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Interaction potential of the H-He system and the hyperfine frequency shift of H in He buffer gas

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The van der Waals potential of the H-He interaction and the hyperfine frequency shift of H in He are predicted using the Tang-Toennies model. This model damps the long-range *ab initio* dispersion terms individually using a universal damping function and adds to this a simple Born-Mayer repulsive term. The Born-Mayer parameters are derived from self-consistent-field calculations. The resulting potential is found to be in good agreement with two molecular-beam experiments and its well parameters, in excellent agreement with the complete configuration-interaction calculation. In order to compare with experiment, the hyperfine frequency shift is thermally averaged over the potential both quantum mechanically and classically. The thermally averaged results are in excellent agreement with experiment in the high-temperature range but there are some discrepancies with the measurements at 0.5 and at 1.15 K. These discrepancies may be due to the fact that the long-range coefficient K_{10} used is too small. The quantum and classical results are practically identical for temperature above 40 K. The classical statistics fails completely only for temperature below 5 K. Also in the quantum calculation, the isotope effect between ^{3}He and ^{4}He is found to show up only for temperature below 10 K. The theoretical isotope effect is in qualitative agreement with experiment.

I. INTRODUCTION

The interaction potential of the H-He system has been studied using a variety of techniques. This system provides a particularly sensitive and useful test for theoretical and experimental methods for determining van der Waals potentials since it is the simplest heteronuclear system and it has perhaps the smallest well depth of all atom-atom partners. It turns out that it is extremely difficult to precisely determine the well region of the potential. The calculated well depths differ from each other as much as one order of magnitude. Although recent *ab initio* calculations of the well depth seem to converge to the area of 0.5 meV, there are still some discrepancies between theory and experiment.

A quantity that offers a strong complement to the study of interaction potentials is the hyperfine frequency shift (HFS). The magnetic hyperfine splitting of the hydrogen atom is caused by the spin-spin interaction between the electron and the proton. The interaction with the helium atom perturbs the density of electron spin at the proton and leads to a small shift in the hyperfine frequency. The hyperfine splitting constant, denoted as $a(R)$, is therefore a function of the internuclear separation R. The fractional hyperfine frequency shift is defined as

$$\frac{\Delta a(R)}{a}=\frac{a(R)-a(\infty)}{a(\infty)} . \tag{1}$$

The interpretation of the observed HFS involves an average of $\Delta a(R)$ over the relative motion of the colliding atoms as determined by the interaction potential $V(R)$. Thus a theoretical calculation of HFS requires the knowledge of both $a(R)$ and $V(R)$ over a wide range of R. As mentioned earlier, it is difficult to determine $V(R)$. It is equally difficult, if not more so, to determine $a(R)$. The difficulty in the *ab initio* calculation is mainly due to antisymmetrization of the wave function that leads to complex formal problems. These problems are well known in calculations of interatomic potentials. While there are many calculations for $V(R)$, there are only a few calculations for $\Delta a(R)$. Considerable discrepancies exist between the results.

Because of the complexity involved in the *ab initio* calculation, in recent years some simple models have been developed for $V(R)$. Most of these models begin with values for the potential at small and large internuclear separations. At small R, the first-order Coulomb and exchange energy, which are accounted for in a self-consistent-field (SCF) calculation, dominates the potential. The result is a repulsive potential that can often be described by a Born-Mayer form $A\exp(-bR)$. At large R, the potential is given by the dispersion series which is determined by the known van der Waals coefficients. The dispersion series is then damped by some damping functions as R is getting smaller. By adding the short-range potential to the damped dispersion potential, a simple expression is obtained for the entire van der Waals potential including the all-important intermediate well region. Some results from these models are shown to be remarkably accurate.[1]

The physical origin of $V(R)$ and $\Delta a(R)$ is the same, namely the distortion of the wave function. Therefore, it is not surprising that they have a similar qualitative behavior. Both $V(R)$ and $\Delta a(R)$ are positive for small R and decrease to negative values as R becomes larger. For very large R, both of them approach zero in the form of a series with a R^{-6} leading term. Therefore, it is not unreasonable to expect that a similar procedure used in the potential model will also give a fairly accurate model for the hyperfine frequency shift.

Among all potential models, the Tang-Toennies model[1] is particularly suited for this purpose. Other than the Born-Mayer range parameter b, there is no free parameter in the damping function of the Tang-Toennies model. Since the SCF short-range results of $\Delta a(R)$ also have a Born-Mayer behavior, the Tang-Toennies model can thus be directly applied to the determination of the entire $\Delta a(R)$.

In this paper we will use the Tang-Toennies model to calculate the van der Waals potential $V(R)$ of the H-He system. We find that in the well region the results are in excellent agreement with the recent complete configuration-interaction (CI) calculations. The same model is also used to calculate $\Delta a(R)$, which are compared with other theoretical results. But these comparisons are less meaningful since previously calculated $\Delta a(R)$ differ so much from each other. In order to compare directly with experiment, we average the present $\Delta a(R)$ with $V(R)$ of this paper and obtain the temperature dependence of the HFS. We find that the results so obtained are in excellent agreement with high-temperature observations in the temperature range of $-140\ \mathrm{K} \le T \le 620\ \mathrm{K}$. But the agreement with the negative HFS measured at 1 K is only fair.

Since the present $\Delta a(R)$ and $V(R)$ are reasonably realistic, we carried out both quantum and classical averages to determine the range of validity of the classical statistics. Generally, classical statistics is believed to be accurate for $T \gtrsim 300$ K. We are surprised to find that our classical and quantum results are practically identical all the way down to 40 K. The isotopic effect between ^{3}He and ^{4}He also does not show up until the temperature gets below 10 K.

