

Hyperfine Pressure Shift and van der Waals Interactions. I. Hydrogen-Helium System*

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The origin of the hyperfine pressure shift (HPS) for hydrogen atoms in a helium atmosphere has been analyzed quantitatively. The theory is discussed in terms of three distinct regions of interaction. Calculations are carried out explicitly for the short-range and long-range regions, and the importance of the intermediate region is investigated. At short range, the Pauli distortion effect is treated through an orthogonalization procedure, and a variation-perturbation approach is utilized to consider the long-range van der Waals interaction. Our theoretical result for the HPS is 1.9×10^{-9} /mm Hg as compared with the experimental value of $3.7 \pm 0.7 \times 10^{-9}$ /mm Hg. The major sources for the discrepancy between these results appear to be neglect of correlation effects and uncertainties with respect to the intermediate-range contribution.

I. INTRODUCTION

There has been sustained interest for more than thirty years in the theory of interatomic and intermolecular forces.¹ With the availability of improved computing techniques and refined treatments for perturbation effects and many-body effects in atomic systems, there has been a recent enhancement in efforts to understand interatomic forces quantitatively. Concurrently, optical pumping techniques² have provided accurate values for properties, the interpretation of which requires not only a knowledge of interatomic energies, but also a detailed understanding of wave functions. Among these properties are the dependence of the magnetic hyperfine constant of paramagnetic atoms on pressure of a rare gas atmosphere and also the lifetimes of polarized spin states. Our primary concern is with the former phenomena referred to as hyperfine pressure shift (HPS). The trend of observed HPS for hydrogen atoms in various rare-gas atmospheres has been qualitatively explained as arising from a competition between short-range and long-range effects, the latter increasing in relative importance in heavier rare-gas atmosphere.³ The short-range effect has been explained as arising from the overlap between hydrogen and rare gas atom orbitals³ and an estimate of the HPS due to this mechanism has been made for hydrogen-helium system.⁴ In the present work we have undertaken a quantitative analysis of both short-range and long-range effects for the H-He system. Our aim is not only to obtain improved agreement between theory and experiment but also to determine the limitations of current approaches to the calculation of properties of interacting atoms.

In Sec. II we describe the procedure that we have utilized to obtain the long-range effect on the hyperfine constant. This procedure also yields a value of the van der Waals energy. In Sec. III, the short-range calculation is described and the dependence of the hyperfine frequency on interatomic separation presented. Section IV deals with the combination of short-range and long-range effects and the statistical averaging procedure used to evaluate

the HPS as well as a discussion of our results.

II. VAN DER WAALS EFFECT

When the separation between the two atoms of the system is sufficient that overlap effects are negligible, then the predominant interaction arises out of mutual polarizations of the atoms referred to as the van der Waals effect. For the hydrogen-helium (H-He) system in this region, the interaction Hamiltonian in atomic units is

$$\mathcal{H}'_{\text{VDW}} = \frac{2}{R} - \frac{1}{r_{\text{H2}}} - \frac{1}{r_{\text{H3}}} - \frac{2}{r_{\text{He1}}} + \frac{1}{r_{12}} + \frac{1}{r_{13}}, \quad (1)$$

where electron 1 is associated with a hydrogen nucleus and electrons 2 and 3 belong to helium. As is customary, we expand this Hamiltonian (1) in terms of spherical harmonics.⁵ In this work we have included the first three terms in this expansion. These are: the dipole-dipole term

$$\mathcal{H}'_{\text{dd}} = \frac{1}{R^3} \sum_{m=-1}^1 C_{11}(m) r_1 Y_{1,m}^*(1) [r_2 Y_{1,m}(2) + r_3 Y_{1,m}(3)], \quad (2)$$

$$\text{where } C_{11}(m) = (-1)^{m+1} (1 + \delta_{|m|,0})^4 \pi/3; \quad (3)$$

the dipole-quadrupole term

$$\mathcal{H}'_{\text{dq}} = \frac{1}{R^4} \sum_{m=-1}^1 \sum_{i=2}^3 C_{12}(m) \times [r_1 r_i^2 Y_{1,m}^*(1) Y_{2,m}^{(i)} - r_1^2 r_i Y_{2,m}^*(1) Y_{1,m}^{(i)}], \quad (4)$$

$$\text{where } C_{12}(m) = (-1)^m (12\pi/\sqrt{15}) (1 + 2\delta_{|m|,1})^{-1/2} \quad (5)$$

and the combined quadrupole-quadrupole and dipole-octupole interaction

$$\begin{aligned} \mathcal{H}'_{\text{qq}} = & \frac{1}{R^5} \sum_{i=2}^3 \left\{ \sum_{m=-1}^1 C_{13}(m) \right. \\ & \times [r_1^3 r_i Y_{3,m}^{*(1)} Y_{1,m}^{(i)} + r_1 r_i^3 Y_{1,m}^{*(1)} Y_{3,m}^{(i)}] \\ & \left. + \sum_{m=-2}^2 C_{22}(m) r_1^2 r_i^2 Y_{2,m}^{*(1)} Y_{2,m}^{(i)} \right\}, \quad (6) \end{aligned}$$

where $C_{13}(m) = (-1)^{m+1} (4\pi/\sqrt{21}) (4\delta_{|m|,0} + \sqrt{6}\delta_{|m|,1})$,

$$\begin{aligned} C_{22}(m) = & (-1)^m (4\pi/5) (6\delta_{|m|,0} \\ & + 4\delta_{|m|,1} + \delta_{|m|,2}). \quad (7) \end{aligned}$$

This last interaction will henceforth be referred to simply as the quadrupole-quadrupole term. The range of validity of this expansion has been analyzed by several authors and broadly the criterion is that the interatomic separation be larger than the sum of the radii of the two atoms.

With the Hamiltonian expressed as in Eqs. (2), (4), and (6), one is naturally led to consider the perturbation theory technique for solving this problem. The zero-order wave function describes the separated atoms and can be taken as a product of the isolated atom wave functions. However, the first-order equation presents difficulties arising from the inherent two-electron nature of the perturbation operator. Thus, it becomes obvious immediately that any perturbation procedure which attempts to set up differential equations for the perturbed one-electron states will lead to coupled equations which are particularly troublesome to handle. In view of this, we have utilized a variational approach which avoids this difficulty.

