_3$. Furthermore, the integrand $G_9 - G_6G_3$ of (8) falls exponentially to zero in region II over a distance of order λ, so that most of the contribution to (8) from region II comes when either $s_1 - a$ or $s_2 - a$ or both are of order λ. Thus the contribution to the integral in (8) from region II is down by a factor of λ/a compared to the contribution from region I.[9] Using the volume element (45) in (8) now yields

$$b_3(\text{exch-1}) = -[1/(2V)] \int_I G_6(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_2, \mathbf{r}_1; \beta) G_3(\mathbf{r}_3; \mathbf{r}_3; \beta)\, d^3\mathbf{R} \times \prod_{i=1}^{3} s_i\, ds_i\, d\alpha \sin\beta\, d\beta\, d\gamma\, [1 + O(\lambda/a)] \tag{51}$$

Now $G_6(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_2, \mathbf{r}_1; \beta)$ depends only on $s_3 = |\mathbf{r}_1 - \mathbf{r}_2|$, and $G_3(\mathbf{r}_3; \mathbf{r}_3; \beta) = \lambda^{-3}$. Furthermore, if $A(s_3)$ is defined by

$$A(s_3) = \int_I s_1\, ds_1\, s_2\, ds_2 \tag{52}$$

then it is easy to show that for $a \leqslant s_3 \leqslant 2a$

$$\begin{aligned} A(s_3) &= \int_{s_3-a}^{s_3+a} s_2 \left(\int_{|s_2-s_3|}^{a} s_1\, ds_1 \right) ds_2 + \int_a^{s_3+a} s_1 \left(\int_{|s_1-s_3|}^{a} s_2\, ds_2 \right) ds_1 \\ &= -(1/24)s_3^4 + \tfrac{1}{2}s_3^2a^2 + \tfrac{2}{3}s_3a^3 \end{aligned} \tag{53}$$

All of the integrations in (51) except the one over s_3 can now be performed to yield

$$b_3(\text{exch-1}) = -4\pi^2\lambda^{-3} \int_a^\infty G_6(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_2, \mathbf{r}_1; \beta) \times s_3 A(s_3)\, ds_3 [1 + O(\lambda/a)] \tag{54}$$

The behavior of G_6 can be determined by noting that, at high temperature,

$$G_6 \sim \exp[-\tfrac{1}{2}\pi\lambda^{-2}(\text{shortest distance from } \mathbf{r}_1, \mathbf{r}_2 \text{ to } \mathbf{r}_2, \mathbf{r}_1)^2]$$

This shortest distance is $a\{\pi + 2[(\tan\theta) - \theta]\}$ where $\theta = \cos^{-1}(a/s_3)$. An elementary calculation now shows that for $\rho_3 - a \ll a$

$$G_6 \sim \exp\{-\tfrac{1}{2}\pi^3a^2\lambda^{-2}[1 + \tfrac{4}{3}\pi^{-1}(2s_3 - 2a)^{3/2}a^{-3/2}]$$

As a consequence of this exponential falloff, the factor $s_3A(s_3)$ in (54) can be replaced by $aA(a)$ with an error of order $(\lambda/a)^{4/3}$. Hence

$$b_3(\text{exch-1}) = -\tfrac{9}{2}\pi^2\lambda^{-3}a^5 \int_a^\infty G_6(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_2, \mathbf{r}_1; \beta)\, ds_3 [1 + O(\lambda/a)] \tag{55}$$

[9] This kind of observation is the basis of the calculation of the first quantum corrections to all of the direct higher virial coefficients for hard spheres by Jancovici.[22]

The same kind of approximation can be used in (7) to show that

$$b_2(\text{exch}) = 2\pi a^2 \int_a^\infty G_6(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_2, \mathbf{r}_1; \beta)\, ds_3\{1 + O[(\lambda/a)^{4/3}] \tag{56}$$

