TABLE II. Convergence, for the open-shell wave function, of various properties of PsH. The nonlinear parameters are $\alpha = 0.56$, $\beta = -0.1917$, $z_1 = 0.7054$, $z_2 = 1.163$.

N	10	20	35	56	∞
E_d	0.02674	0.04398	0.04836	0.04943	0.0497
λ (nsec)$^{-1}$	1.825	2.229	2.3963	2.459	2.496
t (nsec) $= 1/\lambda$	0.548	0.449	0.417	0.407	0.401
ν	-0.3428	-0.4225	-0.4596	-0.4766	-0.491

than those reported previously[1] as far as the energy is concerned. Nevertheless, the cusp value ν seems better; perhaps the annihilation rate is also. The values of P_n are qualitatively in agreement with the corrected values of Ref. 2, which used a very simple trial function.

The open-shell results in Table II give an improvement in the dissociation energy of 2% for the 56-term function, as well as a good value for ν. (With this type of trial function the evaluation of P_n would be rather time consuming, and we did not carry it out; we do not expect the results to differ too much from those in Table I.) The extrapolated values represent estimates based only on the limited type of trial function used here. Further work using more general functional forms is presently under way.[4]

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High-Temperature Quantum Corrections to the Second Virial Coefficient for a Hard-Core-Plus-Attractive-Well-Potential Model

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High-temperature asymptotic expansions of $B_{\rm dir}$ for a hard-core-plus–attractive-well potential are calculated using a method developed by Hill and reformulated by D'Arruda and Hill. To lowest order, we find the first quantum correction from the well to be independent of the shape of the well and to depend only on the value of the potential at the core.

I. GENERAL FORMULATION

We begin with the formulation of Boyd, Larsen, and Kilpatrick[1] and write the second virial coefficient B in the form

$$B = B_{\rm dir} + B_{\rm exch}\ , \tag{1}$$

where

$$B_{\rm dir} = \sqrt{2}\, N\lambda^3 \int d\vec{r}\,[2^{-3/2}\lambda^{-3} - G(\vec{r}, \vec{r}; \beta)] \tag{2}$$

and

$$B_{\rm exch} = \mp \sqrt{2}\, N\lambda^3 (2S+1)^{-1} \int d\vec{r}\, G(\vec{r}, -\vec{r}; \beta)\ . \tag{3}$$

The minus (upper) sign in $B_{\rm exch}$ is associated with Bose statistics and the plus sign with Fermi statistics. Here S is the spin, $\lambda = (2\pi\hbar\beta/m)^{1/2}$ is the thermal de Broglie wavelength, and $\beta = (kT)^{-1}$.

Since it has already been shown that the repulsive core present in realistic two-body potentials and in hard spheres leads to a rapid suppression of the exchange piece at high temperature, we shall focus our efforts only on $B_{\rm dir}$. Qualitatively, the exchange piece is nontrivial only if the particles are allowed to come closer to each other than the thermal wavelength. If this is not possible because of the presence of the repulsive forces, the exchange is negligible. G is the thermal Green's function for the relative motion:

$$G(\vec{r}\,', \vec{r}; \beta) = \langle \vec{r}\,' \,|\, e^{-\beta H_r} \,|\, \vec{r} \rangle\ , \tag{4}$$

where

$$H_r = -\left(\frac{\hbar^2}{m}\right)\nabla^2 + V(r) \tag{5}$$

is the Hamiltonian for the relative motion of a pair of particles of mass m.

Following the general procedure as given in earlier work,[2,3] we may write

$$B_d = -\sqrt{2}\, N\lambda^3 \Delta\ , \tag{6}$$

$$\Delta = \sum_{l=0}^{\infty} (2l+1)\left((2\pi i)^{-1}\int_{W_0 - i\infty}^{W_0 + i\infty} e^{\beta W} f^{\,l}(W)\, dW\right)\ , \tag{7}$$

where the integration contour in the complex W plane lies to the right of all singularities and where

$$f^l(W)=\frac{d}{dW}\ \ln A_l(W)+\frac{l+\frac{1}{2}}{2W} \quad . \tag{8}$$

Here $A_l(W)$ is determined up to a multiplicative constant independent of W by matching solutions of the negative-energy-W Schrödinger equation inside the attractive well, with the free-particle solutions outside the well, and demanding that $f^l(W)$ have the form given in Eq. (8). The details are given in Ref. 3.

