Molecular theory of hyperfine pressure shifts in H caused by Ar and He buffers

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The general applicability of molecular methods for studying hyperfine pressure shifts (HPS) in a hydrogen atom caused by Ar and He noble-gas buffers has been tested thoroughly by carrying out extensive multiconfigurational self-consistent-field (MCSCF) and single-configuration self-consistent-field (SCF) calculations on ArH and HeH diatomic systems. Calculations show that for a He atom, a light noble-gas buffer, single-configuration SCF molecular wave functions are sufficiently good in reproducing the HPS result quantitatively, although qualitatively the weak, long-range polarization features are not described. However, for a heavier noble-gas buffer, such as the Ar atom, the long-range polarization effects are the strong and dominant features in the ArH binary interaction. Because of a lack of a sufficient number of proper functions for describing the long-range polarization features, the single-configuration SCF molecular wave functions do not reproduce the long-range polarization effects adequately. For ArH, therefore, MCSCF molecular wave functions, constructed with a choice of configurations which describe the dominant polarizations, are employed to reproduce the HPS result quantitatively and the long-range features qualitatively. HPS results computed by using MCSCF molecular wave functions are in excellent agreement with the experimental result.

I. INTRODUCTION

The success of the molecular method in reproducing the hyperfine pressure shift (HPS) in paramagnetic atoms[1,2] which interact with noble-gas buffers has been blurred because of the following reasons. First, the need for a single-configuration or a multiconfigurational molecular method, depending on the physical interactions experienced by a collision pair, has not been explored properly. Second, no real attempts have been made to understand why a single-configurational molecular method works in one system and seems to fail in another. Third, apparent discrepancies that exist need to be removed. Thus, the main objective of this paper is to explore these facts and other special behaviors that make each interacting atom pair unique, and then to prescribe specific measures that must be incorporated in the method, in order to ensure proper representation of such unique features.

The multiconfigurational self-consistent-field (MCSCF) method goes beyond the single-configuration self-consistent-field (SCF) method in the sense that the MCSCF method can include in its representation of wave functions many of the details of an interaction that no single-configuration calculation can possibly describe. By including the right configurations in a MCSCF calculation, a specific effect arising from certain interaction features can be incorporated into the molecular wave functions. Therefore, when a single-configuration SCF method fails, owing to effects arising from the detailed structures of the interaction, the MCSCF method is sought. Thus, the MCSCF method is just like the perturbation method. Higher-order terms are added to the single-configuration SCF term through inclusion of other significant configurations.

In a binary encounter, the colliding atoms experience interactions of various natures[3] as the internuclear separation varies. Broadly speaking, when the internuclear separation is small, the interaction is highly repulsive and can be expressed adequately by first-order perturbation terms. Therefore, a single-configuration SCF molecular calculation may be quite good in the short-range region to reproduce dominant physical properties exhibited by the colliding atom pair, although effects arising from intra-atom correlations would be missing. In the long-range region, however, the interaction is generally weak and attractive (known as Van der Waals interaction or London's dispersion interaction) and can be described by the second-order perturbation terms.[4] To describe the long-range features of any physical properties exhibited by the colliding atom pair, the use of single-configuration SCF molecular wave functions would be a poor choice. Thus, MCSCF molecular wave functions, constructed by a choice of representative configurations, are required to describe the long-range features. This same argument applies while describing the intermediate-range properties. In the intermediate-range region, both the repulsive interaction and Van der Waals attractive interaction are concurrent and thus competing with each other. Unless the repulsive interaction dominates the attractive counterpart, the use of single-configuration SCF molecular wave functions will not be justified in

the intermediate-range region.

From the above discussion, it becomes clear that, except for the colliding atom pair with small polarizability, or in other words, for the colliding pair that has a very weak long-range interaction, the use of the single-configuration SCF method will not be justifiable. For a colliding pair consisting of a hydrogen atom and a noble-gas atom, the long-range attractive interaction becomes gradually stronger when switching from the lighter to the heavier noble-gas atom. The polarizability of a noble-gas atom becomes larger as the atom gets heavier. For He, the lightest of all the noble-gas atoms, with a small polarizability, the long-range attractive interaction in HeH is quite small and not at all dominating. Therefore, as will be seen, the single-configuration SCF molecular wave functions in HeH give rise to a HPS result that is in excellent agreement (quantitative only) with the experimental value. If, however, the He is replaced by any other noble-gas atom, the interaction changes drastically. The long-range attractive interaction become increasingly stronger and dominating as the strength of the polarizability of the noble-gas atom increases. Therefore, for the proper description and representation of long-range and intermediate-range behaviors, the use of MCSCF molecular calculations becomes mandatory.

Achieving the desired computational accuracy becomes increasingly difficult when the interaction gets smaller. Such is always the case with the HeH long-range interaction. Thus, the real root of all the discrepancies may lie in part in not achieving the required computational accuracy. It becomes, therefore, very significant to consider those requirements that are essential to maintain always a sufficient level of computational accuracy. Accordingly, the expansion coefficients of molecular orbitals, accurate to the required significant figures, are obtained by choosing a tighter constraint on the energy convergence in the MCSCF calculation.

Finally, in the case of paramagnetic atoms with cores, core electrons with spins parallel to that of valence electrons see a different exchange potential than that seen by core electrons with spins antiparallel to that of valence electrons. Therefore, the radial part of the electronic wave functions in those atoms becomes spin dependent. This phenomenon is known in the literature as the core polarization.[5] The hyperfine interaction has a significant contribution arising from the core-polarization effect. It is, therefore, necessary that, for all the paramagnetic atoms except isoelectronic atoms, provisions be made to incorporate core-polarization contributions. For example, in diatomic systems involving $N(^4S_{3/2})$ and

$P(^4S_{3/2})$, the contribution to the hyperfine interaction may arise significantly from core-polarization effects. The detailed exposition of the subject with reference to free $N(^4S_{3/2})$ and $P(^4S_{3/2})$ atoms can be found in the literature.[6] Molecular calculations, if employed, must be modified to meet these requirements. At the moment no molecular calculations are conducted on such systems. However, in those cases involving Li and Na, where core-polarization contributions are essentially minor corrections compared to the direct hyperfine interaction terms, the core-polarization contribution to the HPS results is assumed to be quite small and negligible.[2] If, however, the inclusion of such small but legitimate corrections removes existing discrepancies or leads to better qualitative agreement with experiments, core-polarization effects should be added within the framework of molecular calculations.

The molecular method was first applied[1] to HeH and later to the LiHe and NaHe systems.[2] In all these cases the HPS results were positive, and in each case, good quantitative agreement with the experiment was achieved. Das and Ikenberry[7] criticized our work[1] on HeH because it did not reproduce the long-range features correctly. They felt that this was due to the choice of the trial solution in the variational calculation presented in Ref. 1. Furthermore, they claimed that the negative HPS result cannot be obtained by this procedure. The simplest systems that give negative HPS results are $He(1s2s)$ and ArH. Rao and Kestner[8] reported a single-configuration SCF calculation for ArH. They obtained a large positive result for the HPS in ArH. All these unfavorable developments prompted us to initiate a thorough MCSCF molecular calculation on ArH. The main text of this paper is to report the HPS result in ArH, successfully obtained by employing MCSCF molecular wave functions. However, to answer all the other relevant questions that in the meanwhile have been raised, we have carried out three complementary calculations. One is a single-configuration "modified" SCF molecular calculation on ArH. The other two are single-configuration and multiconfigurational SCF calculations on HeH. Here we have employed the same basis set as we have used in the earlier calculation on HeH.[1] This only proves that our failure to obtain the long-range features in our earlier calculation was due to insufficient accuracy of the computation and not to the molecular method or variational principle of Ref. 1.