The variation function which we have used is of the form

$$\delta\Psi_{\text{VDW}} = f\Psi_0, \quad (8)$$

where Ψ_0 is the unperturbed wave function of the total H-He system

$$\Psi_0 = \chi_{\text{H}}(1)\chi_{\text{He}}(2)\chi_{\text{He}}(3)\alpha_1(\alpha_2\beta_3 - \alpha_3\beta_2)/\sqrt{2}. \quad (9)$$

For the three interactions considered, the variation functions f have the forms

$$\begin{aligned} f_{\text{dd}} = & \frac{1}{R^3} \sum_{n,k=1}^{N_0} \sum_{m=-1}^1 C_{11}(m) A_{nk} r_1^n \\ & \times Y_{1,m}^{*(1)} [r_2^k Y_{1,m}^{(2)} + r_3^k Y_{1,m}^{(3)}], \quad (10) \end{aligned}$$

$$\begin{aligned} f_{\text{dq}} = & \frac{1}{R^4} \sum_{n,k}^N \sum_{j=2}^3 \sum_{m=-1}^1 C_{12}(m) A_{nk} \\ & \times [r_1^n r_j^{k+1} Y_{1,m}^{*(1)} Y_{2,m}^{(j)} \\ & - r_1^{n+1} r_j^k Y_{2,m}^{*(1)} Y_{1,m}^{(j)}], \quad (11) \end{aligned}$$

$$\begin{aligned} f_{\text{qq}} = & \frac{1}{R^5} \sum_{n,k}^{N_0} \sum_{j=2}^3 A_{nk} \left\{ \sum_{m=-1}^1 C_{13}(m) \right. \\ & \times [r_1^{n+2} r_j^k Y_{3,m}^{*(1)} Y_{1,m}^{(j)} \\ & \left. + r_1^n r_j^{k+2} Y_{1,m}^{*(1)} Y_{3,m}^{(j)}] \right. \\ & \left. + \sum_{m=-2}^2 C_{22}(m) r_1^{n+1} r_j^{k+1} Y_{2,m}^{*(1)} Y_{2,m}^{(j)} \right\}, \quad (12) \end{aligned}$$

where $C_{11}(m)$, $C_{12}(m)$, $C_{13}(m)$, and $C_{22}(m)$ are given in Eqs. (3), (5), and (7).

The variation function, Eq. (8), is similar to one used earlier by Davison,⁶ except that he utilized for the helium wave function in Ψ_0 a complicated function incorporating correlation effects through the inclusion of interelectronic coordinates. Since we wanted to use the same zero-order function for short-range effects as well, correlated wave functions would have been a little too complicated to use. Also, for larger atoms, use of correlated wave functions would make the calculations prohibitively difficult. It is therefore helpful to test the results with simpler Hartree-Fock wave functions for lighter atoms. A comparison with Davison's van der Waals energy terms can then provide an assessment of the importance of intra-atomic correlation in the hydrogen-helium system. A somewhat different type of variation function has been suggested by Löwdin and Hirschfelder.⁷ This corresponds to using different pairwise excitation functions for each pair of states made up of one orbital from each of the interacting atoms. This modification is indistinguishable from the choice in (8) for the H-He system studied here because each of these atoms has a single orbital leading to only one pair of mutually interacting states.

A variation-perturbation technique was employed to determine the parameters A_{nk} . In this procedure we minimize the functional

$$J(\delta\Psi) = \langle \delta\Psi | \mathcal{H}_0 - E_0 | \delta\Psi \rangle + 2\langle \delta\Psi | \mathcal{H}' | \Psi_0 \rangle, \quad (13)$$

$$\text{where } \mathcal{H}_0 = \mathcal{H}_{\text{H}} + \mathcal{H}_{\text{He}}, \quad E_0 = E_{\text{H}} + E_{\text{He}}. \quad (14)$$

\mathcal{H}_{H} and \mathcal{H}_{He} being the Hamiltonians of the isolated atoms and E_{H} and E_{He} the corresponding energies. Since our unperturbed wave function Ψ_0 is a Hartree-Fock function, we first express the function $J(\delta\Psi)$ in terms of the many-electron Hartree-Fock Hamiltonian \mathcal{H}_{HF}

$$\begin{aligned} J(\delta\Psi) = & \langle \delta\Psi | (\mathcal{H}_{\text{HF}} - E_0) | \delta\Psi \rangle \\ & + \langle \delta\Psi | \Delta\mathcal{H} | \delta\Psi \rangle + 2\langle \delta\Psi | \mathcal{H}' | \Psi_0 \rangle, \quad (15) \end{aligned}$$

$$\text{where } \Delta\mathcal{H} = \mathcal{H}_0 - \mathcal{H}_{\text{HF}} \quad (16)$$

or explicitly, for the H-He system,

$$\Delta\mathcal{H} = \frac{1}{r_{23}} - \left\langle \chi_{\text{He}}(3) \left| \frac{1}{r_{23}} \right| \chi_{\text{He}}(3) \right\rangle - \left\langle \chi_{\text{He}}(2) \left| \frac{1}{r_{23}} \right| \chi_{\text{He}}(2) \right\rangle + \left\langle \chi_{\text{He}}(2) \chi_{\text{He}}(3) \left| \frac{1}{r_{23}} \right| \chi_{\text{He}}(2) \chi_{\text{He}}(3) \right\rangle. \quad (17)$$