Comparison of (55) and (56) now yields (50); the result (6a) for b_3(exch-1) then follows from using the known result[1-3]

$$b_2(\text{exch}) = 4\pi^3 a^3 \lambda^{-6} \exp\left\{-\pi\left[\frac{1}{2}\left(\frac{\pi a}{\lambda}\right)^2 + \beta_1\left(\frac{\pi a}{\lambda}\right)^{2/3} + \frac{4}{45}\beta_1^2\left(\frac{\pi a}{\lambda}\right)^{-2/3}\right]\right\}\left\{1 + O\left[\left(\frac{\lambda}{a}\right)^{4/3}\right]\right\} \tag{57}$$

in (50).

4.3. Calculation of b_3(exch-2)

The calculation of b_3(exch-2) is similar to the calculation of b_2(exch) in Section 3. The use of (10) in (9) yields

$$b_3(\text{exch-2}) = \frac{1}{3V} \lim_{M\to\infty} \left(\frac{M}{\lambda^2}\right)^{9M/2} \int \cdots \int \prod_{k=0}^{M-1} \prod_{i=1}^{3} d^3\mathbf{r}_i^{(k)} \times \exp\left\{-\pi M \lambda^{-2} \sum_{k=1}^{M} \sum_{i=1}^{3} [\mathbf{r}_i^{(k)} - \mathbf{r}_i^{(k-1)}]^2\right\} \tag{58}$$

where $\mathbf{r}_1^{(0)} = \mathbf{r}_3^{(M)}, \mathbf{r}_2^{(0)} = \mathbf{r}_1^{(M)}, \mathbf{r}_3^{(0)} = \mathbf{r}_2^{(M)}$, and the integration region is restricted by $|\mathbf{r}_1^{(k)} - \mathbf{r}_2^{(k)}| \geqslant a$, $|\mathbf{r}_2^{(k)} - \mathbf{r}_3^{(k)}| \geqslant a$, and $|\mathbf{r}_3^{(k)} - \mathbf{r}_1^{(k)}| \geqslant a$.

The path integral (58) is most easily handled in the coordinates described in Section 4.1. It is convenient to define the Euler angles $\alpha^{(k)}, \beta^{(k)}, \gamma^{(k)}$ for $k = 1, 2, \ldots, M$ relative to those for $k = 0$. With this definition $\alpha^{(0)} = \beta^{(0)} = \gamma^{(0)} = 0$, $\alpha^{(M)} + \gamma^{(M)} = 2\pi/3$, and $\alpha_M - \gamma_M = \beta_M = 0$. Also, $s_1^{(0)} = s_3^{(M)}, s_2^{(0)} = s_1^{(M)}$, and $s_3^{(0)} = s_2^{(M)}$. The integration region is restricted by $s_i^{(k)} \geqslant a$.

The shortest path from the initial point $\mathbf{r}_1^{(0)}, \mathbf{r}_2^{(0)}, \mathbf{r}_3^{(0)}$ to the final point $\mathbf{r}_1^{(M)}, \mathbf{r}_2^{(M)}, \mathbf{r}_3^{(M)}$ is one on which $s_i^{(k)} = a$, $\alpha_k + \gamma_k = 2\pi k/(3M)$, $\beta_k = 0$, and $\alpha_k - \gamma_k$ is arbitrary (because the distance is independent of $\alpha_k - \gamma_k$ when $\beta_k = 0$). In order to calculate b_3(exch-2) to the order indicated in (6b), it is sufficient to expand about this shortest path and approximate the distance in the exponent of (58) by

$$\sum_{i=1}^{3} (\mathbf{r}_i^{(k)} - \mathbf{r}_i^{(k-1)})^2 \simeq 3(\mathbf{R}^{(k)} - \mathbf{R}^{(k-1)})^2 + \tfrac{5}{9} \sum_{i=1}^{3} (s_i^{(k)} - s_i^{(k-1)})^2$$