In our earlier reports[1,2] of the molecular method, we did not outline the structural details of the molecular calculations. It is our understanding now that there is a need and growing demand for

recording them so that many readers will obtain
a clearer picture of the method. In Sec. II, we
review the variational method and general proce-
dure for molecular calculations. We also include
in Sec. II the discussion of basis sets used for the
ArH and HeH calculations.

In Sec. III, we give the derivation of an expres-
sion for the electronic spin density in terms of
molecular orbitals (HeH molecular orbitals are
used for the reference). We have felt it necessary
to analyze the molecular-orbital expression of the
spin density in the perturbation picture and identify
its various terms with those of nonvanishing cross-
perturbation terms. In our calculations we have
always neglected the third-order terms because
they are small and do not contribute significantly.
Das and Ikenberry[7] nonetheless added the missing
third-order term to our calculated spin density
in HeH to obtain the long-range feature in their
report of the HeH calculation. We have tried here
to draw the reader's attention to this fact involving
the discrepancy. Our present MCSCF calculation
on HeH with the required computational accuracy
does show that, without adding third-order cor-
rection terms, the long-range feature in HeH can
be obtained. In Sec. III, we also give the expres-
sion for the standard definition of the HPS.

In Sec. IV, we present the details of the MCSCF
calculation for ArH. We outline the general MCSCF
theory in reference to ArH and then detail the HPS
calculation for ArH.

A single-configuration "modified" SCF calcula-
tion on ArH is reported in Sec. V. This calcula-
tion attributes a new feature to a single-configura-
tion SCF calculation. Because of our choice of a
basis set that includes a diffuse function at H for
a fairly good description of polarization effects
arising from Ar, our single-configuration SCF
calculation on ArH is capable of describing the
tendency of the long-range polarization features.
It, however, fails to reproduce them quantitatively.
Therefore, our single-configuration SCF calcula-
tion (which we refer to as a "modified" SCF calcu-
lation) on ArH differs physically from two existing
calculations, one by Rao and Kestner[8] and the
other by Wagner, Das, and Wahl.[9] Nevertheless,
the HPS result calculated by use of our single-
configuration molecular-orbital (MO) wave func-
tions is also a large and positive quantity like the
HPS result of Rao and Kestner.[8] The whole section
is devoted to an analytical discussion on these
topics.

In Sec. VI we document the new MCSCF calcula-
tion on HeH. This calculation shows the consis-
tency in the MCSCF approach and illustrates the
fact that the attainment of sufficient computational
accuracy is the essential requirement. Then, we

have placed a single-configuration SCF calculation
on HeH in Sec. VII. A brief discussion has been
added in the conclusion in Sec. VIII.

II. VARIATIONAL METHOD AND GENERAL PROCEDURE FOR MOLECULAR CALCULATIONS

The general procedure for single-configuration
SCF calculations and MCSCF calculations on di-
atomic systems, based on the variational prin-
ciple,[10] is well documented in the literature.[11-13]
We, however, outline here the essential aspects.
Energy functionals are minimized with respect
to variational parameters involved in molecular
orbitals. Each molecular orbital is a linear com-
bination of basis functions or basis vectors, com-
prised of Slater functions or Gaussian functions.
These variational parameters may include ex-
pansion coefficients, exponents in basis vectors,
and also the configuration-mixing coefficients in
the case of the MCSCF method. If the molecular
orbitals as variational functions approach the
exact eigenfunctions, then the energy obtained by
the minimization principle approaches the exact
energy of the system under consideration. Only
a linear combination of a complete set of basis
vectors, i.e., an infinite summation over the
basis vectors, may satisfy that criterion. In
practice, however, one optimizes a linear com-
bination of a finite number of basis vectors and
their exponents, initially by intuitive guess, and
then by iteration. For each set of basis vectors,
the exponents are optimized through successive
processes of individual exponent optimizations.
Each exponent optimization needs several runs
of energy calculations through the minimization
with respect to the expansion coefficients. These
energies are plotted against the various values of
the exponent, and then, the optimum value for the
exponent is obtained by interpolation. However,
the number of basis functions is optimized through
successive additions of new and relevant basis
functions, whose exponents are in turn optimized.
The whole process can be continued until the low-
est possible energy is achieved.

If, however, this prescription is strictly fol-
lowed, actual calculation become prohibitive.
Thus, in order to make the calculation practical
and feasible, and without sacrificing the essential
spirit, a shortcut procedure is practiced. Use is
made of existing exponent-optimized basis func-
tions, which have been obtained from earlier di-
atomic calculations with at least one atom in com-
mon with that of the diatom concerned. Then, in
addition to the standard procedure of energy mini-
mization as a probe, one may reproduce some
standard physical properties by employing these

optimized wave functions.

When calculations need to be carried out at various internuclear separations, the exponent optimization at each internuclear separation becomes excessive and prohibitively expensive. A compromise is generally sought by choosing an agreeable and intermediate internuclear separation. This, however, poses serious questions about its validity when the same exponents are employed at various other internuclear separations.

In the present calculation, the set of basis functions for ArH has been chosen from several sets of available exponent-optimized basis functions for Ar and H. To be able to complete the calculation within limited resources, we have exercised maximum caution and minimum allowable freedom in choosing the total number of basis functions. We have not allowed alteration of the optimized basis functions chosen for Ar, but several sets of exponent-optimized basis functions[14] are used for H. We have chosen the set that gives the best minimum for the energy and the best agreement with the long-range Van der Waals interaction. Table I lists the set of basis functions used for ArH. The optimization is carried out only once at $R = 8.0$ a.u. There is a need, however, for the further improvement of the wave function through rigorous optimization at each internuclear separa-

TABLE I. Quantum numbers n, L, m, and exponent ζ for the ArH basis set.

Centers	n	L	m	ζ
Ar	1	0	0	19.2500
Ar	2	0	0	16.7810
Ar	3	0	0	11.1910
Ar	2	0	0	6.3320
Ar	3	0	0	3.1430
Ar	3	0	0	1.9800
Ar	4	0	0	2.2547
Ar	2	1	0, ±1	15.3170
Ar	2	1	0, ±1	9.0530
Ar	2	1	0, ±1	5.7700
Ar	3	1	0, ±1	2.8930
Ar	3	1	0, ±1	1.6050
Ar	3	2	0, ±1	2.2547
Ar	4	2	0, ±1	2.2547
H	1	0	0	1.0000
H	1	0	0	0.4500
H	2	0	0	1.0000
H	2	0	0	0.4500
H	2	1	0, ±1	1.2100
H	2	1	0, ±1	0.8500
H	3	1	0, ±1	1.2000
H	3	2	0, ±1	1.0000
H	4	3	0, ±1	1.0000

TABLE II. Configurations used for the MCSCF calculations on ArH.