II. THE MODEL

A. The potential model and its parameters

For the interaction potential we use the model proposed by Tang and Toennies.[1] This model incorporates available dispersion coefficients and damps the asymptotic dispersion series with the universal radial-dependent damping functions. This is then added to a simple Born-Mayer repulsive term to give

$$V(R) = A\exp(-bR) - \sum_{n\ge 3}^{9} f_{2n}(R)C_{2n}/R^{2n} , \qquad (2)$$

where

$$f_{2n} = 1 - \exp(-bR)\sum_{k=0}^{2n}(bR)^k/k! . \qquad (3)$$

The first three dispersion coefficients C_6, C_8, and C_{10} are now well established,[2] and they are listed in Table I. Higher-order terms are estimated by the recursion relation of Tang and Toennies:[3]

$$C_{2n} = (C_{2n-2}/C_{2n-4})^3 C_{2n-6} \qquad (4)$$

for $n \ge 6$. The sum over n is truncated at $n=9$ as was done previously.

TABLE I. Parameters (in a.u.) used in the potential model of Eq. (2) for the H-He interaction.

A	4.8185[a]
b	1.807[b]
C_6	2.823[c]
C_8	41.83[c]
C_{10}	871.3[c]

[a] $A=(1+\gamma)A_{\mathrm{SCF}}$, where $\gamma=0.15$ and A_{SCF} is the amplitude of the Born-Mayer fit of the SCF results of Refs. 4 and 5 [see Eq. (5)].

[b] The range parameter of the Born-Mayer fit of the SCF results of Refs. 4 and 5 [see Eq. (5)].

[c] Reference 2.

The two Born-Mayer parameters A and b can be derived from single-configuration SCF calculations. The SCF values calculated by Ray[4] and by Das, Wagner, and Wahl[5] are shown in Fig. 1. In the range studied here, they can be adequately expressed as

$$V_{\mathrm{SCF}}(R) = A_{\mathrm{SCF}}\exp(-bR) . \qquad (5)$$

The SCF values from Ray's calculation are only slightly different from Das *et al.* The parameters A_{SCF} and b in Eq. (5) are chosen to fit the data in the region of the repulsive wall near the van der Waals minimum (4 a.u. $\le R \le$ 6 a.u.). There are other repulsive contributions to the potential, the most important of which is the exchange dispersion. However, the sum of these contributions is relatively small and is shown to be proportional

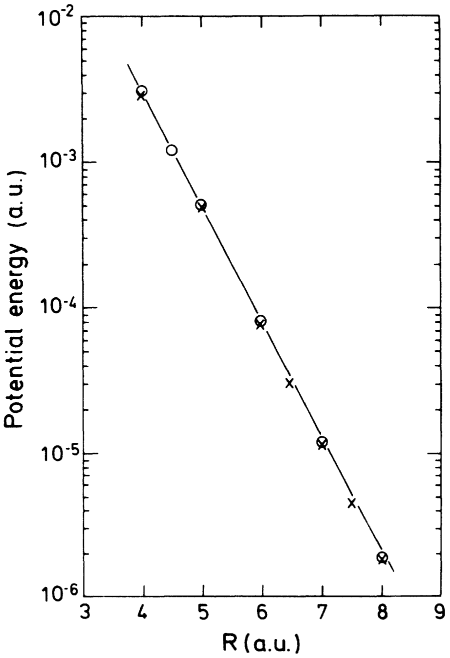

FIG. 1. The Born-Mayer behavior of the single-configuration SCF potential of the H-He system: ×, Das, Wagner and Wahl (Ref. 3); ○, Ray (Ref. 4). The solid line is the present Born-Mayer fit of the SCF potential in the repulsive region of 4 a.u. $\le R \le$ 6 a.u.

to the V_{SCF} in the region of the potential well.[1] That is, b in Eqs. (2) and (3) is determined by the SCF results, whereas A in Eq. (2) is given by

$$A=(1+\gamma)A_{\mathrm{SCF}}\ . \tag{6}$$

The constant γ is found to vary in a narrow range. The value[1] of γ for He-He interaction is $\gamma_{\text{He-He}}=0.17$ and for H-H is $\gamma_{\text{H-H}}=0.14$. For the He-H interaction, we take the geometric mean,

$$\gamma_{\text{He-H}}=(\gamma_{\text{He-He}}\gamma_{\text{H-H}})^{1/2}=0.15\ . \tag{7}$$

All the parameters for the potential are summarized in Table I.

B. The model for the hyperfine frequency shift and its parameters

Since the behavior of the hyperfine frequency shift (HFS) as a function of internuclear separation R is very much similar to the potential, we use the same Tang-Toennies model for the fractional HFS. That is,

$$\frac{\Delta a}{a}=B\exp(-\beta R)-\sum_{n\geq 3}^{9} g_{2n}(R)K_{2n}/R^{2n}\ , \tag{8}$$

where

$$g_{2n}=1-\exp(-\beta R)\sum_{k=0}^{2n}(\beta R)^k/k!\ . \tag{9}$$

The first three long-range coefficients K_6, K_8, and K_{10} of the HFS for H in the presence of He are taken from the recent calculations of Greenwood and Tang.[6] The higher-order terms are again estimated by the recursion relation

$$K_{2n}=(K_{2n-2}/K_{2n-4})^3K_{2n-6} \tag{10}$$

for $n\geq 6$.

