THEORETICAL CHEMISTRY INSTITUTE

THE UNIVERSITY OF WISCONSIN

HARTREE FOCK CALCULATIONS FOR THE GROUND AND FIRST EXCITED STATES OF H_2

by

Joseph D. Bowman, Jr., Arnold C. Wahl, and Joseph O. Hirschfelder

WIS-TCI-373 15 December 1969

MADISON, WISCONSIN

ERRATA to WIS-TCI-373

HARTREE FOCK CALCULATIONS FOR THE GROUND AND FIRST EXCITED STATES OF H_2

Joseph D. Bowman, Jr., Arnold C. Wahl, and Joseph O. Hirschfelder

Abstract In the fifth line, it should read $R < 5a_o$.

page 3 Eq. (2b) and (2c) should read:

$$\alpha \equiv 2(\cdots) + <\cdots> - < {}^1\sigma_u \; {}^1\sigma_u | \frac{1}{r_{12}} | {}^1\sigma_u \; {}^1\sigma_u >$$

$$\beta \equiv < {}^1\sigma_g \; {}^1\sigma_g | \frac{1}{r_{12}} | {}^1\sigma_u \; {}^1\sigma_u >$$

page 4 The right hand side of Eq. (3a) is: $\frac{{}^1\varepsilon_g}{A_g^2} \, {}^1\sigma_g$.

The right hand side of Eq. (3b) is: $\frac{{}^1\varepsilon_u}{A_u^2} \, {}^1\sigma_u$.

page 5 The line above Eq. (6), omit "is"; the line below Eq. (6) change "dissociated" to "dissociates" and add a period after "atoms".

page 7 In the second paragraph, it should read: $\beta = 5/8$.

page 17 The next to last line, change "σ_g" to "σ_u" .

page 18 Line 13, change "indestinguishable" to "indistinguishable".

HARTREE-FOCK CALCULATIONS FOR THE GROUND AND FIRST EXCITED STATES OF H_2 *

by

Joseph D. Bowman, Jr., Arnold C. Wahl, and Joseph O. Hirschfelder

The University of Wisconsin Theoretical Chemistry Institute
Madison, Wisconsin

and

The Chemistry Division, Argonne National Laboratory
Argonne, Illinois

ABSTRACT

The Hartree-Fock energy and orbitals are calculated with high precision for both the ground state ($^1\Sigma_g^+$) and the first excited state ($^3\Sigma_u^+$) of H_2 for separations ranging from the United Atom to $10a_o$. The σ_g orbital obtained from the $^1\Sigma_g^+$ is almost the same as that from the $^3\Sigma_u^+$ for all separations. However when $R > 5a_o$, the σ_u from the $^3\Sigma_u^+$ is larger than that from the $^1\Sigma_g^+$. The correlation energy ($E_{HF} - E$) is 4 times larger for the $^1\Sigma_g^+$ than for the $^3\Sigma_u^+$ at the equilibrium separation, $1.4a_o$. For separations greater than $8a_o$, the two correlation energies become equal.

---

* This work was supported by the National Science Foundation Grant GP-12832, and in part by the National Aeronautics and Space Administration Grant NGL-50-002-001.

I. Introduction

The Hartree-Fock approximation plays an important role in our understanding of molecular quantum mechanics. In this paper, HF potential energy curves are calculated with high precision for both the ground state $({}^1\Sigma_g^+)$ and the first excited state $({}^3\Sigma_u^+)$ of the H_2 molecule for separations from 0 to 10 a_o. These two states have been important test cases for theories of molecular structure and intermolecular forces. This HF calculation for H_2 should therefore be useful, as an accurate starting point for the many recent treatments which improve upon Hartree-Fock.

If the ground state of H_2 is to dissociate into two ground state hydrogen atoms, an extended (or double configuration) Hartree-Fock treatment is necessary. However, the usual single configuration HF suffices for the triplet state. The wave functions for both states contain only σ_g and σ_u molecular orbitals. The MO's are expressed by a basis set of Slater-type orbitals.

In order to obtain the genuine Hartree-Fock properties which are independent of the basis set, we expanded our set of STO's until the total energy converged to within bounds considerably smaller than the correlation and exchange energies.

