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THEORETICAL STUDY OF THE INTERACTION POTENTIAL AND THE HYPERFINE PRESSURE SHIFTS IN HeH[†]

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The interaction of a noble-gas atom with a paramagnetic atom is studied by the use of optimized configuration mixing. It is shown (with actual computation for the helium-hydrogen system) that the optimized mixing of the Hartree-Fock ground state with polarization states is adequate for reproducing the interaction over almost the entire range of the internuclear distance. The computed wave function is used to calculate the hyperfine pressure shift for hydrogen in the atmosphere of helium buffer gas atoms, with results in good agreement with experiment.

It is well known that the Hartree-Fock approximation fails to yield the long-range attractive forces of noble-gas atoms since the Hartree-Fock function is unable to represent adequately the polarization of the interacting atoms. For a proper representation of the interaction it is necessary to mix in polarization states with the Hartree-Fock function. Using the technique of optimized valence configurations[1-3] we have made an extensive study of these polarization states in HeH. For internuclear distances greater than 3.0, the resulting wave function consisting of five configurations corresponding to the Hartree-Fock function and the "induced dipole moment states" gives a fairly accurate picture of the interaction of HeH.

One of the reasons we undertook the present calculations is to obviate some of the quantitative uncertainties that exist in literature[4,5] regarding the theoretical determination of the hyperfine pressure shift (HPS). The calculation to be reported below as well as the following reasoning convinces us of the importance of the Hartree-Fock wave function in the determination of the fractional HPS. Let us consider the formula for HPS, derived on the basis of classical statistics and believed to differ negligibly from the corresponding quantum statistical formula:

$$f_\rho = [6.502\,14\times 10^{-8}(\mathrm{mm\ Hg})^{-1}] \times \int_0^\infty \left[\frac{\Delta\nu(R)}{\nu_0}\right] e^{-V(R)/kT} R^2 dR, \qquad (1)$$

where R is the internuclear distance,

$$\frac{\Delta\nu(R)}{\nu_0} = \frac{\rho_{\mathrm{H}}(R)-\rho_{\mathrm{H}}(\infty)}{\rho_{\mathrm{H}}(\infty)},$$

$\rho_{\mathrm{H}}(R)$ being the spin density at the hydrogen nucleus, and $V(R)$ is the interaction potential, all these quantities being evaluated in atomic units. We notice that at $T \sim 50°\mathrm{C}$, kT is of the order of 0.001 a.u. and $V(R)$ quickly becomes small compared with kT for $R > 6.0$, making the exponential factor very nearly unity. For smaller internuclear distances the Hartree-Fock approximation in HeH is known to be quite good energetically. The spin density at the hydrogen nucleus is given by

$$\rho(R) = \langle \Psi(R) | \textstyle\sum_i s_{iz}\delta(\vec{r}_i - \vec{r}_{\mathrm{H}}) | \Psi(R)\rangle,$$

where Ψ is the complete wave function of the system. Let us write down Ψ in the following form:

$$\Psi = \textstyle\sum_c A_c \Phi_c + \sum_h A_h \Phi_h,$$

where Φ's are a complete set of configurations,

Φ_c's corresponding to those which primarily correlate the He atom while Φ_h's correspond to those that represent primarily the interatomic correlation. The first sum also includes the Hartree-Fock term. Because of the fact that in these sums there cannot be any terms that represent single excitations from the Hartree-Fock state (Brillouin's theorem being valid in the HeH system), we can write $\rho_{\rm H}(R)$ as $\sim(\sum A_c^2)\varphi_{\rm H}^2(0)$, where $\varphi_{\rm H}(r)$ is the Hartree-Fock orbital for the hydrogen. Since A_h's are small owing to the weakness of the van der Waals term, $\sum A_c^2 \sim 1$ to a good approximation. Extending the argument, for other cases such as Na-He, the terms in the wave function that correlate the atom should be more important than those that represent interatomic correlation. Calculations are under way for these and other similar systems and preliminary results indicate that the HPS is already well reproduced by the Hartree-Fock approximation.

As discussed above, the wave function for HeH must be of the following form in order to take account of the long range interaction:

$$\Psi = a(1\sigma^2 2\sigma) + b[1\sigma(3\sigma 4\sigma);{}^2\Sigma^+ \times {}^1\Sigma^+] + c[1\sigma(3\sigma 4\sigma);{}^2\Sigma^+ \times {}^3\Sigma^+] + d[1\sigma(1\pi 2\pi);{}^2\Sigma^+ \times {}^1\Sigma^+] + e[1\sigma(1\pi 2\pi);{}^2\Sigma^+ \times {}^3\Sigma^+], \qquad (2)$$

where the molecular orbital functions 1σ, 2σ, 3σ, 4σ, 1π, and 2π are approximately $1S_{\rm He}$, $1S_{\rm H}$, $2p\sigma_{\rm He}$, $2p\sigma_{\rm H}$, $2p\pi_{\rm He}$, and $2p\pi_{\rm H}$, respectively. The notations ${}^2\Sigma^+ \times {}^1\Sigma^+$, etc., represent the pairing scheme of the open shells in the different configurations.