For our system, the explicit forms of \mathcal{H}_{HF} and E_0 are given by

$$\mathcal{H}_{\text{HF}} = -\frac{1}{2} \sum_i \nabla_i^2 - \frac{1}{r_{1\text{H}}} - \frac{2}{r_{2\text{He}}} - \frac{2}{r_{3\text{He}}} + \int \frac{\chi_{\text{He}}^2(3)}{r_{23}} d\tau_2 + \frac{\chi_{\text{He}}^2(2)}{r_{23}} d\tau_3 - \int \frac{\chi_{\text{He}}^2(2) \chi_{\text{He}}^2(3)}{r_{23}} d\tau_2 d\tau_3, \quad (18)$$

$$E_0 = \epsilon_{\text{H}} + 2\epsilon_{\text{He}} - \int \frac{\chi_{\text{He}}^2(2) \chi_{\text{He}}^2(3)}{r_{23}} d\tau_2 d\tau_3,$$

where ϵ_{H} and ϵ_{He} are one-electron energies for the 1s orbitals of hydrogen and helium atoms. With the help of Eqs. (18) and substituting for $\delta\Psi$ from Eq. (8), Eq. (15) may be re-expressed as

$$J(\delta\Psi) = \frac{1}{2} \left\langle \Psi_0 \left| \sum_{i=1}^3 \left| \frac{\partial f}{\partial r_i} \right|^2 \right| \Psi_0 \right\rangle + \frac{1}{2} \left\langle \Psi_0 f \left| \sum_{i=1}^3 \frac{1}{r_i^2} [L_i^2, f] \right| \Psi_0 \right\rangle + \left\langle \Psi_0 \left| |f|^2 \Delta\mathcal{H} \right| \Psi_0 \right\rangle + 2 \left\langle \Psi_0 f \left| \mathcal{H}' \right| \Psi_0 \right\rangle, \quad (19)$$

where L_i is the electronic angular momentum operator.

The minimization of the functional (19) with respect to the variation parameters results in a system of linear equations, the solutions of which are the A_{nk} . In carrying out this procedure, it is necessary to express the four integrals of $J(\delta\Psi)$ in Eq. (19) in terms of radial integrals. For the dipole-dipole case, these expressions are

$$\frac{1}{2} \left\langle \Psi_0 \left| \sum_{i=1}^3 \left| \frac{\partial f}{\partial r_i} \right|^2 \right| \Psi_0 \right\rangle = \frac{4}{6R^6} \sum_{n,n',k,k'} A_{nk} A_{n'k'} \times [nn'I(\text{HH}, n+n'-2)I(\text{HeHe}, k+k') + kk'I(\text{HH}, n+n')I(\text{HeHe}, k+k'-2)], \quad (20)$$

$$\frac{1}{2} \left\langle \Psi_0 f \left| \sum_{i=1}^3 \frac{1}{r_i^2} [L_i^2, f] \right| \Psi_0 \right\rangle = \frac{4}{3R^6} \sum_{n,k,n',k'} A_{nk} A_{n'k'} \times [I(\text{HH}, n+n'-2)I(\text{HeHe}, k+k') + I(\text{HH}, n+n')I(\text{HeHe}, k+k'-2)], \quad (21)$$

$$\left\langle \Psi_0 \left| |f|^2 \Delta\mathcal{H} \right| \Psi_0 \right\rangle = \frac{4}{9R^6} \sum_{n,k,n',k'} A_{nk} A_{n'k'} \times (\text{HH}, n+n')J(k, 1, k'), \quad (22)$$

$$2 \left\langle \Psi_0 \left| f^* \mathcal{H}' \right| \Psi_0 \right\rangle = \frac{8}{3} \frac{1}{R^6} \sum_{n,k} A_{nk} I(1, n+1)I(2, k+1). \quad (23)$$

Here the one- and two-electron radial integrals are defined by

$$I(ij, n) = \int_0^\infty P_i(r_1) P_j(r_1) r_1^n dr, \quad (24)$$

$$J(m, k, n) = \int_0^\infty \int_0^\infty r_1^m \frac{r_1^k}{r_2^{k+1}} r_2^n \times |P_{\text{He}}(r_1)|^2 |P_{\text{He}}(r_2)|^2 dr_1 dr_2, \quad (25)$$

and the radial functions $P(r_1)$ are defined by

$$\chi(\vec{r}) = [P(r)/r] Y_{l, m}(\theta, \phi). \quad (26)$$

Similar expressions were obtained for the dipole-quadrupole and quadrupole-quadrupole interactions.

For our calculations we have utilized Clementi's⁸ helium atom wave function; the isolated hydrogen atom wave function is, of course, exact. Once the variational parameters have been obtained, the second-order perturbation energy due to the van der Waals interaction is given by $J(\delta\Psi)$ with the values of the parameters substituted in (19). This yields an expression for the energy in the familiar form

$$E_{\text{VDW}} = C_{\text{dd}}/R^6 + C_{\text{dq}}/R^8 + C_{\text{qq}}/R^{10}. \quad (27)$$

The terms arising from $\Delta\mathcal{H}$ in $J(\delta\Psi)$ merit special attention. These terms represent a type of intra-atomic correlation (within the helium atom) in the perturbed state. In carrying out the calculation of energy, we have investigated the importance of this effect in the case of the dipole-dipole interaction by repeating the calculation with and without the $\Delta\mathcal{H}$ term. As is seen in Table I, where these results are listed, this correlation effect is about 3%.

The results in Table I indicate that good convergence was obtained with 49 variational parameters for all three interaction terms. Two earlier theoretical results are available for the dipole-dipole term. One of these was obtained by Karplus and Kolker,⁹ using time-dependent perturbation technique neglecting intra-atomic correlation effects completely. Their value for $C_{\text{dd}} = -3.0116$ is in excellent agreement with our result without correlation. A later result, $C_{\text{dd}} = -2.8173$, was obtained by Davison⁶ who used a correlated wave function for the isolated helium atom and a variation function f similar to our choice. Davison's result is about 3.5% smaller than our value including $\Delta\mathcal{H}$ terms. It is interesting that the 3%

TABLE I. Coefficients in the van der Waals energy expansion.

Number of variation parameters	C_{dd} without $\Delta\mathcal{H}$	C_{dd} with $\Delta\mathcal{H}$	C_{dq} with $\Delta\mathcal{H}$	C_{qq} with $\Delta\mathcal{H}$
9	-3.0214	-2.9085	-41.903	-858.76
16	-3.0218	-2.9132	-41.906	-858.90
25	-3.0218	-2.9134	-41.906	-858.91
36	-3.0218	-2.9140	-41.906	-858.92
49	-3.0218	-2.9142	-41.907	-858.93

intra-atomic correlation effect introduced through $\Delta\mathcal{H}$ in the Hamiltonian is comparable¹⁰ with the correlation effect from the ground-state wave functions. Davison's value compares very well with the best semiempirical estimates $C_{dd} = -2.82$ and -2.83 made by Dalgarno and Kingston¹¹ and Bell,¹² respectively.