Past calculations of the ${}^1\Sigma_g^+$ state have nearly ignored this two configuration MO wavefunction. The Heitler-London[1] wavefunction, Weinbaum[2] wavefunction and all the subsequent variations are special cases of this function, but only Callen,[3] McLean, Weiss, and Yoshimine,[4] and Das and Wahl[5] used this form without restrictions. Only Das and Wahl calculated the potential energy curve out to large R. Das and Wahl, however, used a limited basis set picked at the equilibrium separation, so the results at large R are not dependable. At their largest internuclear separation, $R = 8a_o$, the energy is further from the accurate Hartree-Fock result than Hartree-Fock is from the exact energy.

There seem to be no MO calculations for the $^3\Sigma_u^+$ state of H_2 in any sense. The only calculations at the present time are based on various free form wavefunctions, the best of which is by Kolos and Wolniewicz.[6]

In the rest of the paper, the calculation is presented in detail, and the results are analyzed. Section II reviews the Hartree-Fock theory and uses those equations to predict the behaviour of the singlet and triplet states when the nuclei are infinitely separated. Section III describes the procedure used in the calculation. In section IV, the results are presented, and the molecular orbitals and correlation energies obtained from the calculations are discussed.

The results show several interesting trends. The σ_g and σ_u orbitals for both states are very nearly the same for internuclear separations down to $4\ a_o$. For smaller separations, the σ_g orbitals remain approximately the same, but the σ_u $(^1\Sigma_g^+)$ gets much smaller than the σ_u $(^3\Sigma_u^+)$ orbital. The electron correlation energy for the $^1\Sigma_g^+$ is 4 times larger than for the $^3\Sigma_u^+$ at the equilibrium separations; twice as large at $5\ a_o$; and approximately equal for $8\ a_o$ and larger.

II. Theory

For both the singlet and triplet states, only σ_g and σ_u orbitals were necessary to give the wavefunction the proper symmetry and to insure dissociation into two ground state hydrogen atoms. For the ${}^1\Sigma_g^+$ state, the spatial wavefunction is:

$$ {}^1\psi = A_g \, {}^1\sigma_g(1) \, {}^1\sigma_g(2) + A_u \, {}^1\sigma_u(1) \, {}^1\sigma_u(2) \qquad (1) $$

where A_g and A_u are real constants.

The variational principle is used to find the mixing co-efficients, A_λ, and the molecular orbitals. First, a guess for the orbitals is put into ${}^1\psi$, and the A_λ are varied until $\tilde{E} = < {}^1\psi|\mathcal{H}|{}^1\psi >/< {}^1\psi|{}^1\psi >$ is a minimum, keeping the total wavefunction normalized. The optimum co-efficients from this minimization are:

$$ A_{\substack{g\\u}} = \pm\, 2^{-\frac{1}{2}}(1 \pm \alpha(\alpha^2 + 4\beta^2)^{-\frac{1}{2}})^{\frac{1}{2}} \qquad (2a) $$

where

$$ \alpha \equiv 2(< {}^1\sigma_g|h|{}^1\sigma_g > - < {}^1\sigma_u|h|{}^1\sigma_u >) $$

$$ + < {}^1\sigma_g \, {}^1\sigma_g|\frac{1}{r_{12}}|{}^1\sigma_g \, {}^1\sigma_g > + < {}^1\sigma_g {}^1\sigma_g|\frac{1}{r_{12}}|{}^1\sigma_g \, {}^1\sigma_g > \qquad (2b) $$

$$ \beta \equiv < {}^1\sigma_g \, {}^1\sigma_g|\frac{1}{r_{12}}|{}^1\sigma_g \, {}^1\sigma_g > \qquad (2c) $$

and

$$ h \equiv -\tfrac{1}{2}\nabla^2 - \frac{1}{r_a} - \frac{1}{r_b} $$

(Our notation is: $|{}^1\sigma_\lambda\ {}^1\sigma_u > \equiv |{}^1\sigma_\lambda(1)\ {}^1\sigma_u(2) >$ and $< {}^1\sigma_\lambda\ {}^1\sigma_u| \equiv < {}^1\sigma_\lambda(1)\ {}^1\sigma_u(2) >$). Putting the A_λ into ${}^1\psi$ and optimizing E by varying the orbitals gives the Fock-type equations:

$$h\,{}^1\sigma_g + {}^1\sigma_g \int \frac{[{}^1\sigma_g(2)]^2}{r_{12}}\, d\tau_2 + \frac{A_u}{A_g}\,{}^1\sigma_u \int \frac{{}^1\sigma_g(2)\ {}^1\sigma_u(2)}{r_{12}}\, d\tau_2 = \frac{{}^1\varepsilon_g}{A_g}\ {}^1\sigma_g \tag{3a}$$

