PHYSICAL REVIEW
LETTERS

VOLUME 27 12 JULY 1971 NUMBER 2

Hyperfine Pressure Shift for Interacting Atoms: Pitfalls of a Variational Procedure*

Dennis Ikenberry† and T. P. Das‡
Department of Physics, University of Utah, Salt Lake City, Utah 84112
(Received 25 March 1971)

In a recent Letter on the hyperfine shifts in HeH the conclusion was reached that the hyperfine shift is never negative, even at the largest separations. This conclusion, which is in disagreement with fundamental ideas regarding the role of the van der Waals interaction in hyperfine pressure shifts, is traced to an uncritical use of Brillouin's theorem. Upon making the necessary corrections, we obtain a long-range negative shift of proper magnitude.

Optical pumping methods have provided accurate measurements of the hyperfine pressure shift[1] (HPS) and its temperature dependence[2] for paramagnetic atoms in various buffer gases. The theoretical analysis of such data has been one of the most illuminating developments in the theory of interacting atoms in the past few decades since it involves fine details of their wave functions and thus offers a strong complement to the study of intermolecular forces which require only a knowledge of energies. One of the important problems in the field of HPS is that of the hydrogen atom in rare-gas buffers since here the HPS shows a strong variation from positive in H-He to large and negative in H-Xe.

Adrian[3] offered an explanation for this trend in terms of a competition between a positive contribution due to Pauli distortion at short range and a negative one at long range due to van der Waals (vdW) polarization. Quantitative theoretical calculations have been carried out[4-6] showing the correctness of Adrian's ideas, the negative vdW effect dominating for the larger and more polarizable atoms. One of the limitations of these calculations was the necessity of choosing a cutoff for the vdW contribution at short range due to its diverging nature, for example, D/R^6 from the dipole-dipole effect.

In a recent Letter by Das and Ray,[7] hereafter referred to as I, the authors attempted to obviate the need for choosing a cutoff. Instead they obtained the fractional shift

$$f(R)=\Delta\nu(R)/\nu_0=[\rho_H(R)-\rho_H(\infty)]/\rho_H(\infty)$$

by utilizing a molecular-orbital approach with configuration interaction (MO-CI) to allow for van der Waals polarization. Their results and their interpretation, if correct, would place the theoretical understanding of this field in a quandary. They find that for the H-He system the positive contribution due to the Pauli distortion and the one-electron potential distortion (due to the potential terms in the interatomic electronic Hamiltonian) swamp the negative vdW contribution, even at long range. This conclusion leaves without explanation the large negative HPS in H-Ar, H-Kr, and H-Xe. Fundamentally and intuitively, one would think that the vdW effect would dominate at long range since it does not require the wave functions to overlap, which is a necessity for the Pauli and potential distortions.

The main aim of the present paper is to show that the results in I for $f(R)$ are in serious error at long range because of the neglect of single excitations in the MO-CI function. Using cross-perturbation theory, we indicate how one can quantitatively evaluate the effect of the single excitations using the MO-CI function in I and show that such a procedure does indeed lead at long range to the same negative results as have been obtained[8] by many-body perturbation theory for separated atoms. In addition, this process for extracting $f(R)$ from MO-CI functions allows one to obtain the vdW contribution to the fractional shift for all R, eliminating the need for choosing a cutoff in the averaging procedure.

Briefly, what is missing in the calculation in I is the incorporation of singly excited configurations in the MO-CI wave function. Those singly excited configurations which involve excited MO with primarily hydrogen-atom s character are crucial to obtaining the correct $f(R)$ at long range, as will be shown. Physically, the existence and role of these configurations are best illustrated by the two alternate types of diagrams shown in Figs. 1(a) and 1(b).