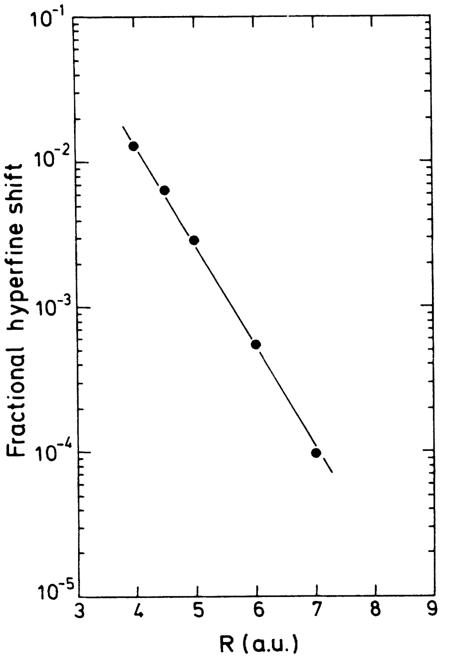

FIG. 2. The Born-Mayer behavior of the single-configuration SCF results of the fractional hyperfine frequency shift of H in He: ●, Ray (Ref. 4). The solid line is the present Born-Mayer fit of Ray's calculation.

TABLE II. Parameters (in a.u.) used in Eq. (8) of the model for the fractional hyperfine frequency shift of H in He.

B	6.634[a]
β	1.520[b]
K_6	13.294[c]
K_8	278.36[c]
K_{10}	2914.9[c]

[a] $B=(1+\alpha)B_{\mathrm{SCF}}$, where $\alpha=0.15$ and B_{SCF} is the amplitude of the Born-Mayer fit of the SCF results of Ref. 4 [see Eq. (11)].

[b] The range parameter of the Born-Mayer fit of the SCF results of Ref. 4 [see Eq. (11)].

[c] Reference 6.

The results of the single-configuration SCF calculation for the HFS by Ray[4] are shown in Fig. 2. It is seen that they also exhibit a Born-Mayer behavior:

$$\left[\frac{\Delta a}{a}\right]_{\mathrm{SCF}}=B_{\mathrm{SCF}}\exp(-\beta R)\ . \tag{11}$$

We assume that the sum of all other repulsive contributions is small and is proportional to the SCF value—that is, the parameter B in Eq. (8) is given by

$$B=(1+\alpha)B_{\mathrm{SCF}}\ . \tag{12}$$

Furthermore, we assume $\alpha=\gamma$, the value determined for the potential. This is an *ad hoc* assumption. It is possible to use α as an adjustable parameter. However, in the absence of other information, the present choice seems to be a reasonable one. All parameters used in Eq. (8) are listed in Table II.

III. RESULTS

A. The van der Waals potential

The van der Waals potential calculated from Eq. (2) with parameters listed in Table I is shown in Fig. 3 together with some previously determined potentials. The well parameters of the present potential are compared with previous determinations in Table III.

It is seen from Fig. 3 that the repulsive wall of the present potential is essentially identical to the experimentally determined potential of Gengenbeck, Hahn, and Toennies.[7] For that part of the potential, their determination is most direct and probably most accurate. They measured the absolute integral cross sections and their velocity dependence in a molecular-beam experiment. Five potential parameters were selected to best fit their data. Their results are, however, not sensitive to the attractive part of the potential because the collision energies are too high. The attractive part of the potential was determined by another molecular-beam experiment of Toennies, Welz, and Wolf[8] with very low collision energies between 2.2×10^{-5} and $95.5\ \times10^{-5}$ a.u. The relative integral cross sections for H-He and D-He were measured and the atomic Ramsauer-Townsend effect was observed. This enabled them to conclude that the van der Waals potential has a minimum at $R_m = 7.03a_0$ with a well depth of $\epsilon = 1.69 \times 10^{-5}$ a.u. As is seen in Fig. 3 and Table III, the present potential has a well that is only slightly deeper than this value. The present well depth is between the experiment and the one determined by the multiconfiguration SCF (MCSCF) calculation of Das, Wagner, and Wahl.[5] It was shown recently by Jochensen, Berlinsky, and Hardy[9] that the MCSCF potential of Das *et al.* will also reproduce the data of Toennies *et al.* very well. Therefore, it is certain that the present potential will also yield results in good agreement with the low-energy molecular-beam experiment.

In fact, the MCSCF calculation of Das *et al.* was considered to be the best *ab initio* result before 1984. In 1984, Knowles, Murrel, and Braga[10] did a complete CI calculation with a large Gaussian basis set which gives a well depth of $\epsilon = 1.84 \times 10^{-5}$ a.u. at $R_m = 6.88a_0$. They also pointed out that although the basis set used in the MCSCF calculation of Das *et al.* is large enough, the basis-set superposition error was not corrected. If this were done, the results would be in closer agreement with their complete CI calculation. It is seen in Fig. 3 and Table III that the well parameters of the present potential are almost in perfect agreement with the complete CI results.