$$- \tfrac{2}{9}[(s_1^{(k)} - s_1^{(k-1)})(s_2^{(k)} - s_2^{(k-1)}) + (s_2^{(k)} - s_2^{(k-1)})(s_3^{(k)} - s_3^{(k-1)})$$
$$+ (s_3^{(k)} - s_3^{(k-1)})(s_1^{(k)} - s_1^{(k-1)})]$$
$$+ \frac{4\pi^2 a}{27M^2\lambda^2} \sum_{i=1}^{3} (s_i^{(k)} + s_i^{(k-1)} - 2a) + \frac{4\pi^2 a^2}{9M^2} + \frac{4\pi a^2}{3M}\left(\alpha^{(k)} - \alpha^{(k-1)} + \gamma^{(k)}\right.$$
$$\left. - \gamma^{(k-1)} - \frac{2\pi}{3M}\right) + a^2\left(\alpha^{(k)} - \alpha^{(k-1)} + \gamma^{(k)} - \gamma^{(k-1)} - \frac{2\pi}{3M}\right)^2$$
$$+ \tfrac{1}{2}a^2[(\beta^{(k)})^2 + (\beta^{(k-1)})^2 - 2\beta^{(k)}\beta^{(k-1)}\cos(\alpha^{(k)} - \alpha^{(k-1)})]$$
$$- \frac{\pi^2 a^2}{9M^2}[(\beta^{(k)})^2 + (\beta^{(k-1)})^2] \tag{59}$$

The approximation (59) follows readily from (46) by neglecting the terms $F_2S_2 + F_3S_3 + F_4S_4$ and using (48a), (49a), and (49b). To the same order, the volume element (45) can be approximated by

$$\prod_{i=1}^{3} d^3r_i^{(k)} \simeq a^3 \prod_{i=1}^{3} s_i^{(k)}\, ds_i^{(k)}\, \beta^{(k)}\, d\beta^{(k)}\, d\alpha^{(k)}\, d\gamma^{(k)} \tag{60}$$

Because $\beta^{(k)}$ and $\alpha^{(k)}$ enter the approximations (59) and (60) like polar coordinates, it is convenient to make a change of variables to

$$x^{(k)} = \beta^{(k)}\cos\alpha^{(k)}, \qquad y^{(k)} = \beta^{(k)}\sin\alpha^{(k)}, \qquad z^{(k)} = \alpha^{(k)} + \gamma^{(k)} - (2\pi k/3M) \tag{61}$$

The use of (59)–(61) in (58) produces

$$b_3(\text{exch-2}) = \frac{8\pi^2}{3} I_{\text{cm}} I_1 I_2^2 I_3 \exp\left(-\frac{4\pi^3 a^2}{9\lambda^2}\right)\left\{1 + O\left[\left(\frac{\lambda}{a}\right)^{2/3}\right]\right\} \tag{62}$$

where

$$I_{\text{cm}} = \lim_{M\to\infty} \left(\frac{3M}{\lambda^2}\right)^{3M/2} \int\cdots\int \prod_{k=1}^{M-1} d^3\mathbf{R}^{(k)} \exp\left[-\frac{3\pi M}{\lambda^2}\sum_{k=1}^{M} (\mathbf{R}^{(k)} - \mathbf{R}^{(k-1)})^2\right] \tag{63a}$$

$$I_1 = \lim_{M\to\infty} \left(\frac{Ma^2}{\lambda^2}\right)^{M/2} \int\cdots\int \prod_{k=1}^{M-1} dz^{(k)} \exp\left[-\frac{\pi M a^2}{\lambda^2}\sum_{k=1}^{M} (z^{(k)} - z^{(k-1)})^2\right] \tag{63b}$$