In Fig. 1(a) $\Psi(\sigma HKs)$ represents a singly excited configuration where the unpaired hydrogen 1s-like orbital is replaced by a higher s-like orbital. $\Psi(\sigma HKp, \sigma HeKp)$ represents a doubly excited configuration where the hydrogen 1s-like and helium 1s-like orbitals are simultaneously excited to higher p-like states as a result of the vdW interaction. $\mathcal{H}_{\text{hfs}}$ is the hyperfine structure operator; the form of $\mathcal{H}_{\text{vdW}}$ will be commented on later. By way of explanation of Figs. 1(a) and 1(b), it is necessary to recall that at long range the lowest order[3,4] of perturbation theory giving rise to the HPS is second order in $\mathcal{H}_{\text{vdW}}$ and first order in $\mathcal{H}_{\text{hfs}}$. The important point is that through two orders in $\mathcal{H}_{\text{vdW}}$, it is possible to obtain a mixing between Ψ_0 [the first term in Eq. (2) of I] and singly excited configurations as seen from both Figs. 1(a) and 1(b).

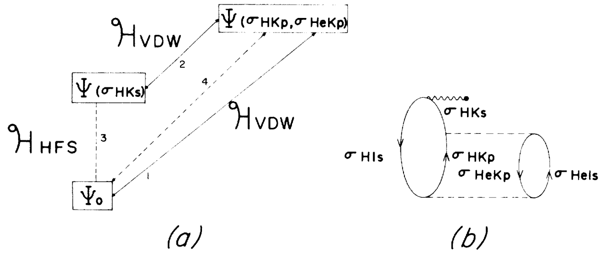


FIG. 1. vdW contribution to $f(R)_{\text{vdW}}$: (a) pathway and (b) diagrammatic representation. In (a) solid lines stand for vdW interaction and dotted ones for hyperfine interaction. σH1s and σHe1s refer to ground-state molecular orbitals with predominant H1s and He1s character, respectively. σHKs, σHKp, and σHeKp are corresponding excited states. Although not shown, excited π states, πHKp and πHeKp, can also occur in double excitations. In (b), the two dashed lines refer to the vdW interaction, while the vertex at the top refers to the hyperfine operator $\mathcal{H}_{\text{hfs}}$.

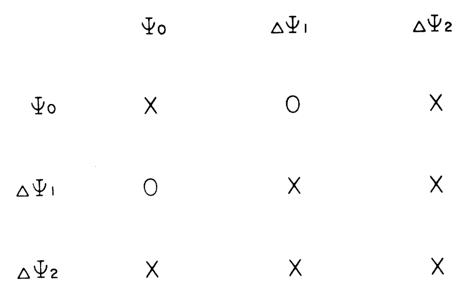
Das and Ray invoked Brillouin's theorem[9] as a reason for excluding singly excited configurations in their calculations for the total Ψ for the two interacting atoms. Brillouin's theorem states that starting with Ψ_0, the first-order changes represented by the singly excited configurations are zero when Ψ_0 has been determined by energy minimization through the Hartree-Fock procedure. However, when one adds two-particle excitations $\Psi(\sigma HKp, \sigma HeKp)$, to Ψ_0 and attempts to obtain the net Ψ by energy minimization, singly excited configurations can and should be added without violating Brillouin theorem. This is already clear from the diagram in Fig. 1(b) but can also be illustrated from a consideration of the secular equation used for solving Ψ variationally. Figure 1(a) is particularly useful in looking at the problem this way. Consider the wave function

$$\Psi = \Psi_0 + \Delta\Psi, \tag{1}$$

where

$$\Delta\Psi = \Delta\Psi_1 + \Delta\Psi_2,$$
$$\Delta\Psi_1 = \textstyle\sum_i c_i \Psi(i),$$
$$\Delta\Psi_2 = \sum_{i>j} c_{ij}\Psi(i,j), \tag{2}$$

with $\Psi(i)$ and $\Psi(i,j)$ representing single and double excitations, respectively. According to Brillouin's theorem, $\langle\Psi_0|\mathcal{H}|\Psi(i)\rangle$ vanishes ($\mathcal{H}$ being the Hamiltonian of the system); and hence in the absence of $\Delta\Psi_2$, the parameters c_i are zero for all i. However, once $\Delta\Psi_2$ is included, one can have finite off-diagonal matrix elements between $\Delta\Psi_1$ and $\Delta\Psi_2$ (see Fig. 2) so that when one solves the requisite secular equation for c_i and c_{ij}, the c_i come out finite. Thus, while the direct mixing between Ψ_0 and $\Delta\Psi_1$ is zero, Ψ_0 mixes indirectly with $\Delta\Psi_1$ via $\Delta\Psi_2$. The same idea is conveyed in