The only experimental data that the present potential is unable to fully explain is the extreme low-temperature diffusion coefficient measured by Hardy *et al.*[11] at 1 K. According to Jochensen *et al.*,[9] the diffusion cross section at 1 K obtained from the experimental potential of Toennies *et al.*[8] is about 20% higher than the observed one. Since the present potential is only slightly deeper than the potential of Toennies *et al.*, presumably the diffusion cross section at 1 K from the present potential will also not be in good agreement with the experiment. Jochensen *et al.*[9] constructed another empirical potential that fits both the diffusion coefficient at 1 K and the cross sections of the low-energy molecular-beam experiment. This potential is also shown in Fig. 3. It is seen that this empirical potential is further away from the complete CI potential than the MCSCF potential of Das *et al.*

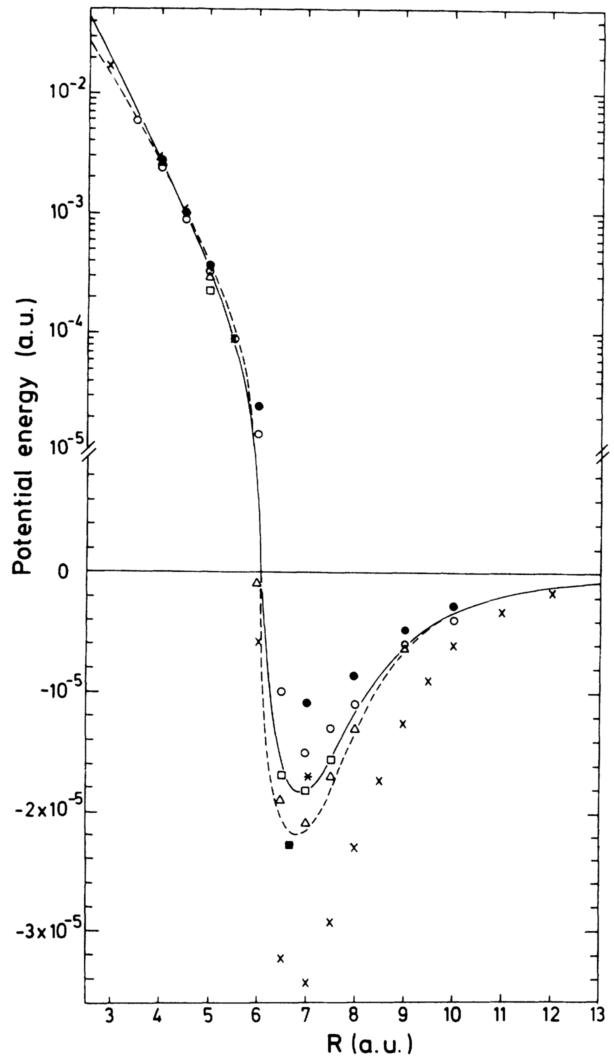

FIG. 3. Interaction potentials for H-He: ●, MCSCF of Ray (Ref. 4); ×, generalized VB of Davison and Liew (Ref. 19); △, MCSCF of Das *et al.* (Ref. 5); ○, MRD-CI of Theodorakopoulos *et al.* (Ref. 28); □, complete CI of Knowles *et al.* (Ref. 10); — — —, empirical potential, the repulsive part by Gengenbach *et al.* (Ref. 7) and the attractive part by Jochensen *et al.* (Ref. 9); ■, well bottom of the Scoles potential (Ref. 9); ∗, well bottom of the experimental potential of Toennies *et al.* (Ref. 8); ——, the present potential predicted by Eq. (2).

TABLE III. Comparison of the well depth ϵ (in a.u.) and well minimum R_m (in a.u.) of the van der Waals potential of the H-He interaction.

Method	ϵ $(\times 10^5)$	R_m
CI (Ref. 27)	11.91	6.56
MRD-CI (Ref. 28)	1.50	6.99
Electron gas (Ref. 29)	2.02	6.80
Experiment (Ref. 8)	1.69	7.03
Empirical (Ref. 9)	2.21	6.78
Scoles model (Ref. 9)	2.27	6.67
GVB (Ref. 19)	3.53	6.80
MCSCF (Ref. 4)	1.10	7.00
MCSCF (Ref. 5)	2.15	6.86
Complete CI (Ref. 10)	1.83	6.88
Present	1.84	6.87

In fact, the potential that best fit the diffusion data at 1 K is the Scoles potential.[9] This potential is based on a theory similar to the present one. It uses the short-range SCF results together with the long-range dispersion series. The damping function in this potential is, however, given by the prescription of Douketis *et al.*[12] While this potential gives a diffusion coefficient at 1 K in perfect agreement with experiment, the velocity dependence of the total integral cross sections obtained from this potential between 2.2×10^{-5} and 95.5×10^{-5} a.u. does not agree with the measurement. Furthermore, the well of this potential is considerably deeper and has a much shorter equilibrium distance than the complete CI potential as shown in Fig. 3 and Table III. The difference is apparently quite significant as Knowles *et al.*[10] noted that "if the Scoles potential is correct, then all theoretical calculations are much worse than is the common experience with comparable molecules."

Thus, it is still difficult to conclude unequivocally what the true potential of this system should be. It seems clear, however, that the accuracy of the present model is comparable to the best theoretical calculation. The result is realistic enough to make it interesting for us to examine the closely related hyperfine frequency shift obtained from the same model.