Description	Configurations
	$(1s\sigma_{Ar}^2 2s\sigma_{Ar}^2 2p\sigma_{Ar}^2 2p\pi_{Ar}^4)X$
Hartree-Fock	$(3s\sigma^2 3p\sigma^2 3p\pi^4)_{Ar} 1s\sigma_H$
$(3p_{Ar}, 1s_H)$ dispersion excitations	$(3s\sigma^2 3p\sigma 3d\sigma 3p\pi^4)_{Ar} 2p\sigma_H$
	$(3s\sigma^2 3p\sigma^2 3p\pi^3 3d\pi)_{Ar} 2p\sigma_H$
	$(3s\sigma^2 3p\sigma 3d\pi 3p\pi^4)_{Ar} 2p\pi_H$
	$(3s\sigma^2 3p\sigma^2 3p\pi^3 3d\pi)_{Ar} 3d\sigma_H$
$(3s_{Ar}, 1s_H)$ dispersion excitations	$(3s\sigma 3p\sigma^2 3d\sigma 3p\pi^4)_{Ar} 2p\sigma_H$
	$(3s\sigma 3p\sigma^2 3d\pi 3p\pi^4)_{Ar} 2p\pi_H$

tion, but it is at present beyond our reach.[15]

In the case of the MCSCF calculations, we have to decide what are the dominant configurations. The wave functions which represent the long-range Van der Waals interaction consists of three kinds of terms: the most dominant Hartree-Fock-like configuration, the dispersion excitation involving simultaneous interatomic excitations from the two atoms, and the "overlap-transfer" excitation. For ArH, 13 configurations were used in the present calculation and these are given in Table II. Given an adequate basis set, the dispersion excitations used are sufficient to yield the C_6, etc., Van der Waals interaction coefficients correctly.

For HeH, the same basis set used in our previous work[1] is employed. Table III lists the HeH basis set.

III. ELECTRONIC SPIN DENSITY, EXPRESSION OF HPS IN TERMS OF MOLECULAR ORBITALS

Either in a single-configuration or a multiconfiguration the molecular-orbital theory, for each orbital, imposes the constraint

$$\langle \phi_i | \phi_j \rangle = \delta_{ij} . \qquad (1)$$

For any operator representing a physical observ-

TABLE III. Quantum numbers n, L, m, and exponent ζ for the HeH basis set.

Centers	n	L	m	ζ
He	1	0	0	1.4530
He	1	0	0	2.9060
He	2	1	0, ±1	1.4530
He	2	1	0, ±1	2.9060
H	1	0	0	1.0000
H	1	0	0	2.4300
H	2	1	0, ±1	1.0000

able involving electron spins, the nonvanishing criterion of a matrix element of that operator depends on the electron or spin occupancy of the MO's involved.

Thus, the expression for the electronic spin density at the hydrogen nucleus, when use is made of the molecular wave function ψ given by Eq. (2) of Ref. 1, reads precisely

$$\rho(R) = a^2 \langle (1\sigma^2 2\sigma) | H_{hfs} | (1\sigma^2 2\sigma) \rangle + \{b^2 \langle 1\sigma(3\sigma 4\sigma) | H_{hfs} | 1\sigma(3\sigma 4\sigma) \rangle_A + c^2 \langle 1\sigma(3\sigma 4\sigma) | H_{hfs} | 1\sigma(3\sigma 4\sigma) \rangle_B$$

$$+ d^2 \langle 1\sigma(1\pi 2\pi) | H_{hfs} | 1\sigma(1\pi 2\pi) \rangle_A + e^2 \langle 1\sigma(1\pi 2\pi) | H_{hfs} | 1\sigma(1\pi 2\pi) \rangle_B \} , \tag{2}$$

where A is the coupling $^2\Sigma^+ \times ^1\Sigma^+$ and B is the coupling $^2\Sigma^+ \times ^3\Sigma^+$, and $H_{hfs} = \sum_i S_{iz} \delta(\vec{r}_i - \vec{r}_H))$ is the Fermi contact term[16] for the hyperfine interaction. Now, our intention is to analyze and understand the expression in Eq. (2) in the perturbation picture so that we can compare our method with Das and Ikenberry's perturbation approach.[7] We express $H_{vdW} = H$ (total Hamiltonian) $- H_{HF}$ (corresponding HF potential) and treat it as a perturbation to H_{HF}. For two simultaneous perturbations, namely, H_{vdW} and the hyperfine contact interaction H_{hfs}, there are two terms in the third-order correction to the spin density (the second-order terms vanish):

$$\Delta\rho_3(R) = \langle \delta\psi_{vdW} | H_{hfs} | \delta\psi_{vdW} \rangle + 2 \langle \delta\psi_{vdW} | H_{vdW} | \delta\psi_{hfs} \rangle , \tag{3}$$

where $\delta\psi_{vdW}$ and $\delta\psi_{hfs}$ are perturbed wave functions due to H_{vdW} and H_{hfs}, respectively. In the molecular calculation, however, the H_{vdW} terms is included in the total Hamiltonian H, but the H_{hfs} term is not included. Thus, in the perturbation picture, the molecular wave function ψ, which is an eigenfunction of the Hamiltonian H, does not contain a term equivalent to $\delta\psi_{hfs}$. Consequently, the expression of the third-order correction to the spin density, calculated from the MCSCF or SCF wave functions, does not contain the second term of $\Delta\rho_3(R)$ as shown in Eq. (3). Let us take from the expression given by Eq. (2) the first term giving the first-order contribution, while terms inside the { } constitute a part of the third-order contribution, and can be identified with the first term of Eq. (3). Here we have assumed that the very first configuration of ψ, i.e., a $(1\sigma^2 2\sigma)$, is the eigenfunction of H_{HF} and the rest of the configuration gives $\delta\psi_{vdW}$. Again, it is easy to determine that the first term of $\Delta\rho_3(R)$ as given by Eq. (3) is a positive quantity. Now if the second term of $\Delta\rho_3(R)$ turns out to be a negative quantity, it will be incorrect to include only one of the two terms of $\Delta\rho_3(R)$ as corrections to the spin density. In doing so, one may cause serious impairment to the spin density by destroying the delicate balance between the third-order terms. In our molecular calculations, in computing $\rho(R)$, we have always neglected the terms inside the { } of Eq. (2) be-

cause they are small, and thus we have retained only the first-order term. If this kind of perturbation interpretation has any relevancy, one can see what $\Delta\rho_3(R)$ really means. $\Delta\rho_3(R)$ should be small. Das and Ikenberry,[7] however, have described the absence of the second term of $\Delta\rho_3(R)$ in the spin-density expression of our HeH calculation[1] as "a pitfall of the variational principle." They have added this missing term to our calculated HeH spin density when they have treated H_{vdW} as the interatomic interaction and have used our ψ in place of $\delta\psi_{vdW}$, and again, without regarding the fact that we also have not included the first term of $\Delta\rho_3(R)$ in the HeH spin density. It is certainly a discrepancy which speaks for itself. Their calculated values of the second term of $\Delta\rho_3(R)$ are negative and that has helped to lower our calculated $\Delta\nu(R)/\nu_0$ values. Thus, in the long-range region $\Delta\nu(R)/\nu_0$ becomes negative and it was therefore thought to be physically acceptable.

No new calculations are required to clarify the discrepancy, the simple logic discussed here should be sufficient. Nevertheless, our new precision MCSCF calculation on HeH, presented in Sec. VI, is to show that the long-range features in HeH can be reproduced without inclusion of third-order correction terms as given by $\Delta\rho_3(R)$.