	Ψ_0	$\Delta\Psi_1$	$\Delta\Psi_2$
Ψ_0	X	0	X
$\Delta\Psi_1$	0	X	X
$\Delta\Psi_2$	X	X	X

FIG. 2. Illustration of secular-equation matrix elements. Here X represents a finite contribution and 0 a vanishing one.

the pathway diagram in Fig. 1(a) showing the indirect connection of Ψ_0 and $\Delta\Psi_1$ through two orders in the correlation part of $\mathcal{H}$. The part of this correlation potential which is of interest for interatomic interactions at long range is referred to as $\mathcal{H}_{\rm vdW}$. Once such singly excited configurations are introduced into Ψ, an alternate pathway is allowed for contributions to the HPS as shown in Fig. 1(a) and denoted by $(1\rightarrow 2\rightarrow 3)$. This effect is missing in I, since singly excited configurations were not included in the variational wave function. The only pathway that was included in I corresponds to $(1\rightarrow 4)$ in Fig. 1(a).

Having diagnosed the source of error in I we now present the procedure for calculating the neglected contribution to $f(R)$ using the presently available wave function of Das and Ray. In perturbation language, the vdW contribution for the single-excitation mechanism is given by

$$f(R)_{\rm vdW}=2\sum_n\sum_m\frac{\langle\Psi_0|\mathcal{H}_{\rm vdW}|\Psi_n\rangle\langle\Psi_n|\mathcal{H}_{\rm vdW}|\Psi_m\rangle\langle\Psi_m|\mathcal{H}_{\rm hfs}|\Psi_0\rangle}{(E_0-E_n)(E_0-E_m)},\tag{3}$$

where Ψ_n represents doubly excited configuration and Ψ_m singly excited ones due to the one-electron nature of the operator $\mathcal{H}_{\rm hfs}$. As is usual in cross-perturbation theory, $f(R)_{\rm vdW}$ can be written[5] in two alternate forms:

$$f(R)_{\rm vdW}=2\langle\Delta\Psi_1|\mathcal{H}_{\rm hfs}|\Psi_0\rangle\tag{4}$$

or

$$f(R)_{\rm vdW}=2\langle\Delta\Psi_2|\mathcal{H}_{\rm vdW}|\Delta\Psi_{\rm hfs}\rangle,\tag{5}$$

where

$$|\Delta\Psi_1\rangle=\sum_n\sum_m\frac{|\Psi_m\rangle\langle\Psi_m|\mathcal{H}_{\rm vdW}|\Psi_n\rangle\langle\Psi_n|\mathcal{H}_{\rm vdW}|\Psi_0\rangle}{(E_0-E_n)(E_0-E_m)},$$

$$|\Delta\Psi_2\rangle=\sum_n\frac{|\Psi_n\rangle\langle\Psi_n|\mathcal{H}_{\rm vdW}|\Psi_0\rangle}{E_0-E_n},$$

and

$$|\Delta\Psi_{\rm hfs}\rangle=\sum_m\frac{|\Psi_m\rangle\langle\Psi_m|\mathcal{H}_{\rm hfs}|\Psi_0\rangle}{E_0-E_m}.$$

The two forms in Eqs. (4) and (5) are equivalent. However, using (4) would require a new MO-CI calculation including single excitations, while the form in Eq. (5), on the other hand, makes possible the evaluation of $f(R)_{\rm vdW}$ using only the presently available MO-CI wave functions and a knowledge of $\mathcal{H}_{\rm hfs}$. Before proceeding, we would like to comment on an apparent paradox in I, namely, that while the vdW energy had the correct form[10] for large R, $f(R)$ did not. This paradox can be explained by examining the lowest-order perturbation expression for the vdW energy, namely,

$$E_{\rm vdW}=\sum_n\frac{\langle\Psi_0|\mathcal{H}_{\rm vdW}|\Psi_n\rangle\langle\Psi_n|\mathcal{H}_{\rm vdW}|\Psi_0\rangle}{E_0-E_n},\tag{6}$$

where the Ψ_n refer only to doubly excited configurations. Since these latter were included properly in I, this explains why good agreement was found for $E_{\rm vdW}$ with earlier results. The singly excited configurations can influence vdW energy only in higher orders.