B. The hyperfine frequency shift

The fractional hyperfine frequency shift (HFS) as a function of internuclear separation R calculated from Eq. (8) with parameters listed in Table II is shown in Fig. 4. It is seen that the shape of the function is very similar to the interaction potential. There are only a few previous theoretical calculations of this function. Adrian[13] was the first one to recognize that the HFS consists of a positive contribution due to Pauli distortion at short range and a negative one at long range due to van der Waals polarization. Earlier calculations[14-18] have shown that this idea is essentially correct. However, these calculations suffer from the lack of a reliable way to combine the long-range and short-range effects. The necessity of choosing a more or less arbitrary cutoff point for the van der Waals contribution due to its divergent nature makes these calculations remain on the qualitative level. In an *ab initio* calculation, this uncertainty can only be removed by using a two-center wave function that is sufficiently flexible to represent the electron distribution accurately in both the short-range and long-range regions. As far as we are aware, there are only two previous calculations that were aimed at achieving this goal. One is the generalized valence-band calculation by Davison and Liew,[19] the other is the multiconfiguration SCF calculation by Ray.[4] Their results are also shown in Fig. 4. It is seen that in the short range, they more or less agree with each other, but in the well region there are large differences. The dashed line is simply the average of these two *ab initio* shifts that was used by Jochensen and Berlinksy[20] in their calculation. The single-configuration SCF results[4] are also shown in Fig. 4. The negative portion of the shift cannot be produced by such a calculation, but in the repulsive region it is fairly accurate. The results obtained from the present model of Eq. (8) are shown as the solid line in Fig. 4. It falls between the two *ab initio* calculations. It is interesting to compare the fractional HFS shown in Fig. 4 with the interaction potentials shown in Fig. 3. Both Ray[4] and Davison and Liew[19] have used their respective methods to calculate both the shift $\Delta a(R)$ and the potential $V(R)$. Figure 3 shows that neither the *ab initio* potential of Ray nor that of Davison and Liew is very accurate. The Ray potential is too shallow while the potential of Davison and Liew is much too deep. Presumably, their HFS results are of similar quality since each of them has used the same basis set to calculate these two quantities. Figures 3 and 4 show that the relative positions between the results from the present model and these two *ab initio* calculations are approximately the same for both the interaction potential and the hyperfine frequency shift. This suggests that the present HFS is more accurate than either of the two *ab initio* calculations.

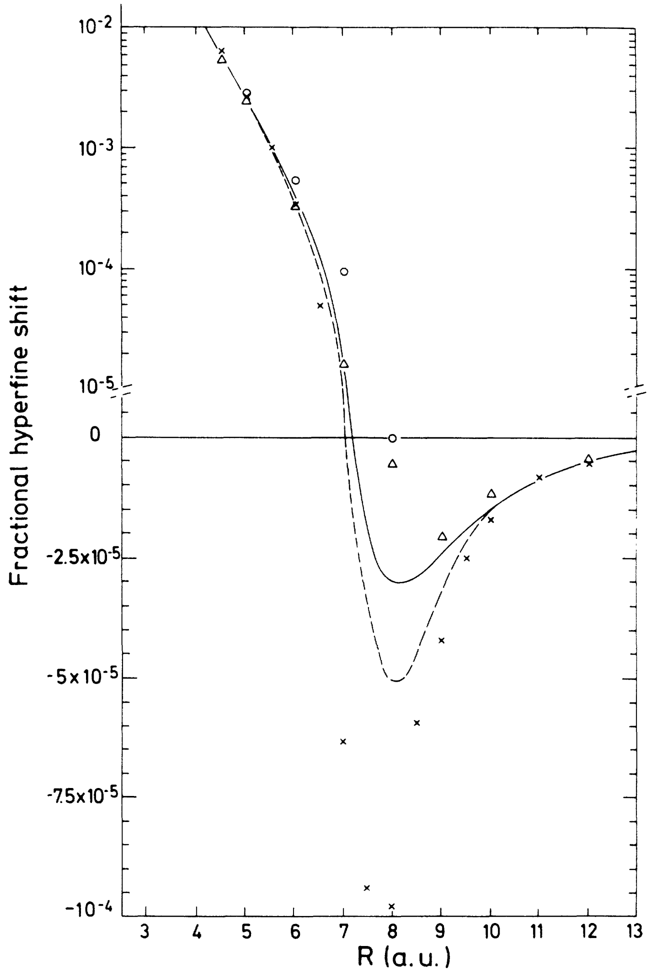

FIG. 4. Fractional hyperfine frequency shift of H in He: ○, single-configuration SCF by Ray (Ref. 4); △, MCSCF by Ray; ×, generalized VB of Davison and Liew (Ref. 19); — — —, average of MCSCF and GVB used by Jochensen and Berlinsky (Ref. 20); ——, the present result predicted by Eq. (8).

IV. THE THERMAL AVERAGE OF THE HYPERFINE FREQUENCY SHIFT

In order to compare with experiment, the fractional HFS obtained from Eq. (8) must be thermally averaged with the interatomic potential to give the temperature dependence. At room temperature and above, the classical Boltzmann statistics should be adequate. At low temperature, the quantum-mechanical average becomes necessary. The isotope effect in the HFS between He^3

and He^4 that was observed can be obtained only from quantum mechanics. To compare with experiment and to establish the region of validity for the classical statistics, we thermally average the HFS with both quantum and classical statistics.

A. Quantum average

To calculate the temperature dependence of the HFS quantum mechanically, we must first average the fractional HFS over the scattering wave function for a given energy E:

$$A(E)=\rho\int|\psi_E(R)|^2[\Delta a(R)/a(\infty)]d^3R\ , \qquad (13)$$

where ρ is the number density of the helium buffer gas. The scattering wave function ψ_E is the solution of the equation

$$\nabla^2\psi_E+\frac{2\mu}{\hbar^2}[E-V(R)]\psi_E=0\ , \qquad (14)$$

where μ is the reduced mass of the H-He system and E is the center-of-mass energy. With usual partial-wave expansion, ψ_E can be expressed as

$$\psi_E=\frac{1}{kR}\sum_l i^l(2l+1)\exp(i\delta_l)P_l(\cos\theta)F_l(kR)\ , \qquad (15)$$

where $k=(2\mu E/\hbar^2)^{1/2}$ and the partial wave $F_l(kR)$ is obtained from the equation

$$\frac{d^2}{dR^2}F_l(kR)+\left[k^2-\frac{2\mu}{\hbar^2}V(R)-\frac{l(l+1)}{R^2}\right]F_l(kR)=0\ . \qquad (16)$$

with $V(R)$ given by Eq. (2), this equation can be solved numerically with a boundary condition $F_l(kR)=0$ at $R=0$. While the phase shift δ_l is uniquely determined by Eq. (16), the amplitude of the partial wave $F_l(kR)$ is not. After δ_l is obtained, $F_l(kR)$ must be normalized so that in the region where $V(R)$ has practically vanished it is equal to

$$F_l(kR)=kR\,[\cos\delta_l j_l(kR)-\sin\delta_l\eta_l(kR)]\ , \qquad (17)$$

where j_l and η_l are the spherical Bessel and Neumann functions.