Finally, once $\rho(R)$'s are computed for various internuclear separations, we then tabulate the quantity

$$\frac{\Delta\nu(R)}{\nu_0} = \frac{\rho(R) - \rho(\infty)}{\rho(\infty)} \tag{4}$$

as a function of R. A statistical averaging of these quantities, $\Delta\nu(R)/\nu_0$, over the entire phase space gives rise to

$$\int_0^\infty [\Delta\nu(R)/\nu_0] R^2 e^{-V(R)/kT} dR , \tag{5}$$

which when multiplied by certain physical constants defines the HPS.[17] In expression (5),

$$V(R) = E(R) - E(\infty) \tag{6}$$

refers to the calculated potential surface as a function of R. k and T refer to the Boltzmann constant and the temperature of measurements in the absolute scale.

IV. GENERAL MCSCF THEORY AND COMPUTATION OF $\Delta\nu(R)/\nu_0$ AND HPS FOR ArH

The general MCSCF theory has been fully discussed in previous publications.[12] Therefore, the repetition of the entire subject matter once again is not needed. Rather, we summarize here only the essential and relevant facts from those earlier publications.[11-13] Let $\{\phi_{\lambda m}^{Ar}\}$ and $\{\phi_{\lambda m}^{H}\}$ be functions centered at the two nuclei of Ar and H. A configuration-interaction (CI) wave function, consisting of terms obtained by double excitations from the Hartree-Fock (HF) configuration into these functions,

$$\Psi = a_0\{\psi_0\} + \sum c_{\lambda m, \lambda'm'}\{\phi_{\lambda m}^{Ar}\phi_{\lambda'm'}^{Ar}\}$$

$$+ \sum d_{\lambda m, \lambda'm'}\{\phi_{\lambda m}^{Ar}\phi_{\lambda'm'}^{H}\} \tag{7}$$

is considered. The first term in Eq. (7) represents the near HF function consisting of a set of more-or-less nonoverlapping localized orbitals, and also it is the predominant term with proper antisymmetrization in the particle indices, etc. Thus, the said excitations, represented by the third and second terms of Eq. (7), respectively, can be divided into two classes: one that corresponds to single excitation from the two centers and the other to both excitations from the same center. In pair-theory language, the third term relates to the interatomic correlation and the second term to the intra-atomic correlation. The MCSCF method consists in optimizing the coefficients a_0, $c_{\lambda m, \lambda'm'}$, and $d_{\lambda m, \lambda'm'}$, as well as the orbitals. The optimization of $\{\phi_{\lambda m}^{Ar}\phi_{\lambda'm'}^{Ar}\}$ or $\{\phi_{\lambda m}^{Ar}\phi_{\lambda'm'}^{H}\}$ depends crucially on the maximization of the coupling integral:

$$E_{0ii'} = \int \{[\phi_i^{Ar}(1)\phi_{i'}^{Ar}(2)]$$

$$\text{or } [\phi_i^{Ar}(1)\phi_{i'}^{H}(2)]\psi_0(1)\psi_0(2)/r_{12}\} d\tau_1 d\tau_2. \tag{8}$$

As has been shown, within the MCSCF formalism the functions that contribute less are also the functions that are more localized. The intra-atomic correlation functions, such as $\{\phi_i^{Ar}\phi_{i'}^{Ar}\}$, are found to be localized functions. On the other hand, the interatomic correlation terms are represented by dispersion-type diffused excitation functions. Therefore, the coupling between intra-atomic and interatomic terms,

$$\langle\phi_{dis}^{H}(1)\phi_0^{H}(1)|\frac{1}{r_{12}}|\phi_{\text{intra-atom corr.}}^{Ar}(2)\phi_0^{Ar}(2)\rangle$$

$$\times\langle\phi_{dis}^{Ar}|\phi_{\text{intra-atom corr.}}^{Ar}\rangle, \tag{9}$$

which is, at most, as large as the coupling between the dispersion-type interatomic function and the dominant near HF one multiplied by the overlap integral $\langle\phi_{dis}^{Ar}|\phi_{\text{intra-atom corr.}}^{Ar}\rangle$. Since $\phi_{\text{intra-atom corr.}}^{Ar}$ is localized while ϕ_{dis}^{Ar} is diffused, the overlap is small and thus one arrives at a contribution that is almost two orders of magnitude smaller than that from the dispersion-type interatomic terms. While this work has been completed and the publication process was in progress, a recent published work by Liu and McLean[18] was brought to our attention. They have demonstrated that in the case of the Van der Waals interaction of two ground-state He atoms, our prescribed coupling of inter- and intra-atomic correlation leads to a discrepancy in estimating the theoretical potential depth. Our calculation is supposed to give a deeper potential.

Now, for the proper representation of the intra-atomic correlation in Ar, one would need a set of very large localized basis functions centered at Ar, in addition to near HF functions and dispersion-type-interatomic correlation functions. This requires working with a very large set of basis functions and a host of required configurations which leads to several practical problems such as the handling of extra large supermatrices, excessive computational time, etc. In order to avoid these practical problems, one can partition the calculation into three independent steps: (i) Obtain a high precision HF function; (ii) evaluate the intra-atomic correlation using only the dominant Ar-atomic correlating MCSCF orbitals as a function of internuclear separation; and (iii) evaluate the contribution from the dispersion-type-interatomic correlation by employing the near HF set, coupled with a usually small number of dispersion-type-interatomic correlation functions.

In accordance with an earlier calculation[12] for HeH and LiHe, the contributions to the long-range and the intermediate-range interatomic potentials, which arise from the intra-atomic terms, are assumed to be quite small in ArH compared to those arising from the dispersion-type-interatomic correlation terms. However, in the short-range region, these intra-atomic correlation terms should make a significant contribution that should be properly incorporated in order to produce an accurate short-range interatomic potential surface in ArH. Again, for ArH, the dominant contribution to the HPS arises from $\Delta\nu(R)/\nu_0$ in the intermediate-range and long-range internuclear separation, and depends mainly on the intra-atomic correlation function in H in the ArH environment. Thus, except for the short-range interatomic potential, the calculation of the intra-atomic correlation from localized functions at Ar can be neglected. To avoid expensive intra-atomic correlation cal-

culations in the short-range region, we have em-
ployed, for the statistical averaging, the short-
range HF potentials calculated by precision HF
functions.

Even if the deviation of the HF potential from
the exact potential is sizable in the short-range
region, the over-all contribution of the repulsive
short-range potential is quite small because of
the statistical averaging factor, $R^2 e^{-V(R)/kT}$. If,
however, the deviation is very large, it will in-
fluence the HPS result quantitatively if not qualita-
tively. But from the analysis made by Das and
Wahl[12] in HeH, it appears that for R between the
small and near intermediate region, both inter-
atomic and intra-atomic correlation terms be-
come comparable and competitive. The cumula-
tive effects of these two added terms to the HF
potential may not be very significant when we are
only considering the Boltzmann factor. However,
over a narrow range of intermediate R, the devia-
tion of the HF potential from the exact potential
could become serious, but its influence on the
average nature of the HPS result would not be
drastically felt if the calculations of quantities re-
main fairly accurate for all other values of R.