This formulation may be further extended by noting that for the hard-sphere case

$$A_l^{\rm hc}(W)=K_{l+1/2}(\gamma a) , \tag{9}$$

where a is the radius of the core, $\gamma^2=mW/\hbar^2$ and $K_{l+1/2}(\gamma a)$ is the modified Bessel function of the third kind. Equation (8) may then be put in the form

$$f^l(W)=f^l_{\rm hc}(W)+F^l(W) , \tag{10}$$

where

$$f^l_{\rm hc}(W)=\frac{d}{dW}\ \ln K_{l+1/2}(\gamma a)+\frac{l+\frac{1}{2}}{2W} \tag{11}$$

and

$$F^l(W)=\frac{d}{dW}\ \ln\left(\frac{A_l(W)}{K_{l+1/2}(\gamma a)}\right) \quad . \tag{12}$$

A similar decomposition of Eqs. (6) and (7) gives

$$\Delta=\Delta_{\rm hc}+\delta , \tag{13}$$

$$B_{\rm dir}=B_{\rm hc}+B_1 , \tag{14}$$

where

$$\Delta_{\rm hc}=\sum_{l=0}^{\infty}\ (2l+1)\left((2\pi i)^{-1}\int_{W_0-i\infty}^{W_0+i\infty}\ e^{\beta W}f^l_{\rm hc}(W)\,dW\right) \tag{15}$$

and

$$\delta=\sum_{l=0}^{\infty}\ (2l+1)\left((2\pi i)^{-1}\int_{W_0-i\infty}^{W_0+i\infty}\ e^{\beta W}F^l(W)\,dW\right) . \tag{16}$$

The contribution of $\Delta_{\rm hc}$ to $B_{\rm dir}$ has already been evaluated as[2,3]

$$B_{\rm hc}=\frac{2}{3}\,\pi N a^3\left\{1+\frac{3}{2\sqrt{2}}\ \left(\frac{\lambda}{a}\right)\right.$$
$$\left.+\frac{1}{\pi}\left(\frac{\lambda}{a}\right)^2+\frac{1}{16\pi\sqrt{2}}\ \left(\frac{\lambda}{a}\right)^3+O\left[\left(\frac{\lambda}{a}\right)^4\right]\right\} . \tag{17}$$

The task now remains to calculate B_1, which is

$$B_1=-\sqrt{2}\,N\lambda^3\delta . \tag{18}$$

II. ATTRACTIVE-WELL POTENTIAL

We now assume a general attractive-well potential of the form

$$V(r)=0 , \qquad b\leq r<\infty$$

$$V(r)=-\mathcal{V}(r) , \quad a\leq r<b$$

$$V(r)=\infty , \qquad r<a .$$

Only the solutions of the radial Schrödinger equation, which obeys the inner boundary conditions and satisfies the conditions imposed on $f^l(W)$, are needed for the computation of $A_l(W)$. Such solutions are obtained, inside the well, from

$$\left[\frac{d^2}{dr^2}+\frac{2}{r}\ \frac{d}{dr}-\left(\frac{l(l+\frac{1}{2})}{r^2}+\frac{mW}{\hbar^2}-\frac{m\mathcal{V}(r)}{\hbar^2}\right)\right]U^l(r)=0 , \tag{19}$$

with

$$\nu=l+\tfrac{1}{2} , \qquad U(r)=\frac{mv(r)}{\hbar^2} \ ;$$

$$U^l=\frac{y_\nu}{r^{1/2}} , \quad \gamma^2=\frac{mW}{\hbar^2} \quad .$$

Equation (19) may be cast into the form

$$\left[\frac{d^2}{dr^2}+\frac{1}{r}\ \frac{d}{dr}-\left(\frac{\nu^2+\gamma^2r^2-r^2U(r)}{r^2}\right)\right]y_\nu(r)=0 . \tag{20}$$