Most applications of partial-wave analysis are aimed at obtaining the cross sections that need only the phase shift. However, for the quantum average expressed in Eq. (13), the scattered wave function itself in all space is required. For this purpose, the amplitude of the partial wave must be normalized[21,22] according to Eq. (17). The number of necessary partial waves ranges from 4 at 0.3×10^{-5} a.u. to 40 at 120×10^{-5} a.u.

With the fractional shift $\Delta a/a(\infty)$ given by Eq. (8) and ψ_E by Eq. (15), $A(E)$ can be calculated from Eq. (13) by carrying out the integration numerically. Finally, $A(E)$ must be thermally averaged over the energy to give the temperature dependence

$$\bar{A}(T)=\frac{2}{(KT)^{3/2}}\frac{1}{(\pi)^{1/2}}\int_0^\infty E^{1/2}A(E)\exp(-E/kT)dE\ , \qquad (18)$$

where K is the Boltzmann constant and T is absolute temperature. With a given T, Eq. (18) can be evaluated by numerical integration. Following Jochensen and Burlinsky,[20] we report our results in terms of $a(\infty)\bar{A}(T)/\rho$, where $a(\infty)=1.420405\times10^9$ Hz. The results are listed in Table IV and shown in Figs. 5 and 6.

TABLE IV. The thermally averaged hyperfine frequency shift $A(\infty)\bar{A}(T)/\rho(10^{-18}\ \text{Hz cm}^3)$ of H in ^{4}He.

T (K)	Quantum	Classical
0.2	−3.80	
0.5	−6.22	
1	−5.92	864.90
2	−4.78	34.26
3	−3.66	5.48
4	−2.61	0.10
5	−1.62	−1.19
6	−0.69	−1.20
7	0.14	−0.78
8	1.01	−0.18
9	1.90	0.61
10	2.84	1.62
20	12.06	11.04
30	20.99	20.45
40	28.71	28.64
50	36.45	36.40
100	69.42	69.39
150	98.33	98.31
200	124.01	123.99
250	147.46	147.43
300	169.29	169.27
350	189.86	189.85
400	209.42	209.39

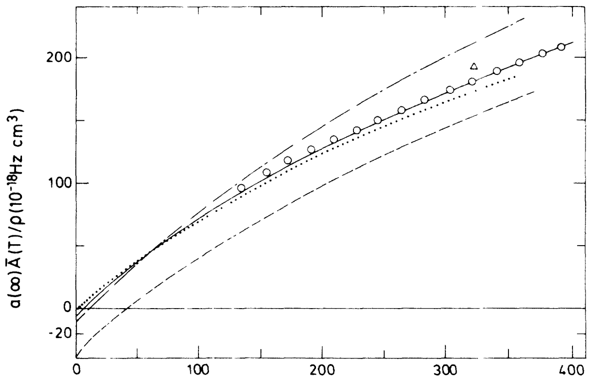

FIG. 5. The thermally averaged hyperfine frequency shift of H in He as a function of temperature: ——, the present result; ○, experimental result of Wright *et al.* (Ref. 21); △, measurement by Pipkin and Lambert (Ref. 30); —·—·—·, calculation of Jochensen and Berlinsky (Ref. 20); · · · ·, calculation of Ray (Ref. 4); — — —, calculation of Davison and Liew (Ref. 19). Except the present result, the rest of the data are taken directly from Ref. 20.

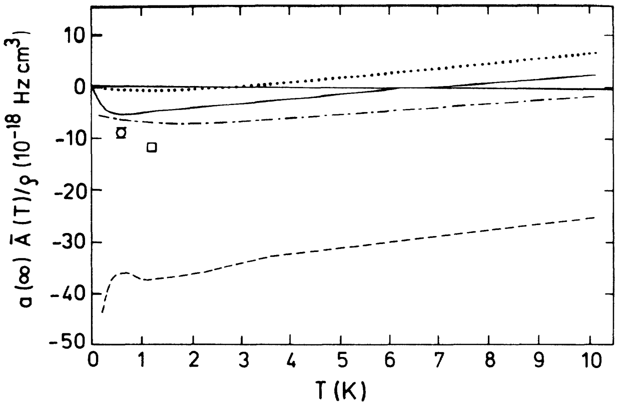

FIG. 6. The thermally averaged hyperfine frequency shift of H in He in the low-temperature range: ——, the present result; —·—·—, calculation of Jochensen and Berlinsky (Ref. 20); · · · ·, calculation of Ray (Ref. 4); — — —, calculation of Davison and Liew (Ref. 19); □, experimental result of H in ^{4}He at $T=1.15$ K by Hardy *et al.* (Ref. 11); ○, experimental results of H in ^{3}He at $T=0.5$ K by Hardy *et al.* (Ref. 24). Except the present result, the rest of the data are taken directly from Ref. 20. All calculations are for H in ^{4}He.

It is seen from Eq. (16) that there is an isotope effect because the wave function depends on the reduced mass of the system. We have calculated the averaged shifts for both ^{3}He and ^{4}He. The results are shown in Fig. 7.