Taking advantage of the simplicity of the pro-
cedure, we have carried out the HF and disper-
sion-type configuration mixing at the same step,
using the basis set shown in Table I. In deter-
mining the dispersion-type functions we have con-
sidered the coupling term

$$\iint \phi_0^H(1)\phi_{\lambda m}^H(1)\frac{1}{r_{12}}\phi_0^{Ar}(2)\phi_{\lambda'm'}^{Ar}(2)\,d\tau_1\,d\tau_2\,. \quad (10)$$

For large R this becomes

$$\sim(R^{\lambda+\lambda'})^{-1}\int \phi_0^H r^\lambda Y_{\lambda m}(\theta,\,\phi)\phi_{\lambda m}^H\,d\theta$$

$$\times\int \phi_0^{Ar} r^{\lambda'} Y_{\lambda'm'}(\theta,\,\phi)\phi_{\lambda'm'}^{Ar}\,d\theta\,. \quad (11)$$

When each of these integrals is optimized individ-
ually, one obtains

$$\phi_{\lambda m}^H = r^\lambda \phi_0^H(r)Y_{\lambda m}(\theta,\,\phi)\,,$$
$$\phi_{\lambda'm'}^{Ar} = r^{\lambda'} \phi_0^{Ar}(r)Y_{\lambda'm'}(\theta,\,\phi)\,. \quad (12)$$

Thus, the dispersion-type functions are simply
$r^\lambda Y_{\lambda m}(\theta,\,\phi)$ times the corresponding HF functions.

For ArH, the MCSCF wave function with 13 dom-
inant configurations is given by

$$\Psi = a_1(1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 6\sigma 1\pi^4 2\pi^4)$$

$$+a_2[1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma(7\sigma 8\sigma)1\pi^4 2\pi^4;\ {}^2\Sigma^+\times{}^1\Sigma^+]+a_3[1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma(7\sigma 8\sigma)1\pi^4 2\pi^4;{}^2\Sigma^+\times{}^3\Sigma^+]$$

$$+a_4[1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma(3\pi 4\pi)1\pi^4 2\pi^4;{}^2\Sigma^+\times{}^1\Sigma^+]+a_5[1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma(3\pi 4\pi)1\pi^4 2\pi^4;{}^2\Sigma^+\times{}^3\Sigma^+]$$

$$+a_6[1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 8\sigma(2\pi^3 3\pi)1\pi^4;{}^2\Sigma^+\times{}^1\Sigma^+]+a_7[1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 8\sigma(2\pi^3 3\pi)1\pi^4;{}^2\Sigma^+\times{}^3\Sigma^+]$$

$$+a_8[1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 7\sigma(2\pi^3 3\pi)1\pi^4;{}^2\Sigma^+\times{}^1\Sigma^+]+a_9[1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 7\sigma(2\pi^3 3\pi)1\pi^4;{}^2\Sigma^+\times{}^3\Sigma^+]$$

$$+a_{10}[1\sigma^2 2\sigma^2 3\sigma 4\sigma^2 5\sigma^2(7\sigma 8\sigma)1\pi^4 2\pi^4;{}^2\Sigma^+\times{}^1\Sigma^+]+a_{11}[1\sigma^2 2\sigma^2 3\sigma 4\sigma^2 5\sigma^2(7\sigma 8\sigma)1\pi^4 2\pi^4;{}^2\Sigma^+\times{}^3\Sigma^+]$$

$$+a_{12}[1\sigma^2 2\sigma^2 3\sigma 4\sigma^2 5\sigma^2(3\pi 4\pi)1\pi^4 2\pi^4;{}^2\Sigma^+\times{}^1\Sigma^+]+a_{13}[1\sigma^2 2\sigma^2 3\sigma 4\sigma^2 5\sigma^2(3\pi 4\pi)1\pi^4 2\pi^4;{}^2\Sigma^+\times{}^3\Sigma^+]\,, \quad (13)$$

where the molecular orbitals 1σ, 2σ, 3σ, 4σ, 5σ,
6σ, 7σ, 8σ, 1π, 2π, 3π, and 4π are approximately
$1s\sigma_{Ar}$, $2s\sigma_{Ar}$, $3s\sigma_{Ar}$, $2p\sigma_{Ar}$, $3p\sigma_{Ar}$, $1s\sigma_H$, $3d\sigma_{Ar}$, $2p\sigma_H$,
$3p\pi_{Ar}$, $3d\pi_{Ar}$, and $2p\pi_H$, respectively. The nota-
tions ${}^2\Sigma^+\times{}^1\Sigma^+$, etc., represent the pairing scheme
of the open shells in the different configurations.

In terms of computer CPU time, the most time-
consuming part of the calculation is the creation
of two-centered one-electron and two-electron in-
tegrals at each R. The numerical accuracy of
these integrals, computed by the standard compu-
tational code BISON,[15] depends upon the choice of
higher values of Gaussian grid sizes (NXI, NETA,
NSIMP, NBIAS). For a numerical accuracy of these
integrals to 10 significant figures, NXI = NETA = 100,
NSIMP = 95, NBIAS = 50 are suggested. But, an ac-
curacy of that high level is not really warranted,
particularly for the ArH system, where the long-
range interactions are quite large. Thus, to reach

an acceptable compromise, this research has been
carried out with three Slater (ns) functions of ex-
ponents, $\zeta_{Ar} = 19.25$, $\zeta_{Ar} = 16.781$, and $\zeta_H = 1.00$ at
various R. A reasonable compromise choice of
grid sizes with NXI = NETA = 50, NSIMP = 50, NBIAS
= 30 has been reached since the very small inte-
grals ($\sim 10^{-8}$) are found to be accurate to eight
significant figures. For each R, the CPU time
for computing the integrals for ArH on an IBM
370/165 computer is an hour. The level of compu-
tational accuracy of our calculation is quite ade-
quate to give a reliable value for the ArH HPS re-
sult. The entire calculation including the construc-
tion of wave functions, interatomic potentials, and
other results involving scattering of the ArH colli-
sion pair will soon be reported in a separate paper.
For ArH, the calculated a_1, $V(R)$, and $[\Delta\nu(R)/$
$\nu_0]R^2 e^{-V(R)/kT}$, the integrand of the statistical
averaging expression that defines the HPS, are

presented in Table IV. The numerical integration of (5) is carried out by use of a spline interpolation program.[19] The HPS value, for ArH, computed by employing MCSCF wave functions at T $=26°$C is -4.38×10^{-19}/Torr at $0°$C compared to the latest experimental HPS (at $26°$C) result of -4.80×10^{-19}/Torr at $0°$C.[20,21]

V. CALCULATION OF THE HPS RESULT FOR ArH BY EMPLOYING SINGLE-CONFIGURATION "MODIFIED" SCF WAVE FUNCTIONS

There have not been many HF or single-configuration SCF calculations carried out on ArH, except one by Rao and Kestner[8] and one by Wagner-Das-Wahl (WDW).[9] The polarizability of Ar is very high. In the intermediate- and long-range internuclear separations, the polarization effect on the ArH interaction should be strongly felt. Thus, for single-configuration SCF calculations on ArH, if one chooses a fairly large basis set including some diffuse functions for H, these polarization effects partially appear in the calculations for intermediate- and long-range separations. Rao and Kestner[8] used three basis functions for H. Two of them are $1s$- and $2p$-type free hydrogenic functions. The third one is a compact $1s$-type function. So, their basis functions for H do not offer enough flexibility to describe intermediate- and long-range polarization effects in the ArH interaction. The choice of basis set by Wagner-Das-Wahl[9] is certainly superior. However, they have emphasized Ar by their choice of functions. To represent polarization effects arising from Ar, they have not taken any diffuse functions on H.