Davison⁶ has also evaluated the dipole-quadrupole term and obtains $C_{dq} = -41.782$ which agrees within 0.3% with our value. This seems to indicate that intra-atomic correlation effects associated with the wave function for the helium atom are even less significant for the dipole-quadrupole effect. No other result is available for comparison with our quadrupole-quadrupole term, but experience with the other two terms indicates that our C_{qq} should be quite reliable.

We next consider the calculation of the HPS. For this purpose we have to obtain the hyperfine energy for the van der Waals perturbed wave function. For this purpose, we consider formally a system subjected to two perturbations described in our case by

$$\mathcal{H}' = \mathcal{H}'_{\text{VDW}} + \mathcal{H}'_{\text{hfs}}, \quad (28)$$

where $\mathcal{H}'_{\text{VDW}}$ is defined by Eqs. (1) through (7). The term $\mathcal{H}'_{\text{hfs}}$ describes the Fermi-contact interaction¹³

$$\mathcal{H}'_{\text{hfs}} = A_c \vec{I} \cdot \sum_i \vec{s}_i \cdot \delta(\vec{r}_i), \quad (29)$$

where $A_c = (16\pi/3)(\mu_N/I)\mu_0 a_0^{-3}$, μ_N and I being the nuclear moment and spin and μ_0 the Bohr magneton, $\delta(\vec{r}_i)$ being expressed in atomic units. The dipole-dipole interaction term is not of interest here because it makes vanishing contribution to HPS after statistical averaging.¹⁴ Since we are interested in linear hyperfine effects, we want to retain terms in the energy of the system which involve one order in $\mathcal{H}'_{\text{hfs}}$ and various orders in $\mathcal{H}'_{\text{VDW}}$. On introducing the first-order perturbed wave function

$$\delta\Psi = \delta\Psi_{\text{VDW}} + \delta\Psi_{\text{hfs}}, \quad (30)$$

where $\delta\Psi_{\text{VDW}}$ and $\delta\Psi_{\text{hfs}}$ are individually orthogonal to Ψ_0 , it is easy to show that first-, second-, and third-order energies are given by¹⁵

$$\delta E = \langle \Psi_0 | \mathcal{H}' | \Psi_0 \rangle, \quad (31)$$

$$\delta^2 E = \langle \Psi_0 | \mathcal{H}' | \delta\Psi \rangle, \quad (32)$$

$$\delta^3 E = \langle \delta\Psi | \mathcal{H}' - \delta E | \delta\Psi \rangle. \quad (33)$$

On substituting for \mathcal{H}' from (28) in (31), we get the first-order van der Waals energy δE_{VDW} which vanishes and the hyperfine energy for the isolated atoms. The only part of (32) that we are interested in is the one involving linear terms in both $\mathcal{H}'_{\text{hfs}}$ and $\mathcal{H}'_{\text{VDW}}$. Thus

$$\delta^2 E_{11} = \langle \Psi_0 | \mathcal{H}'_{\text{hfs}} | \delta\Psi_{\text{VDW}} \rangle + \langle \Psi_0 | \mathcal{H}'_{\text{VDW}} | \delta\Psi_{\text{hfs}} \rangle, \quad (34)$$

the suffixes of $\delta^2 E_{mn}$ indicating m th order in hyperfine and n th order in the van der Waals effect. On examining the two matrix elements on the right, it can be seen that $\delta^2 E_{11}$ vanishes. This then leaves $\delta^3 E$ as the lowest-order nonvanishing contribution. On extracting linear hyperfine terms out of (33), we get

$$\begin{aligned} \delta^3 E_{12} = & 2 \langle \delta\Psi_{\text{VDW}} | \mathcal{H}'_{\text{VDW}} | \delta\Psi_{\text{hfs}} \rangle \\ & + \langle \delta\Psi_{\text{VDW}} | \mathcal{H}'_{\text{hfs}} | \delta\Psi_{\text{VDW}} \rangle \\ & - \delta E_{\text{hfs}} \langle \delta\Psi_{\text{VDW}} | \delta\Psi_{\text{VDW}} \rangle. \end{aligned} \quad (35)$$

In Eq. (35), the first-order hyperfine energy δE_{hfs} is given by

$$\begin{aligned} \delta E_{\text{hfs}} & = \langle \Psi_0 | \mathcal{H}'_{\text{hfs}} | \Psi_0 \rangle \\ & = \frac{1}{2} A_c I \chi_{\text{H}}^2(\text{H}) = A_c I / 2\pi, \end{aligned} \quad (36)$$

since $\chi_{\text{H}}^2(\text{H}) = 1/\pi$ in atomic units, and where we have assumed that the nuclear and electron spins of the hydrogen atom are in states $m_I = I$ and $m_S = 1/2$. The perturbed wave function $\delta\Psi_{\text{hfs}}$ due to the proton hyperfine field requires a solution of the first-order equation

$$(\mathcal{H}_0 - E_0) \delta\Psi_{\text{hfs}} = \mathcal{H}'_{\text{hfs}} \Psi_0 \quad (37)$$

for the separated atoms. Equation (37) may be shown to reduce to the perturbation equation for the isolated hydrogen atom for which the solution can be obtained analytically. Thus

$$\begin{aligned} \delta\Psi_{\text{hfs}} = & \delta\chi_{\text{H, hfs}}^{(1)} \chi_{\text{He}}^{(2)} \chi_{\text{He}}^{(3)} \alpha_1 (\alpha_2 \beta_3 \\ & - \alpha_3 \beta_2) / \sqrt{2}, \end{aligned} \quad (38)$$

where $\delta\chi_{\text{H, hfs}} = (A_c I / 4\pi) (F(r_{\text{H}}) - \langle \chi_{\text{H}} | F | \chi_{\text{H}} \rangle) \chi_{\text{H}}$,

$$F(r_{\text{H}}) = -1/r_{\text{H}} + 2 \ln r_{\text{H}} + 2r_{\text{H}}. \quad (39)$$