$$I_2 = \lim_{M\to\infty} \left(\frac{Ma^2}{2\lambda^2}\right) \int\cdots\int \prod_{k=1}^{M-1} dx^{(k)} \exp\left[-\frac{\pi M a^2}{2\lambda^2}\sum_{k=1}^{M} (x^{(k)} - x^{(k-1)})^2 + \frac{2\pi^3 a^2}{9M\lambda^2}\sum_{k=1}^{M-1} (x^{(k)})^2\right] \tag{63c}$$

$$I_3 = \lim_{M\to\infty} \left(\frac{4M^3}{27\lambda^6}\right)^{M/2} \int\cdots\int \prod_{k=0}^{M-1}\prod_{i=1}^{3} ds_i^{(k)} \exp\left\{-\frac{\pi M}{9\lambda^2}\sum_{k=1}^{M}\left[5\sum_{i=1}^{3}(s_i^{(k)}\right.\right.$$

$$- s_i^{(k-1)})^2 - 2(s_1^{(k)} - s_1^{(k-1)})(s_2^{(k)} - s_2^{(k-1)}) - 2(s_2^{(k)} - s_2^{(k-1)}(s_3^{(k)} - s_3^{(k-1)})$$

$$- 2(s_3^{(k)} - s_3^{(k-1)})(s_1^{(k)} - s_1^{(k-1)})] - \frac{8\pi^3 a}{27M\lambda^2} \sum_{k=1}^{M} \sum_{i=1}^{3} (s_i^{(k)} - a)\Bigg\} \qquad (63d)$$

The factor of $8\pi^2$ in (62) comes from integrating out over $\alpha^{(0)}$, $\beta^{(0)}$, and $\gamma^{(0)}$; the factor of $1/V$ in (58) has been cancelled by the integral over $\mathbf{R}^{(0)}$. Because the exponentials decrease so rapidly for M large, the variables $\mathbf{R}^{(k)}$, $x^{(k)}$, $z^{(k)}$ in (63a)–(63c) can be integrated from $-\infty$ to ∞ and the variables $s_i^{(k)}$ in (63d) from a to ∞.

Also, $\mathbf{R}^{(0)} = \mathbf{R}^{(M)}$, $x^{(0)} = x^{(M)} = z^{(0)} = z^{(M)} = 0$, and $s_1^{(0)} = s_3^{(M)}$, $s_2^{(0)} = s_1^{(M)}$, $s_3^{(0)} = s_2^{(M)}$. The error estimate in (62) is arrived at by the following assignments of orders of magnitude in the regions in which significant contributions occur:

$$\alpha^{(k)} + \gamma^{(k)} = (2\pi k/3M) + O(\lambda/a), \qquad \alpha^{(k)} = O(1), \quad \beta^{(k)} = O(\lambda/a)$$
$$s_i^{(k)} - s_i^{(k-1)} = O[a(\lambda/a)^{2/3}], \qquad s_i^{(k)} = a\{1 + O[(\lambda/a)^{4/3}]\}$$

The integrals I_{cm} and I_1 can be evaluated with the aid of the convolution theorem for the Fourier transform (see Appendix A); the results are

$$I_{\mathrm{cm}} = (3/\lambda^2)^{3/2} \qquad (64)$$

and

$$I_1 = a/\lambda \qquad (65)$$

I_2 can be evaluated with the aid of a formula given in the review article by Gel'fand and Yaglom[10]; the result is

$$I_2 = (4\pi^2/27)^{1/4}(a/\lambda) \qquad (66)$$

The path integral I_3 can be evaluated by comparing (63d) with (10), which shows that

$$I_3 = \int G_3(s_1, s_2, s_3; s_2, s_3, s_1; \beta)\, ds_1\, ds_2\, ds_3) \qquad (67)$$

where $G_3(s_1, s_2, s_3; s_1', s_2', s_3'; t)$ is that solution of

$$[H_3(s_1, s_2, s_3) + (\partial/\partial t)]G_3(s_1, s_2, s_3; s_1', s_2', s_3'; t) = 0 \qquad (68)$$