In carrying out a single-configuration self-consistent-field calculation on ArH we employ the same basis set and integrals as those already used for the MCSCF calculation on ArH. First of all, this choice is computationally economic. Second, in comparing both other choices of an ArH basis set, our choice offers H some flexibility for representing the polarization effects of Ar on the ArH interaction. Therefore, our single-configuration self-consistent-field calculations on ArH give an interatomic potential which is physically different from the other two potentials discussed here. Our potential becomes attractive beyond $R = 7.0$ and slowly goes to the separated-atom limit at R $=20.0$ a.u. The potential reported by Rao and Kestner[8] is, on the other hand, repulsive throughout and with a separated-atom limit of 9.0 a.u. Wagner-Das-Wahl[9] do not report their SCF results beyond $R = 9.0$ a.u. and the interatomic potential up to that point is repulsive.

In standard or conventional calculations, the HF or single-configuration potentials are found to be repulsive throughout. There is, however, no mathematical justification for such occurrences except that the HF wave functions are approximate functions, not the exact wave functions of Schrödinger's equation. That does not, however, rule out the possibility of the HF wave functions approaching the exact wave functions. A good choice of basis functions that describe the essential and dominating interactions can close the gap between the HF function and the exact function.

Wagner-Das-Wahl[9] have plotted the experimentally derived ArH potentials. From that plot one sees that around 6.5 a.u. the ArH potential becomes attractive and around 9.0 a.u. it is still strongly attractive. The separated-atom limit can easily be extended beyond 20.0 a.u. Now, if a choice of

TABLE IV. Mixing coefficient a_1, interaction potential $V(R)$, and the integrand $[\Delta\nu(R)/\nu_0] R^2 e^{-V(R)/kT}$ for ArH.

| R (a.u.)	a_1	$V(R)$ $(10^{-4}$ a.u.)	$\Delta\nu(R)/\nu_0$ $(10^{-4}$ a.u.)	$[\Delta\nu(R)/\nu_0]R^2$ $\times e^{-V(R)/kT}$
4.0	0.999150	+168.8000	+51.3047	0.0
5.0	0.999670	+40.5000	+68.7905	+0.002388
6.0	0.999860	+6.7123	+13.5936	+0.024088
6.5	0.999900	+2.0727	+2.8796	+0.009774
7.0	0.999900	−1.3338	−1.5204	−0.008577
7.5	0.999934	−1.4673	−2.3777	−0.015533
8.0	0.999946	−1.3118	−2.5118	−0.018464
9.0	0.999963	−1.0345	−1.5840	−0.014312
9.5	0.999970	−0.9237	−1.2650	−0.012586
10.0	0.999976	−0.8347	−1.1076	−0.012096
11.0	0.999984	−0.7096	−0.7126	−0.009293
12.0	0.999990	−0.6354	−0.3359	−0.005173
15.0	0.999998	−0.5509	−0.1193	−0.002844
20.0	1.000000	0.0	0.0	0.0
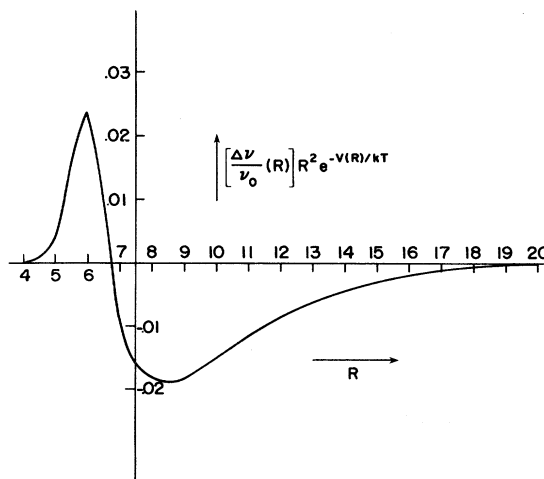
FIG. 1. Integrand $[\Delta\nu(R)/\nu_0]R^2 e^{-V(R)/kT}$ vs R for ArH. MCSCF wave functions are employed.

HF function produces the ArH potential repulsive throughout and its separated-atom limit is reached at a point where it is supposed to be strongly attractive, it only means that the gap between the chosen HF function and the exact function is unreasonably wide. That HF function should only remotely be considered as an approximate eigenfunction.

Unfortunately, to close the gap between the HF function and the exact function is a difficult task. There is no one prescribed method for achieving this. Thus, in most cases, not having a good choice of basis functions gives HF functions which fail to field the correct physical behavior. However, in accordance with the conventional standard, both Rao-Kestner[8] and Wagner-Das-Wahl's[9] single-configuration self-consistent-field calculations correspond to the current usage of the phrase "SCF calculation."

Our single-configuration self-consistent-field results on ArH appeared drastically different from the other two calculated potentials and were closer to the exact nature of the interaction. We should, therefore, refrain from identifying them as results of a single-configuration SCF calculation. To make a distinction, our single-configuration calculations are designated "modified" SCF calculations. To make sure that our calculations do not involve errors arising from hidden sources, we have taken the following precautionary steps. First, we have checked again our two-centered integrals by calculating integrals for the same three basis functions quoted in Sec. IV. But this time we have used a different "BISON" system,[15]

operating on a CDC 6400 computer at the University of Virginia, Charlottesville. The BISON system at Charlottesville has been widely tested by reproducing known results for several systems. We have found no discrepancies in the stated accuracy of our ArH integrals. They are accurate to eight significant figures. Second, to check our modified SCF convergencies, we have requested Dr. G Das of Argonne National Laboratory to redo our ArH SCF calculations. Our ArH integrals (stored in several tapes) are with Dr. Das, who is employing them to complete another joint project on ArH. The new results that he has recently sent to us are presented in Table V. They are identical to our earlier results.

The most interesting aspect of our modified SCF calculation is the improvement that can be obtained over conventional single-configuration calculations through a simple modification allowing a diffuse function in the basis set. It demonstrates how simply one can describe the physical behavior by employing some intuitiveness. It would appear that the term $be^{-0.45r}$ in the ArH basis set was just a good guess which gives much of the polarization effects. This function effectively doubles the range of the interaction of the hydrogen atom, which of course should allow the calculated energy to approach closer to the actual energy. This silent feature of the modified SCF calculation needs further explorations. We hope the method would develop into a powerful technique in calculating interatomic potentials.

We now present our single-configuration modified SCF results on ArH. The columns 3, 4, and

TABLE V. Single-configuration SCF calculation on ArH. The columns 2–4 refer to $V(R)$ of Rao-Kestner, Wagner-Das-Wahl, and the present calculations. The column 5 refers to $\Delta\nu(R)/\nu_0$ of the present calculation. The columns 6–8 refer to $\Delta\nu(R)/\nu_0$ of the present calculation. The columns 6–8 refer to $[\Delta\nu(R)/\nu_0]R^2 e^{-V(R)/kT}$ with $V(R)$ of Rao-Kestner, Wagner-Das-Wahl, and the present calculations. Atomic units are used everywhere. [Note: $V(R)$'s of both Rao-Kestner (Ref. 8) and Wagner-Das-Wahl (Ref. 9) are obtained from their given analytic fits.]