The multiconfiguration self-consistent field technique is now applied to the wave function (2). The Roothaan expansion scheme, on which our computer program BISON is based,[6] requires the self-consistent field basis set for HeH to be augmented by suitable functions that will properly represent the orbitals 3σ, 4σ, 1π, and 2π. We have found the following technique to be useful. Approximately speaking the contribution of the configurations that employ these orbitals comes through terms such as

$$\Delta E_n = -|\langle 0|H|n\rangle|^2/(E_n - E_0). \qquad (3)$$

We also observe that $E_n - E_0$ is more or less insensitive to the changes in the orbitals compared with $|\langle 0|H|n\rangle|^2$. Thus our criterion for the choice of the basic functions would be to extremize $\langle 0|H|n\rangle$. We have approximately

$$K_{0n} \sim R^{-3}(\textstyle\int Z_{\rm H} 1S_{\rm H} 2p_{\rm H}\, dT)(\int Z_{\rm He} 1S_{\rm He} 2p_{\rm He}\, dT), \qquad (4)$$

which obviously leads to the long-range $1/R^6$ effect by virtue of (3). Maximization of (4) gives the ζ values of the p functions as

$$\zeta_{\rm He}' = \zeta_{\rm He}, \quad \zeta_{\rm H}' = \zeta_{\rm H}, \qquad (5)$$

$\zeta_{\rm He}$, $\zeta_{\rm H}$ being the ζ's of the predominant functions in the $1S_{\rm He}$ and $1S_{\rm H}$ orbitals. A similar treatment can yield reliable ζ's for other kinds of functions, too. It is found by direct optimization that to the accuracy we are concerned with, (5) represents indeed the optimized ζ's. We believe that our basis set for HeH, which appears in Table I, is both compact and rather accurate up to as close as 3 a.u. in the internuclear separation.

In Table II we show in the eighth column the interaction potential as a function of R as calculated by the above procedure. The second through sixth columns in Table II give the mixing coefficients of the primary (near Hartree-Fock) configuration. The seventh column corresponds to the Hartree-Fock values of the potential obtained with a bigger basis set. On the basis of our fairly extensive exploration of both the basis set as well as the configurations we feel that the discrepancy between our values of the interaction potential and the exact ones cannot exceed more than about 15% at all distances of significance. We do not have sufficient experimental data to check our curve at all internuclear distances. At small internuclear distances our results compare with Mason and Amdur's[7] experimental values to within 15%. The sources of this error are, of course, the basis set which needs to be optimized at all the internuclear distances and the absence of configurations that correlate the He atom, which becomes particularly serious at short in-

Table I. Quantum numbers n, l, m, and exponent ζ for HeH basis set.

Center	n	l	m	ζ
H	1	0	0	1.000
H	1	0	0	2.430
H	2	1	0	1.000
He	1	0	0	1.453
He	1	0	0	2.906
He	2	1	0	1.453
He	2	1	0	2.906

Table II. Mixing coefficients, interaction potential, and $[\rho(R)-\rho(\infty)]/\rho(\infty)$ as a function of internuclear distance.

R (a.u.)	a	b	c	d	e	$V_{H\cdot F}(R)$ x 10^4 (a.u.)	$V_{7\text{-conf}}(R)$ x 10^4 (a.u.)	$\frac{\rho(R)-\rho(\infty)}{\rho(\infty)}$ x 10
2.0	.99935	.01901	-.01318	.02245	-.01593	720.455	709.995	-3.43784
3.0	.99972	.00956	-.01277	.01293	-.01155	286.738	149.830	3.52361
4.0	.99990	.00503	-.00931	.00631	-.00717	33.0019	26.300	1.19129
4.5	.99994	.00408	-.00763	.00453	-.00575		10.236	.57365
5.0	.99995	.00382	-.00643	.00366	-.00486	5.0153	3.694	.24724
6.0	.99998	.00223	-.00398	.00183	-.00286	.5490	.257	.03487
7.0	.99999	.00149	-.00261	.00112	-.00186		- .108	.00370
8.0	1.00000	.00118	-.00187	.00085	-.00132		- .087	.00188
9.0	1.00000	.00084	-.00132	.00059	-.00093		- .049	.00016
10.0	1.00000	.00059	-.00090	.00042	-.00064		- .027	

ternuclear distances. Since our objective in this communication is just to illustrate the method, we defer a more complete calculation to a later report.

In considering the HPS we observe that the polarization functions have very low mixing coefficients such that to a good degree of accuracy only the primary configurations need be considered in calculating the spin density at the hydrogen nucleus. The computed HPS value (at $T = 50°\text{C}$) is 4.967×10^{-9}/mm Hg compared with $(4.8 \pm 0.09) \times 10^{-9}$/mm Hg obtained experimentally.[8] We find it worth mentioning that the R dependence of the quantity $\Delta\nu/\nu_0$, which is tabulated in column 9 of Table II, is not the same as previous qualitative models[5] predicted. But this might be because only the contribution from van der Waals terms has been considered in the latter model which when combined with the other terms of the wave function would then lead to the vanishingly small but positive values as obtained in the present calculations. We notice further that the influence of the van der Waals terms of the total wave function on the integrand of Eq. (1) comes as a modification of the exponential term rather than the spin density.

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