which reduces to $\delta(s_1 - s_1')\,\delta(s_2 - s_2')\,\delta(s_3 - s_3')$ at $t = 0$ and satisfies the boundary conditions $G_3 = 0$ at $s_1 = a$, at $s_2 = a$, and at $s_3 = a$ and $G_3 \to 0$ as s_1, s_2, and/or $s_3 \to \infty$. Here H_3 is the operator

$$H_3(s_1, s_2, s_3) = -\frac{\hbar^2}{2m}\left[2\left(\frac{\partial^2}{\partial s_1^2} + \frac{\partial^2}{\partial s_2^2} + \frac{\partial^2}{\partial s_3^2}\right) + \frac{\partial^2}{\partial s_1\,\partial s_2} + \frac{\partial^2}{\partial s_2\,\partial s_3}\right.$$

[10] Gel'fand and Yaglom [Ref. 12, Eq. (1.31)]. Gel'fand and Yaglom's λ has the value $\pi^4 a^4/(9\lambda^4)$, their t has the value $2\lambda^2/(\pi a^2)$, and their X has the value zero.

$$+ \frac{\partial^2}{\partial s_3\, \partial s_1}\Bigg] + \frac{16\pi^4\hbar^2 a}{27m\lambda^4}(s_1 + s_2 + s_3 - 3a) \tag{69}$$

Separation of variables produces the solution

$$G_3(s_1, s_2, s_3; s_1', s_2', s_3'; t) = \sum_{n=1}^{\infty} \psi_n(s_1, s_2, s_3)\bar{\psi}_n(s_1', s_2', s_3')e^{-\kappa_n t} \tag{70}$$

where κ_n and ψ_n are the eigenvalues and normalized eigenfunctions of

$$H_3(s_1, s_2, s_3)\psi_n(s_1, s_2, s_3) = \kappa_n\psi_n(s_1, s_2, s_3) \tag{71}$$

The substitutions

$$s_i = a[1 + \tfrac{3}{2}(2\pi^2a^2/\lambda^2)^{-2/3}\sigma_i] \tag{72a}$$

and

$$\kappa_n = (2\pi/9)(2\pi^2a^2/\lambda^2)^{1/3}\beta^{-1}\gamma_n \tag{72b}$$

bring (24) to the form

$$\left\{-\left[2\left(\frac{\partial^2}{\partial\sigma_1{}^2} + \frac{\partial^2}{\partial\sigma_2{}^2} + \frac{\partial^2}{\partial\sigma_3{}^2}\right) + \frac{\partial^2}{\partial\sigma_1\,\partial\sigma_2} + \frac{\partial^2}{\partial\sigma_2\,\partial\sigma_3} + \frac{\partial^2}{\partial\sigma_3\,\partial\sigma_1}\right] + (\sigma_1 + \sigma_2 + \sigma_3)\right\}\psi_n = \gamma_n\psi_n \tag{73}$$

The eigenvalue problem (73) must be solved numerically. A detailed calculation, presented in Appendix C, shows that the eigenfunction ψ_1 belonging to the lowest eigenvalue γ_1 is symmetric in $\sigma_1, \sigma_2, \sigma_3$ and produces the bounds $8.23232 < \gamma_1 < 8.83750$. It now follows from (67), (70), (72b), and the fact that ψ_1 is normalized and symmetric that

$$I_3 = \exp[-(2\pi/9)(2\pi^2a^2/\lambda^2)^{1/3}\gamma_1] \times (1 + O\{\exp[-(2\pi/9)(2\pi^2a^2/\lambda^2)^{1/3}(\gamma_2 - \gamma_1)]\}) \tag{74}$$

The result (6b) for b_3(exch-2) now follows from using (64)–(66) and (74) in (62).