$$h\,{}^1\sigma_u + {}^1\sigma_u \int \frac{[{}^1\sigma_u(2)]^2}{r_{12}}\, d\tau_2 + \frac{A_g}{A_u}\,{}^1\sigma_g \int \frac{{}^1\sigma_g(2)\ {}^1\sigma_u(2)}{r_{12}}\, d\tau_2 = \frac{{}^1\varepsilon_u}{A_u}\ {}^1\sigma_u \tag{3b}$$

To solve these equations, we make a Roothaan expansion of the orbtials.

$${}^1\sigma_{\substack{g\\u}} = \sum_p {}^1C_{\lambda p}\ [\chi_{pa} \pm \chi_{pb}] \tag{4}$$

Here ${}^1C_{\lambda p}$ are real co-efficinets; χ_{pa} and χ_{pb} are Slater-type orbitals (STO) on nucleus a and nucleus b . We used the STO as defined by Wahl.[7] This converts equations (3) into two matrix equations of the form:

$$\mathbb{F}_\lambda\ {}^1\mathbb{C}_\lambda = {}^1\varepsilon_\lambda\ \mathbb{S}_\lambda\ {}^1\mathbb{C}_\lambda \tag{5}$$

Since the matrices $\mathbb{F}_\lambda$ contain the co-efficients ${}^1\mathbb{C}_\lambda$, equation (5) must be solved by iteration until the results are self-consistent. The orbitals obtained in this way are re-inserted into equation (2), and the cycle is repeated until all parameters are self-consistent.

${}^1\varepsilon_g$ and ${}^1\varepsilon_u$ are obtained as the eigenvalues in the solution of equation (5). They can also be derived from equations (3):

$$
{}^1\varepsilon_g = A_g^{\,2} \left[\langle {}^1\sigma_g | h | {}^1\sigma_g \rangle + \langle {}^1\sigma_g {}^1\sigma_g | \frac{1}{r_{12}} | {}^1\sigma_g \, {}^1\sigma_g \rangle \right] + A_g A_u \langle {}^1\sigma_g \, {}^1\sigma_g | \frac{1}{r_{12}} | {}^1\sigma_u \, {}^1\sigma_u \rangle
$$

$$
{}^1\varepsilon_u = A_u^{\,2} \left[\langle {}^1\sigma_u | h | {}^1\sigma_u \rangle + \langle {}^1\sigma_u \, {}^1\sigma_u | \frac{1}{r_{12}} | {}^1\sigma_u \, {}^1\sigma_u \rangle \right] + A_g A_u \langle {}^1\sigma_g \, {}^1\sigma_g | \frac{1}{r_{12}} | {}^1\sigma_u \, {}^1\sigma_u \rangle
$$

Having found ${}^1\sigma_g$ and ${}^1\sigma_u$, these orbitals are re-inserted into Eq. (2) and the whole cycle is repeated until the results are self-consistent. The optimum energy is then

$$
{}^1\tilde{E} = {}^1\varepsilon_g + {}^1\varepsilon_u + A_g^2 \langle {}^1\sigma_g | h | {}^1\sigma_g \rangle + A_u^2 \langle {}^1\sigma_u | h | {}^1\sigma_u \rangle + R^{-1}
$$

For the ${}^3\Sigma_u^+$ state of H_2, the single configuration wave function is

$$
{}^3\psi = \frac{1}{\sqrt{2}} [{}^3\sigma_g(1) \; {}^3\sigma_u(2) - {}^3\sigma_u(1) \; {}^3\sigma_g(2)] \tag{6}
$$

dissociated into two ground state hydrogen atoms, The variational principle produces the Fock equations:

$$
h\,{}^3\sigma_g + {}^3\sigma_g \int \frac{[{}^3\sigma_u(2)]^2}{r_{12}} \, d\tau_2 - {}^3\sigma_u \int \frac{{}^3\sigma_g(2)\,{}^3\sigma_u(2)}{r_{12}} \, d\tau_2 = {}^3\varepsilon_g \, {}^3\sigma_g \tag{7a}
$$

$$h\,{}^3\sigma_u + {}^3\sigma_u \int \frac{[{}^3\sigma_g(2)]^2}{r_{12}}\, d\tau_2 - {}^3\sigma_g \int \frac{{}^3\sigma_g(2)\,{}^3\sigma_u(2)}{r_{12}}\, d\tau_2 = {}^3\varepsilon_u\, {}^3\sigma_u \tag{7b}$$