R	$V(R) \times 10^4$ (RK)	$V(R) \times 10^4$ (WDW)	$V(R) \times 10^4$ (Ray)	$\Delta\nu(R)/\nu_0$	$F1(R)$ (RK)	$F2(R)$ (WDW)	$F3(R)$ (Ray)
4.5	81.200 44	91.489 48	75.878 98	0.018 142	0.000 07	0.000 02	0.000 12
5.5	15.981 01	15.436 13	14.665 63	0.006 436	0.036 01	0.038 14	0.041 38
6.5	2.668 02	2.840 49	2.055 51	0.001 568	0.049 97	0.049 07	0.053 31
7.0	0.995 57	1.179 04	0.420 98	0.000 727	0.032 06	0.031 44	0.034 07
7.5	0.338 62	0.477 04	−0.254 01	0.000 336	0.018 23	0.017 97	0.019 41
8.0	0.099 39	0.188 54	−0.521 72	0.000 145	0.009 15	0.009 07	0.009 77
9.0	0.001 46	0.027 76	−0.645 66	0.000 040	0.003 20	0.003 19	0.003 43
9.5	−0.001 26	0.010 39	−0.642 68	0.000 018	0.001 62	0.001 62	0.001 74
10.0	−0.000 07	0.003 84	−0.628 00	−0.000 002	−0.000 19	−0.000 19	−0.000 21
12.0	0.001 28	0.000 06	−0.566 00	0.000 000	0.000 00	0.000 00	0.000 00
15.0	0.000 11	0.000 00	−0.530 90	0.000 000	0.000 00	0.000 00	0.000 00
20.0	0.000 00	0.000 00	0.000 00	0.000 000	0.000 00	0.000 00	0.000 00

8 of Table V give, respectively, $V(R)$, $\Delta\nu(R)/\nu_0$, and $[\Delta\nu(R)/\nu_0]R^2e^{-V(R)/kT}$, calculated from our single-configuration SCF wave function for ArH. Both $\Delta\nu(R)/\nu_0$ and $[\Delta\nu(R)/\nu_0]R^2e^{-V(R)/kT}$ are positive quantities for all but one internuclear separation. The integral in Eq. (5) is carried out numerically by passing through the values of the integrand at the calculated points an exponential spline curve.[19] The quantitative value of the HPS is found to be $+7.9667\times10^{-19}$/Torr at $0°C$, and is in complete disagreement with the experimental result.[20,21] The columns 2 and 3 of Table V refer to $V(R)$'s obtained from the respective analytic fits as prescribed by Rao-Kestner[8] and Wagner-Das-Wahl,[9] respectively. The columns 6 and 7 of the same Table V give the values of the integrand $[\Delta\nu(R)/\nu_0]R^2e^{-V(R)/kT}$ as obtained from the respective use of Rao-Kestner's[8] and Wagner-Das-Wahl's[9] potentials $V(R)$. This has been done only to display the effects of an arbitrary use of potentials of one kind or another. It makes no sense to find out how much quantitative agreement exists between two wrong results when an arbitrary use of two available potentials is made.

It should be reaffirmed and stated here clearly that the molecular theory does not subscribe to the idea of using an arbitrary potential in carrying out the statistical averaging. The main essence of the molecular theory is to test how accurately the mathematical description or functional representation of the electronic structure of an interacting atomic system has been achieved. We use here the HPS as the probe. We need two quantities, the electronic spin density $\rho(R)$ and the internuclear potential $V(R)$, to describe the HPS. But both $\rho(R)$ and $V(R)$ are natural products of the same interaction experienced by an atom pair. For a particular interaction picture, $\rho(R)$ and $V(R)$ are unique. They are linked through the intricate nature of the interaction involving many electrons and nuclei. They are not independent entities. Whatever happens in one is reflected in the other. Neither of them can be changed while keeping the other intact. It is therefore imperative that both $V(R)$ and $\rho(R)$ are evaluated from one SCF molecular calculation before employing them to derive the HPS. To make any exception to this rule will be a meaningless exercise.

VI. MCSCF CALCULATION ON HeH SHOWING CONSISTENCY IN THE MCSCF APPROACH

In our earlier MCSCF calculation[1] on HeH, the long-range features of $\Delta\nu(R)/\nu_0$ were not properly represented. Now our aim is to examine the cause of our earlier failure and to reveal facts that were not completely clear and explored completely. An order of estimate of $\Delta\nu(R)/\nu_0$ was made in the long-range region by expressing it in terms of $-D_6R^{-6} - D_8R^{-8}$. Good estimates of D_6 and D_8 are available. This told us immediately that our calculated $\Delta\nu(R)/\nu_0$ for HeH in the long-range region was not done accurately enough. Expansion coefficients were accurate only to four or five significant figures, but that was not enough. To obtain barely reliable values of $\Delta\nu(R)/\nu_0$ one must calculate expansion coefficients accurate to six to eight significant figures. In order to attain this, numerical integrals have to be generated accurately (grid sizes with NXI = NETA = 90, NSIMP = 50, NBIAS = 30 are employed) up to nine or ten significant figures and the constraint on the MCSCF energy convergence must be tightened so that energies obtained after each convergence are accurate to 12 significant figures. In light of this, we made the decision to repeat the calculation on HeH by employing the same basis set and configurations as used in the earlier calculation[1] on HeH. Along with the increase of numerical precision we have also extended the calculation beyond $R = 10.0$ a.u. in order to achieve the complete dissociation of He and H.

Calculated $\Delta\nu(R)/\nu_0$ and other relevant quantities are tabulated in Table VI. $[\Delta\nu(R)/\nu_0]R^2e^{-V(R)/kT}$ is plotted, in Fig. 2, against R. The curve crosses the abscissa from the positive side around $R = 7.5$ a.u. and enters the negative region of $[\Delta\nu(R)/\nu_0]R^2e^{-V(R)/kT}$ and then asymptotically approaches zero around $R = 15$ a.u. The curve shows now a physically acceptable behavior throughout R. The new HPS result for HeH is 4.7104×10^{-9}/Torr at $0°C$ and is in excellent agreement with the experimental result[22] of $(+4.8\pm0.09)\times10^{-9}$/Torr, and has not really changed significantly from our previous calculated result. It is, however, easily understandable because the negative values of the integrand $[\Delta\nu(R)/\nu_0]R^2e^{-V(R)/kT}$ are several orders of magnitude smaller than its positive counterparts.

It must be remembered that the present changes in the HeH results arise from the improvement of computational accuracy, not from an improved choice of basis functions and configurations. One should be able to make a distinction between these two ways of improving the results. With a best choice of basis functions and configurations, one may end up with completely wrong results if the necessary level of computational accuracy has not been attained. On the other hand, with a minimal choice of basis functions and configurations, one may be able to produce results that are at least qualitatively correct, if the level of computational accuracy is high. With the present basis set and configurations, a complete realization of the long-range Van der Waals feature was not possible. The calculated $C_6 = -2.769$, compared to the best

TABLE VI. Mixing coefficient a_1, interaction potential $V(R)$, and the integrand $[\Delta\nu(R)/\nu_0]$ $\times R^2 e^{-V(R)/kT}$ for HeH.