APPENDIX A. EVALUATION OF GAUSSIAN PATH INTEGRALS VIA THE CONVOLUTION THEOREM FOR THE FOURIER TRANSFORM

Consider an integral of the form

$$I_l(x_0, x_l) \equiv \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} \prod_{k=1}^{l} f_k(x_k - x_{k-1})\Bigg] \prod_{k=1}^{l-1} dx_k \tag{A.1}$$

The convolution (faltung) theorem for the Fourier transform (Ref. 15, pp. 464–465) reduces this to the single integral

$$I_l(x_0, x_l) = (1/2\pi)\int_{-\infty}^{\infty} \prod_{k=1}^{l} F_k(y)e^{iy(x_0 - x_l)}\, dy \tag{A.2}$$

where

$$F_k(y) \equiv \int_{-\infty}^{\infty} e^{-ixy} f_k(x)\, dx \tag{A.3}$$

is the Fourier transform of f_k. If

$$f_k(x) = \alpha_k^{1/2} \exp(-\pi\alpha_k x^2) \tag{A.4}$$

then

$$F_k(y) = \exp[-y^2/(4\pi\alpha_k)] \tag{A.5}$$

If (A.5) is inserted in (A.2), the integration is easily performed to yield

$$I_l(x_0, x_l) = \left(\sum_{k=1}^{l} \alpha_k^{-1}\right)^{-1/2} \exp\left[-\pi(x_0 - x_l)^2 \Big/ \sum_{k=1}^{l} \alpha_k^{-1}\right] \tag{A.6}$$

APPENDIX B. EXACT EVALUATION OF THE ANGULAR INTEGRALS IN b_2(exch)

If the expansion[11]

$$\begin{aligned}
\exp\Big\{ & M\pi\lambda^{-2} z_k z_{k-1}[\cos\theta_k \cos\theta_{k-1} \\
& + \sin\theta_k \sin\theta_{k-1} \cos(\phi_k - \phi_{k-1})]\Big\} \\
& = 2\pi\left(\frac{2\lambda^2}{M z_k z_{k-1}}\right)^{1/2} \sum_{l=0}^{\infty} I_{l+(1/2)}\left(\frac{M\pi z_k z_{k-1}}{\lambda^2}\right) \\
& \quad \times \sum_{m=-l}^{l} Y_{l,m}(\theta_k, \phi_k)\bar{Y}_{l,m}(\theta_{k-1}, \phi_{k-1})
\end{aligned}$$

is used in the result of inserting (15) into (14), the angular integrations can be performed by exploiting the orthonormality of the spherical harmonics $Y_{l,m}$. The result is

$$\begin{aligned}
b_2(\text{exch}) = 2^{1/2}\lambda^{-3} \lim_{M\to\infty} \left(\frac{M}{2\lambda^2}\right)^{3M/2} & \int\cdots\int \prod_{k=1}^{M} z_k^2\, dz_k\, d\Omega_M \\
\times \sum_{l=0}^{\infty} \exp & \left[-\frac{\pi M}{2\lambda^2}(z_k^2 + z_{k-1}^2)\right]
\end{aligned}$$

[11] See Ref. 23. The quoted expansion follows from the expansion for $\exp(\gamma\rho\cos\phi)$ on p. 108 and the addition theorem for the spherical harmonics.

$$\times \prod_{k=1}^{M} \left[2\left(\frac{2\lambda^2}{Mz_k z_{k-1}}\right)^{1/2} I_{l+(1/2)}\left(\frac{M\pi z_k z_{k-1}}{\lambda^2}\right)\right]$$

$$\times \sum_{m=-l}^{l} Y_{l,m}(\theta_0, \phi_0)\bar{Y}_{l,m}(\theta_M, \phi_M) \tag{B.1}$$

Because the argument of the modified Bessel function $I_{l+(1/2)}$ is always large, it can be replaced by the asymptotic expansion (Ref. 23, p. 139)

$$I_{l+(1/2)}(\omega) = (2\pi\omega)^{-1/2}e^{\omega}\left[1 - \frac{l(l+1)}{2\omega} + O(\omega^{-2})\right]$$