Since the van der Waals perturbation admixes $l \neq 0$ character in the hydrogen atom wave function, the second term on the right in Eq. (35) vanishes, as may be seen from Eqs. (10) to (12). The other two terms can be evaluated by substituting for $\delta\Psi_{\text{VDW}}$ and $\delta\Psi_{\text{hfs}}$ from Eqs. (8) through (12) and (35). Thus, for the dipole-dipole case,

$$\begin{aligned} \langle \delta\Psi_{\text{VDW}} | \mathcal{H}'_{\text{VDW}} | \delta\Psi_{\text{hfs}} \rangle = & \frac{A_c I}{3\pi R^6} \sum_{n,k} A_{nk} I_F^{(n)} \\ & \times I(\text{HeHe}, k+1), \end{aligned} \quad (40)$$

$$\begin{aligned} \langle \delta\Psi_{\text{VDW}} | \delta\Psi_{\text{VDW}} \rangle = & \frac{4}{3R^6} \sum_{n,n',k,k'} A_{nk} A_{n'k'} \\ & \times I(\text{HH}, n+n') I(\text{HeHe}, k+k'), \end{aligned} \quad (41)$$

where the radial integrals $I(2, k+1)$ are defined in Eqs. (24) and

$$I_F(n) = \langle \chi_H | r_H^{n+1} [F(r_H) - \langle \chi_H | F | \chi_H \rangle] | \chi_H \rangle. \quad (42)$$

The terms $I_F(n)$ can be evaluated exactly because of the special forms of χ_H and $F(r_H)$. This evaluation requires the definite integral

$$\int_0^\infty x^n e^{-ax} \ln x dx = \frac{n!}{a^{n+1}} \left(-0.57721567 - \ln a + \sum_{j=1}^n \frac{1}{j} \right). \quad (43)$$

Using this integral,

$$\langle \chi_H | F | \chi_H \rangle = 2.45936866$$

$$\begin{aligned} \text{and } I_F(n) = & 4(- (n+1)!/2^{n+2} + (n+3)!/2^{n+3} \\ & - 2.45936866(n+2)!/2^{n+3} \\ & + 2 \int_0^\infty x^{n+2} e^{-2x} \ln x dx). \quad (44) \end{aligned}$$

Corresponding expressions were derived for the dipole-quadrupole and quadrupole-quadrupole van der Waal terms. The quantity of interest to us is the fractional frequency shift $\Delta\nu(R)/\nu_0$ which may be obtained from $\delta^3 E_{12}$ in (35) by dividing with δE_{hfs} . Using the variation-parameters A_{nk} obtained by energy minimization, we then obtain an expansion for $[\Delta\nu(R)/\nu_0]_{\text{LR}}$ for the long-range region of the form

$$\left(\frac{\Delta\nu(R)}{\nu_0} \right)_{\text{LR}} = \frac{D_{\text{dd}}}{R^6} + \frac{D_{\text{dq}}}{R^8} + \frac{D_{\text{qq}}}{R^{10}}, \quad (45)$$

where $D_{\text{dd}} = -4.0578$, $D_{\text{dq}} = -90.866$,

$$D_{\text{qq}} = -2561.6. \quad (46)$$

Further discussion of this result in the calculation of HPS will be postponed to Sec. IV.

III. SHORT-RANGE CALCULATION

In this section, we shall be concerned with the contribution to the hyperfine constant from short-range interactions. For small interatomic distances, there can be two effects: first that due to the Pauli exclusion principle through the overlap of the orbitals on the two atoms, often referred to as Pauli distortion; and second, an actual deformation of the orbitals due to the additional potential produced by the neighboring atoms. For atoms which do not form a covalent bond, the second type of distortion is usually assumed to be small. We shall thus confine ourselves to a quantitative analysis of the Pauli distortion effect.

When the atoms overlap, this distortion effect can be described by orthogonalizing the orbitals through the Schmidt procedure. After orthogonalization, the three electrons of the H-He system occupy the orbitals $\chi_H'(\vec{r}_H, R)\alpha$, $\chi_{\text{He}}(\vec{r}_{\text{He}})\alpha$ and $\chi_{\text{He}}(\vec{r}_{\text{He}})\beta$, where

$$\chi_H'(\vec{r}_H, \vec{R}) = \frac{\chi_H(\vec{r}_H) - S(R)\chi_{\text{He}}(\vec{r}_{\text{He}})}{[1 - S^2(R)]^{1/2}}, \quad (47)$$

R being the internuclear distance and $S(R)$ the overlap integral,

$$S(R) = \langle \chi_H(\vec{r}_H) | \chi_{\text{He}}(\vec{r}_{\text{He}}) \rangle. \quad (48)$$

To obtain the hyperfine interaction energy of the proton, we need to calculate the expectation value of the hyperfine Hamiltonian $\mathcal{H}'_{\text{hfs}}$ in (29) over a determinantal function composed of the three orthogonal orbitals on the two atoms. In the calculation of $\langle \mathcal{H}'_{\text{hfs}} \rangle$, the contributions from the two paired spin states of the helium atom cancel each other. From the orthogonalized hydrogen atom orbital one then gets the hyperfine energy

$$\delta E_{\text{hfs}}(R) = \frac{1}{2} A_c I [\chi_H'(0, R)]^2, \quad (49)$$

where again we have considered the states $m_I = I$ and $m_S = \frac{1}{2}$.

Had a symmetric orthogonalization procedure been employed instead of the Schmidt procedure, the same result as in Eq. (49) would have been obtained. However, $\delta E_{\text{hfs}}(R)$ would now be composed of finite contributions from both the orthogonalized hydrogen and helium orbitals. The Schmidt procedure is therefore particularly advantageous when one has a number of electronic states on either the paramagnetic or buffer gas atom, since one has then to deal only with the orthogonalized unpaired electronic states.