The procedure we have used for calculating the missing vdW contribution $f(R)_{\rm vdW}$ utilized Eq. (5). In this equation, $\Delta\Psi_2$ is the MO-CI wave function found in Eq. (2) of I. The many-electron perturbed function $\Delta\Psi_{\rm hfs}$ is well approximated except for the smallest internuclear distances ($R<3a_0$) by replacing the hydrogen 1s-like MO (σH1s) in Ψ_0 by the moment-perturbed function, $F_{\Delta{\rm H}1s}$. The weight factor $e^{-V(R)/kT}$ in the statistical averaging[3] makes the contribution to the HPS from $R<3a_0$ vanishing small, making this region unimportant. $F_{\Delta{\rm H}1s}$ is given by

$$F_{\Delta{\rm H}1s}=(A/4\pi)(F_{1s}-\langle{\rm H}1s|F_{1s}|{\rm H}1s\rangle)F_{{\rm H}1s},$$

where

$$F_{1s}=-r^{-1}+2\ln r+2r,$$
$$F_{{\rm H}1s}=(\pi)^{-1/2}\exp(-r)\tag{7}$$

and A is defined by Gaspari, Shyu, and Das and Schwartz.[11] In Eq. (5), the term $\mathcal{H}_{\rm vdW}$ at large distances is conventionally expanded as a multipole expansion. Physically it represents the interatomic correlation potential in the H-He molecular system and one cannot in general use a multipole expansion for it, especially for smaller values of R. Avoiding the multipole expansion, Eq. (5) reduces to just

$$f(R)=2\sum_{i>j}\left\langle\Delta\Psi_2\left|\frac{1}{r_{ij}}\right|\Delta\Psi_{\rm hfs}\right\rangle\tag{8}$$

which also follows from diagram 1(b). The two-center integrals in Eq. (8) were carried out by the α-function technique.[12] The values of $f(R)_{\rm vdW}$ have been obtained as a function of R and are shown in Fig. 3, denoted as curve II. Also in this figure, we have shown the results from I, denoted as curve I, and the total MO-CI results

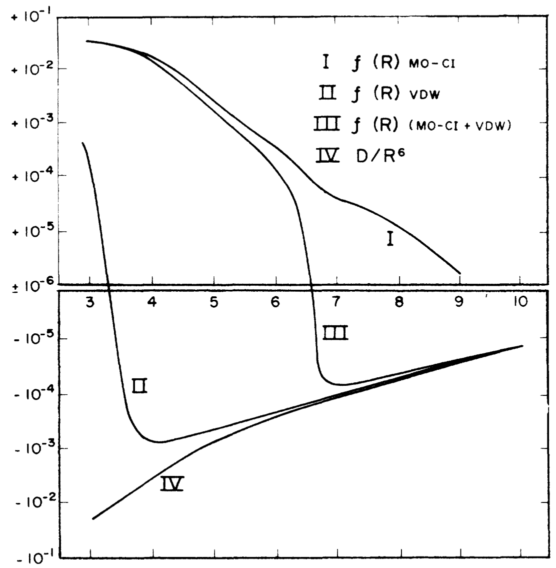


FIG. 3. Fractional frequency shifts versus $R(a_0)$. III represents the sum of the MO-CI results from Ref. 7 and the vdW contribution calculated in this work. Note that the logarithmic scale used here allows a visual compression of the difference between curves such as between II and IV in the range $R = (5-7)a_0$.

which are the sum of the results from I and the present work, denoted as curve III. The latter curve represents the continuous transition from the short-range positive to the long range negative values of $f(R)$ discussed in earlier work.[5,6] Also presented in this figure is the curve representing $D/R^6 = -13.23/R^6$ from perturbation calculations involving multipole expansion for separated atoms.[8]