Furthermore, since $\theta_0 = 0$ and $\theta_M = \pi$,

$$\sum_{m=-l}^{l} Y_{l,m}(\theta_0, \phi_0)\bar{Y}_{l,m}(\theta_M, \phi_m) = (-1)^l(2l+1)/(4\pi)$$

Using these in (B.1) yields

$$b_2(\text{exch}) = 2^{1/2}\lambda^{-3} \lim_{M\to\infty} \left(\frac{M}{2\lambda^2}\right)^{M/2} \int \cdots \int \prod_{k=1}^{M} dz_k$$

$$+ \sum_{l=0}^{\infty} (-1)^l(2l+1) \exp\left[-\frac{\pi M}{2\lambda^2}(z_k - z_{k-1})^2\right.$$

$$\left. - \frac{l(l+1)\lambda^2}{2\pi M} \sum_{k=1}^{M} (z_k z_{k-1})^{-1}\right] \tag{B.2}$$

which is still exact in the $M \to \infty$ limit. Equation (B.2) can be recognized as the result which would be obtained by decomposing the Green's function for the interparticle coordinate in spherical harmonics and then writing a path integral for the radial Green's function.

The sum over l in (B.2) is slowly convergent for $\lambda \ll a$. It can be transformed into a more rapidly convergent series by using one of the transformation formulas for the elliptic theta functions (Ref. 23, pp. 371–373):

$$\sum_{l=0}^{\infty} (-1)^l(2l+1)\exp[-l(l+1)\sigma]$$

$$= \left(\frac{\pi}{\sigma}\right)^{3/2} \exp\left(\frac{\sigma}{4}\right) \sum_{l=0}^{\infty} (-1)^l(2l+1) \exp -\frac{(l+\frac{1}{2})^2\pi^2}{\sigma} \tag{B.3}$$

The formula (B.3), which also arises in the quantum statistics of the rigid rotator, can be readily established with the aid of Poisson's summation formula (Ref. 15, pp. 466–467). The use of (B.3) in (B.2) yields the exact result (19).

APPENDIX C. BOUNDS TO THE EIGENVALUES γ_n

Define operators

$$H(b) \equiv -b\left(\frac{\partial^2}{\partial\sigma_1^2} + \frac{\partial^2}{\partial\sigma_2^2} + \frac{\partial^2}{\partial\sigma_3^2}\right) + \sigma_1 + \sigma_2 + \sigma_3 \tag{C.1}$$

and

$$H' \equiv -\frac{\partial^2}{\partial\sigma_1\,\partial\sigma_2} - \frac{\partial^2}{\partial\sigma_2\,\partial\sigma_3} - \frac{\partial^2}{\partial\sigma_3\,\partial\sigma_1} \tag{C.2}$$

The eigenvalue problem (73) then takes the form

$$[H(2) + H']\psi_n = \gamma_n\psi_n \tag{C.3}$$

The eigenvalues and (unsymmetrized and unnormalized) eigenfunctions of the problem

$$H(b)\phi_{l,m,n}(\sigma_1, \sigma_2, \sigma_3) = \epsilon_{l,m,n}\phi_{l,m,n}(\sigma_1, \sigma_2, \sigma_3) \tag{C.4}$$

are easily found by separation of variables; they are

$$\epsilon_{l,m,n} = b^{1/3}(q_l + q_m + q_n) \tag{C.5}$$

and

$$\phi_{l,m,n} = Ai(b^{-1/3}\sigma_1 - q_l)\,Ai(b^{-1/3}\sigma_2 - q_m)\,Ai(b^{-1/3}\sigma_3 - q_n) \tag{C.6}$$

where q_l is the lth root of $Ai(-q_l) = 0$ with $Ai(z)$ the Airy function.