Combining Eqs. (36) and (49), one obtains for the fractional pressure shift at short range

$$[\Delta\nu(R)/\nu_0]_{\text{SR}} = [\chi_H'(H)/\chi_H(H)]^2 - 1, \quad (50)$$

where the argument H will always indicate the value at the proton site. For numerical accuracy, it is better to deal with small quantities rather than with the difference between large numbers. Thus, it is more convenient to calculate $[\Delta\nu(R)/\nu_0]_{\text{SR}}$ directly by expanding the right-hand side of Eq. (50) in powers of $S(R)$ leading to

$$\begin{aligned} \left(\frac{\Delta\nu(R)}{\nu_0} \right)_{\text{SR}} = & \left[S^2(R) - 2S(R) \frac{\chi_{\text{He}}(H)}{\chi_H(H)} \right. \\ & \left. + S^2(R) \left(\frac{\chi_{\text{He}}(H)}{\chi_H(H)} \right)^2 - 2S^3(R) \frac{\chi_{\text{He}}(H)}{\chi_H(H)} + O(S^4) \right]. \quad (51) \end{aligned}$$

The overlap integral $S(R)$ was calculated by expanding the helium orbital about the proton using Löwdin's α -function technique.¹⁶ Our results for $[\Delta\nu(R)/\nu_0]_{\text{SR}}$ are shown in Fig. 1 and compared with the results obtained, using a single-parameter hydrogenic wave function (effective charge $Z = 1.6875$) for helium as used by Clarke.⁴ The curve of the short-range fractional pressure shift with the more realistic Hartree-Fock wave functions lies consistently higher than the one parameter result since

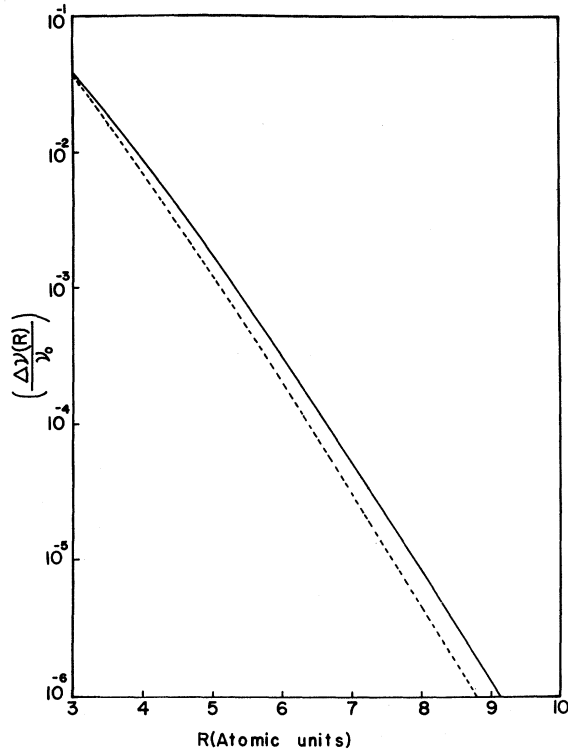


FIG. 1. Variation of short-range fractional frequency shift $(\Delta\nu(R)/\nu_0)_{SR}$ with R . The continuous line represents our results while the dashed line represents results obtained with effective charge $Z=1.6875$ for the helium orbitals (Ref. 4).

the overlaps $S(R)$ are underestimated in the latter case.

IV. PRESSURE SHIFT CALCULATION

The hydrogen atom collides successively with a number of buffer gas helium atoms in a variety of relative configurations. The observed hyperfine constant is therefore an ensemble average of the hyperfine constants for various relative configurations of the hydrogen and helium atoms. Taking a classical average, the pressure shift is given by

$$f_p = \frac{\partial}{\partial P} \langle \frac{\Delta\nu(R)}{\nu_0} \rangle = \frac{1}{kT} \int \frac{\Delta\nu(R)}{\nu_0} e^{-V(R)/kT} d\tau_R. \quad (52)$$

A quantum-mechanical averaging procedure would require a knowledge of the motional wave function for the atom-pair. Clarke⁴ has shown that such a procedure only leads to 3% correction for the H-He system. In Eq. (49), the function $\Delta\nu(R)/\nu_0$ that we use does not depend on the direction of \mathbf{R} . One could get a directional dependence if account was taken of the classical dipole-dipole interaction between the nucleus and electrons, but it has been shown that on statistical averaging, the contribution to the pressure shift from this source vanishes.¹⁴ For $V(R)$ we have utilized the most recent interatomic potential available in the literature.¹⁷

$$\begin{aligned} V(R) &= \left(\frac{4}{R}\right) (1 + 0.265R - 2.419R^2 + 2.616R^3) \\ &= \frac{2}{R} (1 + 0.113R - 2.069R^2 + 2.089R^3 \\ &\quad - 0.259R^4) e^{-2.15R} \quad \text{for } 2 < R \leq 3 \\ &= 4.606 e^{-1.76R} - 3.0116/R^6 \quad \text{for } R > 3. \end{aligned} \quad (53)$$

For large R , the potential is dominated by the van der Waals dipole-dipole term which agrees very well with our calculated result in Sec. III. Clarke⁴ had used a somewhat different choice for $V(R)$ in his calculation. We have used both choices of $V(R)$ in the averaging procedure and find differences only in the fourth significant figure indicating that the final result is not very sensitive to $V(R)$.

In Table II we have listed the values of the long-range and short-range contributions to the fractional frequency shift $(\Delta\nu(R)/\nu_0)$ as well as their sum and the weight factor $R^2 \exp[-V(R)/kT]$ for the averaging process. For the sake of clarification of the relationship between the short-range and long-range results, the entries of Table II are plotted in Fig. 2. Carrying out the average indicated in Eq. (52), we get the short-range and long-range contributions and the total HPS as

$$\begin{aligned} (f_p)_{SR} &= 2.597 \times 10^{-9} / \text{mm Hg}, \\ (f_p)_{LR} &= -1.574 \times 10^{-9} / \text{mm Hg}, \\ f_p &= 1.023 \times 10^{-9} / \text{mm Hg}, \end{aligned} \quad (54)$$

which is substantially smaller than the experimental value.¹⁸

$$(f_p)_{\text{expt.}} = (+3.7 \pm 0.7) \times 10^{-9} / \text{mm Hg}. \quad (55)$$

However, in making a simple addition of $[\Delta\nu(R)/\nu_0]_{LR}$ and $[\Delta\nu(R)/\nu_0]_{SR}$, we assumed the long-range result in Eq. (46) to hold for all values of R , as has been done in the past.¹⁹ However, the expansion in terms of R^{-n} in Eq. (45) is not just-

TABLE II. Fractional frequency shifts and weight factor.