The orbitals ${}^3\sigma_\lambda$ are expanded in terms of the same set of STO which gives the Hartree-Fock-Roothaan equations.[8]

The orbital energies ${}^3\varepsilon_g$ and ${}^3\varepsilon_u$ are determined by the solution of the Roothaan equations, or can be derived from equations (7):

$$\begin{aligned} {}^3\varepsilon_g = {} & < {}^3\sigma_g|h|{}^3\sigma_g > + < {}^3\sigma_g\ {}^3\sigma_u|\frac{1}{r_{12}}|{}^3\sigma_g\ {}^3\sigma_u > \\ & - < {}^3\sigma_g\ {}^3\sigma_u|\frac{1}{r_{12}}|{}^3\sigma_u\ {}^3\sigma_g > \end{aligned}$$

$$\begin{aligned} {}^3\varepsilon_u = {} & < {}^3\sigma_u|h|{}^3\sigma_u > + < {}^3\sigma_u\ {}^3\sigma_g|\frac{1}{r_{12}}|{}^3\sigma_u\ {}^3\sigma_g > \\ & - < {}^3\sigma_u\ {}^3\sigma_g|\frac{1}{r_{12}}|{}^3\sigma_g\ {}^3\sigma_u > \end{aligned}$$

The optimum energy is then

$${}^3\tilde{E} = {}^3\varepsilon_g + {}^3\varepsilon_u + < {}^3\sigma_g|h|{}^3\sigma_g > + < {}^3\sigma_u|h|{}^3\sigma_u > + R^{-1}$$

Large Values of R

Some results can be predicted from the theory even before making any calculations. First, the singlet and triplet wavefunctions have identical molecular orbitals when R is infinite. To see this, note that both states consist of two ground state hydrogen atoms which are not interacting, so the wavefunctions have the Heitler-London form:

$${}^{\substack{1\\3}}\psi = \frac{1}{\sqrt{2}}[\chi_{1sa}(1)\ \chi_{1sb}(2) \pm \chi_{1sb}(1)\ \chi_{1sa}(2)] \qquad (8)$$

Converted into the molecular orbital form of equations (1) and (6), these wavefunctions both consist of the same MO's:

$$\sigma_{\substack{g\\u}} = \frac{1}{\sqrt{2}}(\chi_{1sa} \pm \chi_{1sb}) \qquad (9)$$

When these orbitals are substituted into the Fock equations (3) and (7), the equations are satisfied as R becomes infinite. In this limit, $\alpha = 0$ and $\infty = 5/8$, so that $A_g = -A_u = 2^{-\frac{1}{2}}$. The orbital energies ${}^3\varepsilon_g$ and ${}^3\varepsilon_u$ are $-\frac{1}{2}$a.u., the energy of a 1s hydrogen atom; the ${}^1\varepsilon_g$ and ${}^1\varepsilon_u$ are $-\frac{1}{4}$a.u. Because the mixing co-efficients A_λ appear in equations (3), the ${}^1\varepsilon_\lambda$ are different from the ${}^3\varepsilon_\lambda$.

Small Values of R

The Fock equations (3) can tell us something about the singlet wavefunction for small R. The ratio A_u/A_g can be estimated by approximating the MO in equation (2) by equation (9). Expanding the ratio in powers of $R^n e^{-mR}$ gives:

$$\frac{A_u}{A_g} = -1 + \frac{4}{3} R\, e^{-R} + \mathcal{O}(Re^{-R}) \qquad (10)$$

From the results of the calculation (see Table II), the trends in equation (10) turn out to be correct. As R decreases, the magnitude of A_u/A_g gets smaller. Indeed, as R approaches the equilibrium separation, A_u/A_g becomes small (about $-.1$), so that Equation (3a becomes, in effect,

$$h\,{}^1\sigma_g + {}^1\sigma_g \int \frac{[{}^1\sigma_g(2)]^2}{r_{12}}\, d\tau_2 \cong \left(\frac{{}^1\varepsilon_g}{A_g}\right) {}^1\sigma_g \qquad (11)$$

This is the equation for the orbitals in ${}^1\psi = {}^1\sigma_g(1)\ {}^1\sigma_g(2)$. On the other hand, A_g/A_u becomes large, so that the ${}^1\sigma_u$ orbitals calculated from equation (3b) are very different from the MO's in a ${}^1\sigma_u(1)\ {}^1\sigma_u(2)$ wavefunction. However, most properties of these wavewavefunctions at small R must be determined by a detailed calculation.