It can be easily shown that

$$\langle\phi_{l,m,n}|H'|\phi_{l',m',n'}\rangle = 0 \tag{C.7}$$

if $l = l'$ and $m = m'$ and/or if $m = m'$ and $n = n'$ and/or if $n = n'$ and $l = l'$. The Rayleigh–Ritz variational method with a linear combination of $\phi_{1,1,1}$, $\phi_{2,1,1}$, $\phi_{1,2,1}$, and $\phi_{1,1,2}$ as variational trial functions then shows that the first eigenvalue of $H(2)$ is an upper bound to the first eigenvalue of $H(2) + H'$ and the second eigenvalue of $H(2)$ is an upper bound to the second eigenvalue of $H(2) + H'$.[12] With the boundary condition used, the operator

$$-\frac{1}{2}\left(\frac{\partial^2}{\partial\sigma_1^2} + \frac{\partial^2}{\partial\sigma_2^2} + \frac{\partial^2}{\partial\sigma_3^2}\right) + H' = -\frac{1}{2}\left(\frac{\partial}{\partial\sigma_1} + \frac{\partial}{\partial\sigma_2} + \frac{\partial}{\partial\sigma_3}\right)^2$$

is nonnegative. Hence the nth eigenvalue of $H(3/2)$ is a lower bound[13] to the nth eigenvalue of $H(2) + H'$. The first two eigenvalues γ_1 and γ_2 therefore lie in the intervals $(3/2)^{1/3}(3q_1) \leqslant \gamma_1 \leqslant 2^{1/3}(3q_1)$ and $(3/2)^{1/3}(2q_1 + q_2) \leqslant$

[12] A proof of the fact that the Rayleigh–Ritz method gives upper bounds to the higher eigenvalues as well as the lowest eigenvalue can be found in Ref. 24, pp. 75–78.

[13] This can be easily established by using the minimax characterization of the eigenvalues See Ref. 24, pp. 70–71 and Chapter 12.

$\gamma_2 \leqslant 2^{1/3}(2q_1 + q_2)$. The tabulation of the roots of the Airy function given by Abramowitz and Stegun[18] then yields

$$\begin{aligned} 8.02939 < \gamma_1 < 8.83750 \\ 10.00324 < \gamma_2 < 11.04216 \end{aligned} \tag{C.8}$$

The lower bound to γ_1 given in (C.8) can be improved by making use of the Temple formula[25] (also see Ref. 24, p. 214), which [with $H = H(2) + H'$] yields

$$\gamma_1 \geqslant \frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle} - \left(\gamma^* - \frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle}\right)^{-1}\left[\frac{\langle\psi|H^2|\psi\rangle}{\langle\psi|\psi\rangle} - \left(\frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle}\right)^2\right] \tag{C.9}$$

where γ^* is some number which satisfies $\langle\psi|H|\psi\rangle/\langle\psi|\psi\rangle \leqslant \gamma^* < \gamma_2$. With the choice $\psi = \phi_{1,1,1}$ it can be shown that $\langle\psi|H|\psi\rangle/\langle\psi|\psi\rangle = \epsilon_{1,1,1}$ and $\langle\psi|H^2|\psi\rangle/\langle\psi|\psi\rangle = \epsilon_{1,1,1}^2 + \frac{1}{6}2^{-1/3}q_1^2$. Numerical evaluation of the right-hand side of (C.9) with this ψ and $\gamma^* = 10.00324$ yields

$$8.23232 < \gamma_1 < 8.83750 \tag{C.10}$$

Tighter bounds on γ_1 can be obtained by improving the variational trial function ψ.

The symmetry of the eigenfunction ψ_1 belonging to γ_1 can be argued as follows. Clearly $\phi_{1,1,1}$ is symmetric. The symmetric perturbation H' cannot bring in any admixture of an asymmetric state. Because the lower bound to γ_2 lies above the upper bound to γ_1, an asymmetric lowest state cannot be produced by level crossing as H' is turned on. Thus ψ_1 is symmetric.

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