Furthermore, introducing the ordering parameter ξ, with the prescription to set $\xi=1$ at the end of the calculation, Eq. (20) becomes

$$\left(\frac{d^2}{dr^2}+\frac{1}{r}\ \frac{d}{dr}-\frac{\eta_\nu(r)}{\xi^2}\right)\ y_\nu(r)=0 , \tag{21}$$

where

$$\eta_\nu(r)=\frac{\nu^2+\gamma^2r^2-r^2U(r)}{r^2} \quad . \tag{22}$$

Asymptotic solutions of Eq. (21) can be constructed with the Jeffreys–Wenzel–Kramers–Brillouin (JWKB) *ansatz*

$$y_\nu\sim e^{s/\xi}\Sigma C_m\,\xi^m . \tag{23}$$

Substituting (23) into (21) and collecting terms in the usual fashion generates the desired solutions. Then, following the procedure as given in Ref. 3 and using (13), (14), (17), and (18), we find

$$B_{\rm dir}=\tfrac{2}{3}\pi N a^3\left[1+\frac{3}{2\sqrt{2}}\ \left(\frac{\lambda}{a}\right)+\frac{1}{\pi}\left(\frac{\lambda}{a}\right)^2\right.$$
$$+\frac{1}{16\pi\sqrt{2}}\left(\frac{\lambda}{a}\right)^3-3a^{-3}\int_a^b r^2\,dr(e^{\beta\mathcal{V}(r)}-1)$$
$$\left.+\frac{3}{2\sqrt{2}}\ (\beta\mathcal{V}(a))\left(\frac{\lambda}{a}\right)+O\left(\frac{\lambda^4}{a^4}\right)\right] . \tag{24}$$

This result is valid to the stated order in (λ/a) for $b-a/a$ and $m\mathcal{V}(a)a^2/2\pi\hbar^2$ fixed. It is not uniformly valid for $m\mathcal{V}(a)a^2/2\pi\hbar^2$ large. For helium both $b-a/a$ and $m\mathcal{V}(a)a^2/2\pi\hbar^2$ are near 1, so that

$$\beta\mathcal{V}(a)=\frac{m\mathcal{V}(a)a^2}{2\pi\hbar^2}\ \left(\frac{\lambda}{a}\right)^2=O\left[\left(\frac{\lambda}{a}\right)^2\right] .$$

Equation (24) reduces to the hard-sphere case in the limit $v(a)\rightarrow 0$, but not in the limit $b\rightarrow a$. The nonuniformity in this latter limit can be traced to a rapidly changing potential as $b\rightarrow a$, and hence to a region where the JWKB asymptotic solutions are no longer valid.[4] However, we believe that this difficulity can be treated using a modified form of the Miller–Good method.[5]

III. DISCUSSION

The results of this calculation show that the first quantum correction for a hard-core–plus–attractive-well potential is independent of the shape of the well, and depends only on the value of the potential at the core. Thus for any potential, square well, triangular well, etc., which is continuous near the core, the first quantum correction is given by the term[6]

$$\frac{3}{2\sqrt{2}}\,[\beta v(a)]\left(\frac{\lambda}{a}\right) \quad .$$

Hence, classical arguments alone should suffice in distinguishing which potential-well model best fits experimental data at high temperatures, at least to $O(\lambda^4/a^4)$.

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[4] The author is indebted to Dr. M. Barnhill for discussion on this point.

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Quantum Corrections to the Virial Coefficients for Potentials with Hard Cores

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The leading quantum correction to the virial coefficients is calculated for the case where the intermolecular potential has a hard core. If the potential is bounded and continuous outside the core, the leading quantum correction to the second virial coefficient comes entirely from the region of the hard-core boundary, and depends only on the diameter of the core and the depth of the potential well at the core boundary. The leading quantum correction to the higher virial coefficients also involves the value of the classical radial distribution function at the core boundary. If the potential has discontinuities outside the core, these will give rise to additional first-order corrections.

We investigate the leading quantum correction to the virial coefficients for the case where the intermolecular potential has a hard core. The standard Wigner–Kirkwood method cannot be used, since it requires that the potential be differentiable. Instead we use the method developed in a previous paper[1] (hereafter referred to as I) which is valid for a general potential. The basic quantity is the thermal Green's function $G(\vec{r},\vec{r};\ \beta)$, and this is calculated in the approximation where the curvature of the potential boundaries is neglected. This enables us to obtain the quantum corrections to