The curve II for $f(R)_{\text{vdW}}$ is in essential agreement at large values of R ($> 6a_0$) with the D/R^6 curve for separated atoms. As one goes to values of $R < 6a_0$, the curve for $f(R)_{\text{vdW}}$ departs considerably from the D/R^6 form, goes through a minimum, and in general does not have the divergence feature of the multipole-expansion approach. This behavior of $f(R)_{\text{vdW}}$ provides justification for the cutoff procedure applied in earlier work.[5,6] What is crucially important is that at long range the net value of $f(R)$ as represented by curve III does go negative, in agreement with earlier ideas and calculations.[3,5,6,8] This is true here for even the least polarizable rare-gas atom, helium, and of course is known to be of far greater significance for the heavier rare gases[3,6] where the total HPS is negative.

On carrying out the usual classical averaging of the $f(R)_{\text{vdW}}$ result in curve II using the interatomic potential $V(R)$ in I and combining with the earlier HPS result from I which ignored this contribution, the excellent agreement with experiment obtained in I is no longer valid. The theoretical value is now approximately three-fourths of the most recent experimental result.[13]

In summary then, while the MO-CI procedure[7,14] of Wahl and collaborators for interacting atoms does incorporate two-particle excitations that are of crucial importance for the vdW energy at long range, it must be combined with a procedure such as the present one in order to study hyperfine effects correctly. With the use of such a procedure, it has been demonstrated that, contrary to the recent conclusion in I, but in keeping with the results of several earlier theoretical investigations,[3,5,6,8,15] $f(R)$ for large separations of hydrogen-rare-gas systems is, in fact, negative. Basically then, we have here an example of the pitfalls of using energy alone as a criterion of the detailed accuracy of the wave function of a system in a variational calculation.

The authors are grateful to Dr. S. Ray for kindly providing us with additional information about the wave functions presented in I.

---

*Work supported in part by the National Science Foundation.

†Permanent address: Division of Natural Sciences, California State College, San Bernardino, Calif. 92407.

‡Address after 1 September 1971: Department of Physics, State University of New York, Albany, N. Y. 12203.

[1] L. W. Anderson, F. M. Pipkin, and J. C. Baird, Phys. Rev. 120, 1279 (1960), and 121, 1864 (1961), and 122, 1962 (1961); F. M. Pipkin and R. H. Lambert, Phys. Rev. 127, 787 (1962); R. A. Bernheim, *Optical Pumping* (Benjamin, New York, 1965).

[2] R. A. Brown and F. M. Pipkin, Phys. Rev. 174, 48 (1968); L. C. Balling, R. H. Lambert, J. J. Wright, and R. E. Weiss, Phys. Rev. Lett. 22, 161 (1969); J. J. Wright, L. C. Balling, and R. H. Lambert, Phys. Rev. A 1, 1018 (1970).

[3] F. J. Adrian, J. Chem. Phys. 32, 972 (1960).

[4] G. A. Clarke, J. Chem. Phys. 36, 2211 (1962).

[5] S. Ray, J. D. Lyons, and T. P. Das, Phys. Rev. 174, 104 (1968), and 181, 465 (1969).

[6] B. K. Rao, D. Ikenberry, and T. P. Das, Phys. Rev. A 2, 1411 (1970).

[7] G. Das and S. Ray, Phys. Rev. Lett. 24, 1391 (1970).

[8] C. M. Dutta, N. C. Dutta, and T. P. Das, Phys. Rev. A 2, 30 (1970).

[9] L. Brillouin, Actual. Sci. Ind. No. 71 (1933), and No. 189 (1934); C. Møller and M. S. Plesset, Phys. Rev. 46, 618 (1934).

[10] N. C. Dutta, T. Ishihara, C. Matsubara, and T. P. Das, Int. J. Quantum Chem. 35, 367 (1969).

[11] G. D. Gaspari, W.-M. Shyu, and T. P. Das, Phys. Rev. 134, A852 (1963); C. Schwartz, Ann. Phys. (New York) 6, 156 (1959).