R	$\left(\frac{\Delta\nu(R)}{\nu_0}\right)_{SR}$ $\times 10^2$	$\left(\frac{\Delta\nu(R)}{\nu_0}\right)_{LR}$ $\times 10^2$	$\left(\frac{\Delta\nu(R)}{\nu_0}\right)_{\text{tot.}}$ $\times 10^2$	$R^2 e^{-V(R)/kT}$ (a.u.)
3.0	3.9100	-6.2797	-2.3696	0.0000
3.5	1.8936	-1.5529	0.3408	0.0048
4.0	0.8787	-0.4820	0.3967	0.6526
4.5	0.3942	-0.1781	0.2161	5.6804
5.0	0.1720	-0.0755	0.0966	15.3736
5.5	0.0734	-0.0356	0.0378	25.4264
6.0	0.0307	-0.0183	0.0124	34.1341
6.5	0.0127	-0.0101	0.0025	41.8581
7.0	0.0052	-0.0059	-0.0008	49.2404
7.5	0.0021	-0.0036	-0.0016	56.7098
8.0	0.0008	-0.0023	-0.0015	64.4953
8.5	0.0003	-0.0015	-0.0012	72.7080
9.0	0.0001	-0.0010	-0.0009	81.3982

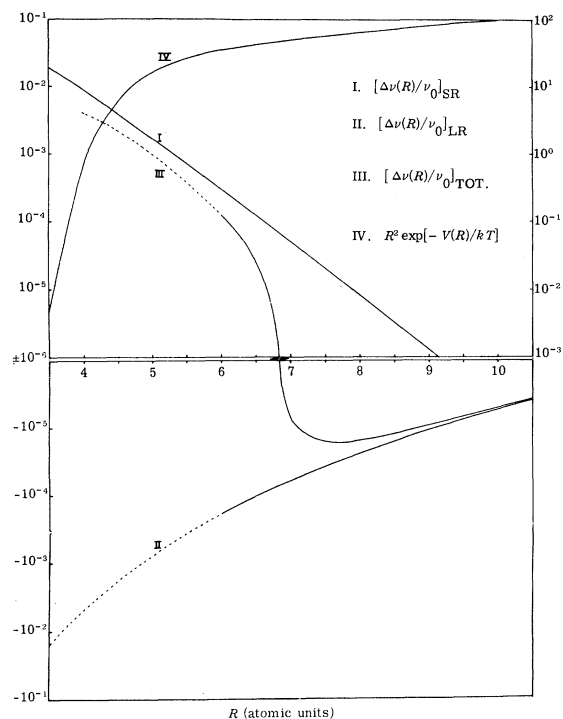


FIG. 2. Fractional frequency shifts and Boltzmann weight factor $\{R^2 \exp[-V(R)/kT]\}$. Dashed portions of total and long-range frequency shift curves for values of $R \lesssim 6$ are unreliable because of the failure of the multipole expansion of the interatomic Hamiltonian.

fiable for small R , since it depends on the validity of the expressions (2) through (7) for the interatomic perturbation Hamiltonian. These expansions do not hold for small R . Since the Boltzmann factor is not sufficiently small in this region to make the contribution to f_p insignificant, one must be careful in handling the long-range effect. Rather than use a wrong result for small R , it is better to use a cut-off R_C for the lower limit in the integration for the averaging process in the long-range case. This cut-off procedure is justified because, in actuality, at short-range the atomic distortion is completely dominated by the Pauli repulsion effect. A value for R_C may be chosen in a number of different ways. The energy expansion in (19) begins to diverge in the neighborhood of $R=4$, the hyperfine expansion showing a similar behavior around $R=5$. These then represent two plausible choices for R_C . The statistical averages for the long-range HPS have been listed in Table III for these values of R_C as well as for some additional values to demonstrate the sensitivity of the final result to R_C . It appears from Table III that the final long-range result in fact depends rather strongly on the choice of R_C . We have chosen $R_C=6$ as a sufficiently large distance to assure convergence of the hyperfine expansion. With this cutoff, the long-range contribution to HPS is

$$(f_p)_{\text{LR}} = -0.443 \times 10^{-9}/\text{mm Hg}. \quad (56)$$

Similar, but less serious, limitations apply to the validity of the averaging procedure for the short-range pressure shift. Thus, in the region where van der Waals effects are important, it is no longer justifiable to take the overlap between undistorted s orbitals on the two atoms. This would not be a significant consideration if the overlap effect were negligible in the long-range region. However, from Table II it appears that $[\Delta\nu(R)/\nu_0]_{\text{SR}}$ is still appreciable over the region beyond $R_C=6$. Values of the short-range HPS for cut-offs at various upper limits R_C are listed in Table III. We have chosen this value of $R_C=6$ as a reasonable upper limit for the average procedure which leads to a short-range HPS of

$$(f_p)_{\text{SR}} = 2.350 \times 10^{-9}/\text{mm Hg}, \quad (57)$$

about 10% less than in Eq. (54). Combining these plausible choices for long-range and short-range contributions, we then get the total HPS as

$$(f_p)_{\text{theo.}} = 1.907 \times 10^{-9}/\text{mm Hg}. \quad (58)$$

This result is substantially better than that in Eq. (54) where no cutoff was used. However, the theoretical result is still only about half the experimental value.

To avoid the uncertainty connected with the validity of the long-range and short-range results for intermediate values of R , it would be best if one could carry out a first-principle calculation of the frequency shift for this region. In this intermediate range, the Pauli distortion and the potential distortion (van der Waals-type effect) are expected to be comparable, and it is therefore necessary to incorporate both effects simultaneously. Thus one would have to use a zero-order function which is a determinant involving the three electrons on the two atoms and consider the perturbation of this wave function by the interatomic potential (1) rather than the multipole expansions in (2) through (7). Such a perturbation calculation could be carried out by a variational procedure resembling a molecular wave function calculation. A calculation of this type would be rather elaborate and beyond the scope of the present work.²⁰ However, we have utilized a rather approximate procedure proposed by Margenau²¹ for calculation of energy in the in-

TABLE III. Dependence of long-range and short-range HPS on cut-off R_C .