R (a.u.)	a_1	$V(R)$ $(10^{-4}$ a.u.)	$\Delta\nu(R)/\nu_0$ $(10^{-4}$ a.u.)	$[\Delta\nu(R)/\nu_0]R^2$ $\times e^{-V(R)/kT}$
3.0	0.999 723	+149.8176	+361.738 97	$+1.42\times10^{-7}$
4.0	0.999 900	+26.3594	+119.049 00	+0.014 48
4.5	0.999 935	+10.2360	+55.709 57	+0.041 48
5.0	0.999 959	+3.6923	+24.797 75	+0.043 21
6.0	0.999 984	+0.2564	+3.253 46	+0.011 42
7.0	0.999 988	−0.109 09	+0.168 12	+0.000 83
8.0	0.999 995	−0.087 71	−0.051 96	−0.000 34
9.0	0.999 997	−0.047 00	−0.204 04	−0.001 66
10.0	0.999 998	−0.027 77	−0.115 76	−0.001 16
12.0	0.999 999	−0.009 71	−0.047 87	−0.000 69
15.0	1.000 000	0.0	0.0	0.0

reported result[23] of −2.8173, indicates that the basis set lacks some important functions and the MCSCF must include additional significant configurations. As we have already implied in our earlier discussion in Sec. V, there cannot be any change in $V(R)$ without a corresponding change occurring in $\rho(R)$. We can be sure that a choice of improved basis functions and configurations would not only lead to an improved $V(R)$, but $\rho(R)$ would also be correspondingly improved. There would then be a combined effect of improvement on the HPS. Therefore, it can be assumed without ambiguity that the quality of the HPS result in HeH can be improved if a better set of basis functions and configurations are employed, which Das and Wahl have essentially implied in their latest MCSCF calculation on HeH. However, our aim here is, essentially, to show that without adding third-order correction terms to $\rho(R)$, the long-range physical feature of $\Delta\nu(R)/\nu_0$ would have been obtained in our earlier work on HeH if we had carried out the cal-

culation with the required numerical precision and the complete dissociation at $R = 15.00$ a.u.

VII. SINGLE-CONFIGURATION SCF CALCULATION ON HeH

Finally, we present here a single-configuration SCF calculation on HeH that has been carried out to examine whether the HPS result deviates significantly from the corresponding MCSCF result. Of course, qualitatively it does deviate, since the long-range features are not represented. The quantitative HPS result, however, is not significantly different from the corresponding MCSCF result. Thus, the HeH system is unlike the ArH system, in which a single-configuration SCF calculation leads to a result that is absurd both qualitatively and quantitatively.

The relevant quantities including $\Delta\nu(R)/\nu_0$ and $[\Delta\nu(R)/\nu_0]R^2 e^{-V(R)/kT}$ are given in Table VII. The calculated HPS result is $+5.32\times10^{-9}$/Torr at $0°$C, which is a little higher than the experimental result.

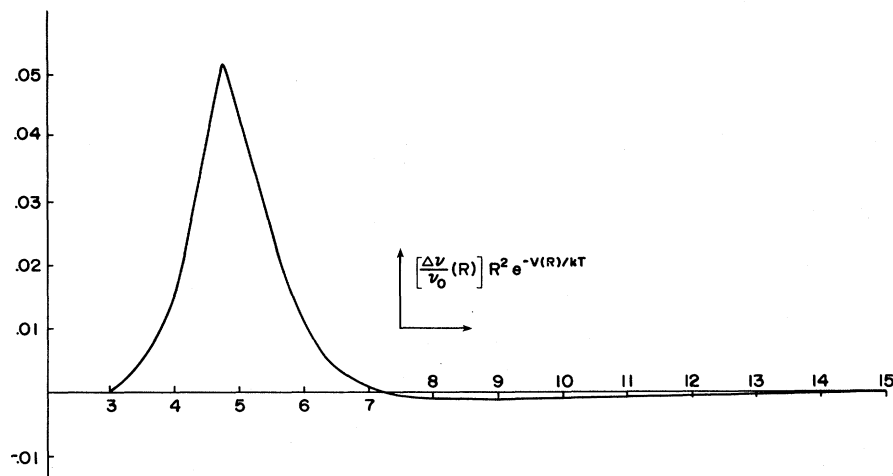
FIG. 2. Integrand $[\Delta\nu(R)/\nu_0]R^2 e^{-V(R)/kT}$ vs R for HeH. MCSCF wave functions are employed.

TABLE VII. For HeH SCF results: $V(R)$, $\Delta\nu(R)/\nu_0$, $[\Delta\nu(R)/\nu_0]R^2 e^{-V(R)/kT}$.

R (a.u.)	$V(R)$ $(10^{-4}$ a.u.)	$\Delta\nu(R)/\nu_0$ $(10^{-4}$ a.u.)	$[\Delta\nu(R)/\nu_0]R^2$ $\times e^{-V(R)/kT}$
3.0	+161.290 456	+396.697 78	+0.507 45 $\times 10^{-7}$
4.0	+30.418 432	+132.010 44	+0.010 79
4.5	+12.671 985	+64.370 68	+0.037 77
5.0	+5.144 136	+29.310 63	+0.036 85
6.0	+0.819 091	+5.552 91	+0.018 45
7.0	+0.123 893	+0.955 08	+0.004 62
8.0	+0.018 091	0.0	0.0
9.0	+0.002 503	0.0	0.0
10.0	+0.000 291	0.0	0.0
12.0	0.0	0.0	0.0
15.0	0.0	0.0	0.0

VIII. CONCLUSIONS

As has already been pointed out, the calculations reported in this paper are not free from deficiencies. There is much that needs further exploration. One should be able to improve these calculations and hence the quality of the results. Among the possible improvements, the important ones are the choice of improved sets of basis functions which will allow formation of various types of orbitals, and the addition of configurations that will significantly contribute to higher-order dispersion and essential intra-atomic correlation. These will improve the quality of the interatomic potentials and the calculated MCSCF wave functions will be the true representative wave functions in the physical sense.

It should be mentioned here that, for ArH, C_6 is found to be −20.75 around the intermediate and the near long-range regions, which is in good agreement with the best result reported by several investigators,[24] but in the far long-range region C_6 is found to be gradually decreasing.[25] We have not tried to calculate C_8, C_{10}, etc. To remove these

discrepancies, it is essential that we improve our choice of a basis set (particularly for Ar) by including functions needed for the higher-order dispersion and intra-atomic correlation, and also by including other important configurations.

In the numerical analysis, the quality of a calculation is determined partly by how certain factors are chosen (such as grids in the numerical integrations) and how constraints are selected to test the energy convergence. Moreover, it is not just a matter of choice, but rather a vital question of availability of resources. Increased hours of computer time are required in order to increase the numerical grids in the integrations and to tighten constraints in the energy convergences.

It must be emphasized here that, compared to the present HeH calculation, our calculation on ArH has been less accurate both in terms of generating two-centered integrals and tightening the energy convergence. The resources available to us have offered us no choice. Nevertheless, calculated HPS results in ArH are good and very reliable. The long-range features are very small in HeH and therefore better accuracy in the calculation has been necessary to describe the small long-range features. But in ArH, the long-range features are dominant effects and their reproduction is assured if a moderate level of computational accuracy is attained.

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