B. Classical average

The correct thermal average should, of course, be given by the quantum-mechanical treatment as described in Sec. IV A. Nevertheless, it is interesting to compare the results with the thermal average obtained in classical physics. According to the classical Boltzmann statistics, the thermal average of the HFS is simply given by

$$\bar{A}(T)=4\pi\rho\int_0^\infty[\Delta a(r)/a(\infty)]\exp[-V(R)/KT]R^2dR\ . \tag{19}$$

Instead of going through the scattering wave function, the classical thermal average is obtained directly. Here the fractional shift $\Delta a(R)/a(\infty)$ of Eq. (8) and the interaction potential $V(R)$ of Eq. (2) appear in the same integral which can be carried out numerically. Clearly this is a much simpler procedure than the quantum average method. The classical results are also listed in Table IV and shown in Fig. 8.

It is generally believed[20] that the classical average is valid for $T\gtrsim 300$ K. It was estimated[14] by wavelength arguments that the difference between quantum and classical average is about 4% at 323 K. We are surprised to find that, although the average procedure is entirely different from the computational point of view, the classical and quantum-mechanical results are essentially identical with each other all the way down to 40 K. Even at temperature as low as 10 K, the classical result is still usable. The classical statistics fails completely only for temperature less than 5 K as seen in Fig. 8.

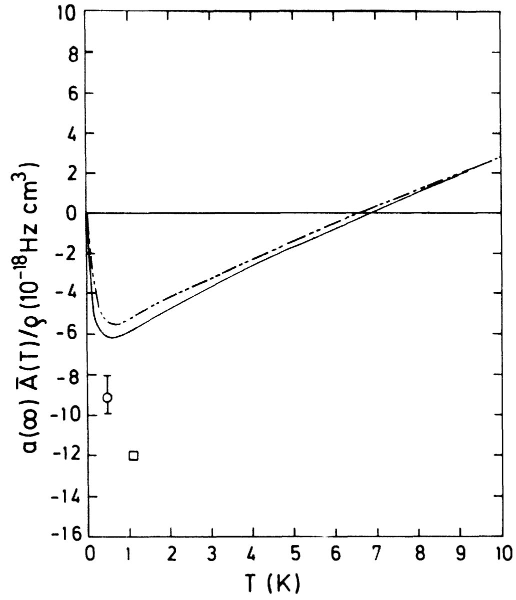

FIG. 7. Isotope effect of the thermally averaged hyperfine frequency shift of H in He: ——, calculated according to Eq. (18) for H in ^{4}He; — — —, calculated according to Eq. (18) for H in ^{3}He; ϕ, experimental result of H in ^{3}He at $T=0.5$ K by Hardy *et al.* (Ref. 24); □, experimental results of H in ^{4}He at $T=1.15$ K by Hardy *et al.* (Ref. 11). The isotope effect between ^{3}He and ^{4}He does not show up until the temperature drops below 9 K.

C. Comparison with experiments and previous theories

The thermally averaged HFS as a function of temperature obtained from the present model is shown in Fig. 5 for the high-temperature range and in Fig. 6 for the low-

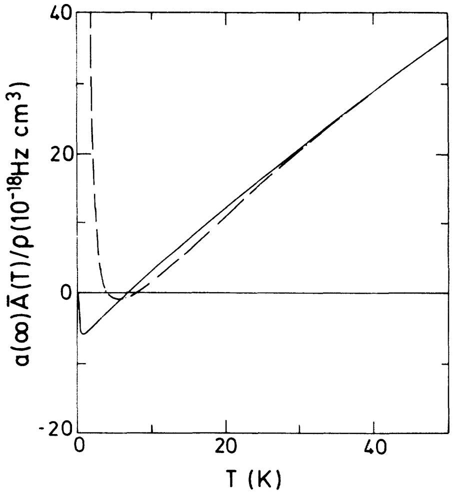

FIG. 8. Comparison between quantum and classical thermal averages of the hyperfine frequency shift of H in He: ——, quantum result calculated according to Eq. (18); —·—·—, classical result calculated according to Eq. (19). The quantum and classical results are practically identical for temperature above 40 K. The classical statistics fails completely only for temperature below 5 K.

temperature range. It is seen in Fig. 5 that the present result is in excellent agreement with the experiment of Wright, Balling, and Lambert[23] over a wide range of temperature. At the extreme low temperature, as shown in Fig. 6, the present result is only in agreement with the negative sign of the shift observed in the experiment. Hardy *et al.*[11,24] measured the HFS of H in ^{3}He at 0.5 K to be $-(9\pm1)\times10^{-18}$ Hz cm^3 and in ^{4}He at 1.15 K to be -11.8×10^{-18} Hz cm^3. The corresponding values obtained from the present calculation are -5.5×10^{-18} Hz cm^3 and -6.2×10^{-18} Hz cm^3, respectively.

Among previous theoretical calculations, the results of Ray[4] are only slightly smaller than the experiment in the high-temperature range but they fail to account for the values of the negative shifts around 1 K. The results of Davison and Liew[19] fall far below the experimental data at all temperatures and are much too negative at 1 K. Jochensen and Berlinsky[20] used the mean value of the fractional shifts of Ray and of Davison and Liew. As a function of R, it has a significantly deeper well than the present result as seen in Fig. 4. They averaged this function over their empirical potential. Their averaged shift of H in ^{3}He at 0.5 K is -6×10^{-18} Hz cm^3 and in ^{4}He at 11.5 K, -7×10^{-18} Hz cm^3. These values are only slightly closer to the experiment than the present results. On the other hand, their results are noticeably too high at high temperatures as shown in Fig. 5.