$R_C(a_0)$	$(f_p)_{\text{LR}}^a$	$(f_p)_{\text{SR}}^b$	$(f_p)_{\text{total}} = (f_p)_{\text{LR}} + (f_p)_{\text{SR}}$
4.0	-1.4626	0.2147	-1.2479
5.0	-0.8437	1.6131	0.7694
6.0	-0.4429	2.3496	1.9067
7.0	-0.2556	2.5425	2.2869
8.0	-0.1615	2.5843	2.4228
9.0	-0.1090	2.5927	2.4837

^aThe range of R in the averaging procedure is $R_C \rightarrow \infty$
^bThe range of R in the averaging process is $0 \rightarrow R_C$.

intermediate range. In this approach, the zero-order wave function is given by

$$\Psi_0 = \det[\chi_H^{\alpha(1)} \chi_{He}^{\alpha(2)} \chi_{He}^{\beta(3)}]. \quad (59)$$

The first-order perturbed wave function is assumed to have the form

$$\Psi = [1 + \lambda(\mathcal{K} - E_0)]\Psi_0, \quad (60)$$

where \mathcal{K} is the total Hamiltonian for the two interacting atoms and E_0 is the total energy for the two separated atoms. The quantity λ has the dimensions of reciprocal energy and is taken as

$$\lambda = 1/E_i, \quad (61)$$

where E_i is the sum of the first ionization potentials for the hydrogen and helium atoms. The hyperfine energy for the hydrogen atom using the perturbed wave function Ψ is then given by

$$\delta E_{\text{hfs}} = A \frac{I}{c} \frac{\langle \Psi | \sum_i S_{zi} \delta(\vec{r}_i - \vec{r}_H) | \Psi \rangle}{\langle \Psi | \Psi \rangle}. \quad (62)$$

On substituting for Ψ from Eq. (60) and after some manipulation using the requisite expressions for the energies E_H and E_{He} of the isolated atoms in terms of one-electron matrix elements, one obtains a fractional frequency shift

$$\begin{aligned} \frac{\Delta\nu(R)}{\nu_0} = & \left(\frac{\Delta\nu(R)}{\nu_0} \right)_{\text{SR}} + \frac{\lambda}{(1 - S^2(R))} \\ & \times \left[\langle \chi_H(1) \chi_{He}(2) \left| \frac{1}{r_{12}} \right| \chi_{He}(1) \chi_H(2) \rangle \right. \\ & - 2S(R) \langle \chi_H(1) \chi_{He}(2) \left| \frac{1}{r_{12}} \right| \chi_{He}(1) \chi_{He}(2) \rangle \\ & \left. + S^2(R) \langle \chi_{He}(1) \chi_{He}(2) \left| \frac{1}{r_{12}} \right| \chi_{He}(1) \chi_{He}(2) \rangle - E_H \right], \end{aligned} \quad (63)$$

where the first term is the short-range effect analyzed earlier and the rest of the terms (referred to as intermediate-range terms) represent the combined effects of interatomic exchange and orbital distortion. Using $E_i = 2.8$ Ry and carrying out the requisite one-center and two-center inte-

grals involved, we find that the intermediate-range terms are orders of magnitude smaller than both the short-range and long-range terms in the corresponding regions. The wave function Ψ in Eq. (60) therefore appears to be inadequate for a description of the perturbed orbitals in the neighborhood of the proton, although Margenau finds it suitable for interatomic energy calculation.

While the uncertainty associated with the intermediate region can influence the final result for pressure shift appreciably, it appears from Table III that the elimination of this uncertainty alone cannot produce agreement with experiment. The short-range effect by itself is appreciably smaller than the experimental value and the long-range effects make a contribution of opposite sign. It seems to us therefore, that the remaining discrepancy with experiment can only be explained by inclusion of correlation effects at short range. This expectation is in keeping with a similar conclusion of Kestner and Sinanoglu²² for the helium-helium system.

V. CONCLUSION

Various contributions to the HPS for the hydrogen atom in a helium atmosphere have been considered quantitatively. The short-range Pauli distortion effect is obtained by considering the overlap between orbitals on the two atoms. A variational procedure is proposed and carried out for the long-range van der Waals energy and long-range hyperfine effects. The results indicate that a proper treatment of the intermediate region is necessary to make a reliable combination of long-range and short-range effects. However, it appears that ultimate agreement between experiment and theory will require explicit treatment of correlation effects at short range. It would be of interest to investigate whether these conclusions apply to other systems involving heavier paramagnetic atoms and buffer gases.

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Hyperfine Pressure Shift and van der Waals Interaction. II. Nitrogen-Helium System*

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In continuation of a series of investigations of hyperfine pressure shifts (HPS) in interacting atoms, an investigation of the long-range interaction of nitrogen atoms in a helium atmosphere is reported. The procedure requires wave functions perturbed to first order in the van der Waals and nuclear hyperfine Hamiltonians, respectively. The van der Waals perturbed wave function is obtained through a variational procedure described previously for the H-He system. The first-order hyperfine wave function is a moment-perturbed (MP) function used in an earlier study of the short-range N-He interaction. The theoretical result for the long-range contribution to HPS is 0.22 cps/mm Hg to be combined with a contribution from short-range of 0.91 cps/mm Hg, as compared with a total experimental HPS of 0.27 ± 0.07 cps/mm Hg. Various factors which might contribute to the difference between theory and experiment are discussed. In particular, the role of correlation at short range is stressed.

I. INTRODUCTION

The present work is a continuation of efforts to arrive at a quantitative understanding of the origin of hyperfine pressure shifts (HPS) of atoms in buffer gas atmospheres.¹ The pressure shift for nitrogen atom has been studied experimentally through the optical pumping technique² in a number of rare gases. In our present investigation we have singled out the N-He system for detailed study. In an earlier paper³ we have analyzed the contribution from short-range effects for this system, arising from an interplay of the overlap effect between the two atoms and the exchange polarization within the nitrogen atom. In the present work we are concerned with long-range effects. For this purpose, we utilize a variational method applied previously to study the van der Waals (VDW) distortion in H-He system.⁴ This work will be referred to hereafter as I.

Calculation of the long-range contribution to HPS requires^{4,5} a knowledge of the third-order energy which consists of two orders in the VDW interaction and one order in the hyperfine effect. We have calculated this energy using the first-order perturbed wave function due to the VDW effect obtained variationally and the first-order wave function due to the action of the nuclear moment determined by the moment-perturbation (MP) procedure.⁶ This method eliminates the need for using conventional perturbation theory with associated uncertainties for the excited states.⁵ It should be noted here that an equivalent procedure would have been to consider the wave function perturbed to second order in the VDW interaction only. In the present case, it is felt that there was likelihood of more error in a second-order wave function calculation than in the procedure utilized here involving two first-order calculations.

Section II deals with variational calculations for