[12] P. O. Löwdin, Advan. Phys. 5, 3 (1969); K. J. Duff, thesis, University of California, Riverside (unpublished).

[13] J. J. Wright, L. C. Balling, and R. H. Lambert, Phys. Rev. A 1, 1018 (1970).

[14] G. Das and A. C. Wahl, J. Chem. Phys. 47, 2934 (1967); P. Bertoncini and A. C. Wahl, Phys. Rev. Lett. 25, 991 (1970); A. C. Wahl and G. Das, Advan. Quantum Chem. 5, 261 (1970).

[15] W. D. Davison, J. Phys. B: Proc. Phys. Soc., London 2, 1110 (1969).

Radial Dependence of Trapped-Particle Instabilities

C. Jablon
Laboratoire de Physique des Plasmas associé au Centre National de la Recherche Scientifique, Faculté des Sciences, 91 Orsay, France

and

G. Laval and R. Pellat
Association EURATOM–Commisariat a l'Energie Atomique, Centre d'Etudes Nucléaires, 92 Fontenay-Aux-Roses, France

(Received 18 May 1971)

The radial localization of trapped-particle instabilities is studied for a peaked diamagnetic-frequency profile and for a realistic profile. In the later case it is shown that modes can be excited only with a high radial wave number. The correspondingly reduced coefficient of turbulent diffusion is computed for the collisionless instability.

The existence of trapped particles in a geometry of the Tokomak type is known to give rise to instabilities in either the collisionless or the collisional regime.[1] Although all the parameters of the problem strongly depend on the radial coordinate r (Fig. 1), the calculations done so far have not taken this into account; it has been assumed more or less explicitly that the modes are strongly localized around a given magnetic surface. We show here that with the experimental density profiles presently available, the trapped-particle instabilities can only be excited with a high radial wave number, thereby giving a small turbulent diffusion.

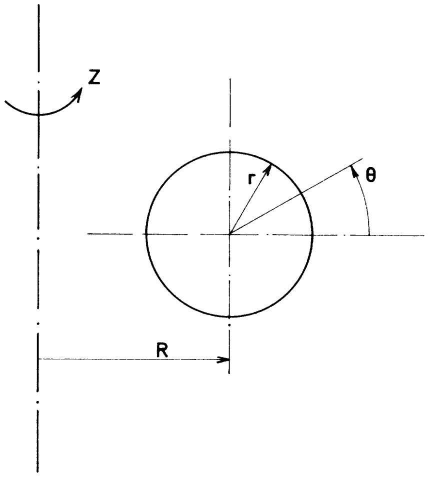


FIG. 1. Coordinates of the problem.

With the "banana" excursions taken into account,[2] the electrostatic potential for the modes fulfills the following integro-differential equation:

$$2\Phi(r,\theta)=\sum_j \epsilon^{1/2}\int_{(1-\cos\theta)/2}^{1} dx^2\,(2x^2-1+\cos\theta)^{-1/2}\frac{\omega-\omega_j^*}{\omega-\omega_{Mj}+i\nu_{j\,\mathrm{eff}}}\left[\langle\Phi\rangle+\left\langle\Lambda_j^2\frac{\partial^2\Phi}{\partial r^2}\right\rangle\right], \tag{1}$$

where $\epsilon=r/R$, $\nu_{j\,\mathrm{eff}}=\nu_j\epsilon^{-1}$ is the effective collision frequency for the species j, Λ_j is the banana thickness, and $\langle\Phi\rangle\equiv[\oint d\theta\,\Phi/V_{\parallel}(\theta)][\oint d\theta/V_{\parallel}(\theta)]^{-1}$. We furthermore have

$$\begin{aligned}
\omega_j^* &= (mT/e_jBr)[(\partial/\partial r)\ln n_0],\\
\omega_{Mj} &= (mT/e_jBrR)\{E(x)/K(x)-0.5+(2q'r/q)[E(x)/K(x)+x^2-1]\},\\
\Lambda_j^2 &= (M_jT/e^2B^2\epsilon)(2x^2-1+\cos\theta),\\
q &= rB_z/RB_\theta.
\end{aligned} \tag{2}$$