V. DISCUSSION

In this paper we have used the Tang-Toennies model to calculate the potential energy curve of the H-He system. The predicted potential agrees well with the potential determined by the two molecular-beam experiments, one probing the repulsive wall and the other, the van der Waals well. The predicted well parameters are almost in exact agreement with the most accurate *ab initio* calculations. The only experimental data the present potential cannot yet fully explain is the diffusion cross section at 1 K measured by Hardy *et al.* The measured value is (20±1) Å^2 whereas the present potential gives 22 Å^2 in a calculation[25] including the second-order approximation in the Chapman-Enskog theory. Since the second-order contribution increases to as much as 30% at low temperature,[9] it is possible that the discrepancy will be resolved in a third-order calculation. However, at this moment the third-order effect is unknown. It should also be pointed out that at such low temperature, the diffusion cross section is rapidly decreasing as the temperature is lowered. A 0.2° deviation in temperature will also explain the difference.

The accuracy of the final result depends on the validity of the model and the quality of the input parameters. The present potential model is on a reasonably good theoretical foundation;[1] its predictive power has been shown previously for many atom-atom, atom-molecule interactions.[26] Among all the parameters for the H-He interaction, the constant γ in Eq. (6) is most uncertain. The term involving γ takes account of the additional repulsion due to the exchange dispersion which can be determined only semiempirically at present for most systems. This constant has been determined previously for the homonuclear H-H and He-He interactions.[1] Since this term contributes only a small fraction of the total potential, it is not unreasonable to expect that the constant $\gamma_{\text{H-He}}$ for the heteronuclear H-He interaction can be determined by a combination of $\gamma_{\text{H-H}}$ and $\gamma_{\text{H-He}}$. In Eq. (7) we have used the geometric combining rule. Actually since $\gamma_{\text{H-H}}$ and $\gamma_{\text{He-He}}$ are very close, the arithmetic combination rule gives about the same answer. To see how large an effect this term will have on the final result, we set $\gamma_{\text{H-He}}=0$ and repeat the calculation. We find that the potential well is 14% deeper. The well depth ϵ becomes 2.1×10^{-5} a.u. which is close to the MCSCF result of Das *et al.*[5] as seen in Table III. This indicates that no serious error can be introduced by the approximation of Eq. (7). In fact, with $\gamma_{\text{H-He}}$ given by Eq. (7), the present result is in close agreement with the complete CI calculation. This can be regarded as a justification for the present procedure.

The same model is applied to the calculation of the hyperfine frequency shift of the H-He system. Overall, the results obtained appear to be the best calculation available in the literature. In the high-temperature range, the agreement with experiment is excellent. However, at 0.5 and 1 K significant differences between the thermally averaged HFS of the present model and the measured ones do exist. Although both theoretical and experimental results show a negative shift at such a low temperature, the absolute magnitude differs from each other by approximately a factor of 2.

The long-range coefficient K_{10} of Greenwood and Tang used in this paper may be too small. The "growth" pattern of K_6, K_8, and K_{10} seems too slow from the point of view of an asymptotic series. Furthermore, the "corrected" variation-perturbation results of K_6, K_8, and K_{10} by Rao, Ikenberry, and Das[16] are 13.26, 269.0, and 7221.0, respectively. While K_6 and K_8 are similar to the values used in this paper, K_{10} is 2.5 times larger. A larger K_{10} will make results of the present model closer to the experimental data at low temperature but will not have much effect at high temperature. It would be interesting to carry out such a calculation with a larger K_{10} in the future when more experimental data covering a wider low-temperature range become available.

The other uncertain component of the present HFS model is the "exchange dispersion" term. It is assumed that its relative contribution is the same as the corresponding term in the interation potential V. This is done by setting $\alpha=\gamma$ in Eq. (12). This is an *ad hoc* assumption as mentioned earlier. However, in the absence of other information, this seems to be a reasonable assumption since there is a one-to-one correspondence between the terms in HFS and in V, and the physical origin and the general shape of these terms are the same. To test the sensitivity of this term, we again set $\alpha=0$ and repeat the calculation. We find that the minimum of the fractional HFS is decreased from -3.0×10^{-5} to -3.45×10^{-5}. In view of the large differences between the existing *ab initio* results, this is a small change, as seen in Fig. 4. Thus, our final conclusion will not be altered.

It is conceivable that a complete *a priori* CI calculation, like the one with 69 964 configurations used in the determination of the potential of this system,[10] can be carried out. However, such a large calculation simply has not yet been done for the HFS. Even if converged *ab initio* results are available, there is still a need to fit the calculated points with an analytical expression for the interplay between theory and experiment. In such a case, the constant γ can be used as an adjustable parameter to summarize the theoretical results. In the absence of such information, the present model enables us to make fairly accurate estimates of the HFS from the more accessible, albeit incomplete, theoretical results.

The theoretical analysis of the hyperfine frequency shift and its temperature dependence was considered[18] to be "one of the most illuminating developments in the theory of interacting atoms in the past few decades." Unfortunately, up until recently such analysis remains more or less on a qualitative level because of the difficult problem of joining the short-range Pauli distortion and the long-range van der Waals effect in the intermediate region. It is seen in this paper that the Tang-Toennies model, which is successful in predicting interaction potentials, also offers a very expedient method to make realistic HFS calculations. Hopefully, this work will stimulate more interests in the accurate determination of the long-range hyperfine-frequency-shift coefficients that are well defined and in principle exactly calculable. With these coefficients, many experimental HFS results can be quantitatively analyzed.

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