United Atom

The United Atom limit for the ${}^1\Sigma_g^+$ state of H_2 is the ground state of helium, ${}^1S(1s)^2$. The ${}^3\Sigma_u^+$ of H_2 goes to the lowest ${}^3P(1s2p)$ state of He. To calculate the electronic energy of these UA states, we used the same wavefunctions, equations (1) and (6), but transformed the basis functions into their UA form. The rules for correlation diagrams[9] link the basis function $\chi_{pa} \pm \chi_{pb}$ to the corresponding STO in the United Atom. All the rest of the theory remains the same, except that $\frac{1}{R}$ is omitted from the energies.

III. The Calculation

The singlet wavefunction requires the iterative solution of two sets of coupled linear equations, containing molecular integrals. The integrals are calculated by the BISON computer system[10] at Argonne National Laboratory, and the equations are solved by the Optimized Valence Configuration (OVC) procedure of Das and Wahl.[11] The triplet wavefunction obeys the Hartree-Fock-Roothaan equations which are also solved by the BISON system.

The BISON system and the OVC program will therefore calculate the singlet and triplet wavefunctions with the lowest energies possible from a given basis set. Our goal was to select the basis sets which would approximate the Hartree-Fock energy and wavefunctions to the desired accuracy for both states over a range of internuclear distances.

To carry out this program, we needed a method for estimating the difference between the Hartree-Fock energy and the energy calculated from a given basis set. Our method is based on the fact that each additional basis function lowers the energy, until the H-F energy is obtained from an infinite set. Gilbert and Wahl[12] devised a system for picking each new function so that the energy converges to the H-F limit at a rate roughly proportional to the distance left to go. This rate was determined from a number of atomic and molecular calculations, including our own. The result is:

$$|E_n - E_{\text{Hartree-Fock}}| < 2|E_{n-1} - E_n| , \tag{12}$$

where E_n is the lowest energy which can be obtained with a wavefunction of n basis functions.

Thus, for a given state and internuclear separation, the procedure is to build up the basis set one by one, at each stage searching to find the function which would lower E the most. Using Eq. (12), we can estimate how close the calculated energy is to the Hartree-Fock energy.

At internuclear diatances from 5 - 10 Bohr, the exponential coefficient ζ in the STO was restricted to unity so that the orbitals could be compared to those used by Hirschfelder and Löwdin[13] who determined the asymptotic form of the natural spin orbitals for H_2 at large separations. In this range of R , the basis sets were chosen to get the energy to within 10^{-6} atomic units of the Hartree-Fock energy (within 10^{-7}a.u. at $R = 10a_o$). This assured sufficient accuracy for the calculated values of the exchange energy, $\frac{1}{2}[E(^1\Sigma_g^+) - E(^3\Sigma_u^+)]$, an important quantity in the theory of intermolecular forces. The basis sets selected at $R = 5a_o$ are given in Table I. For larger values of R two or three of the functions were omitted.[14]

At internuclear distances smaller than $5a_o$, the series of STO converges more slowly to the Hartree-Fock wavefunction. To speed convergence, ζ was no longer restricted to 1, but was optimized to lower the energy. The basis set in Table II was assembled for the triplet state at $R = 1.5a_o$ (where the Hartree-Fock energy was approached within 2×10^{-5}a.u.). This same set was used for the singlet and triplet for all R less than $5a_o$. Providing this basis set is as accurate at other R as it is at $1.5a_o$, these calculations give accurate values for the correlation energy ($E_{\text{Hartree-Fock}} - E_{\text{exact}}$) for the singlet and triplet in this range of R .

Finally, we calculated these wavefunctions in the United Atom limit, using the basis set developed for small R . Since several basis functions were linearly dependent in the UA limit, three had to be discarded in order for the calculation to converge. The resulting basis set is also given in Table II. The deviation of the UA energy from the true Hartree-Fock value was not determined.

In all calculations, the worst computational errors come from the numerical quadrature for the coulomb-hybrid integrals. These integrals were always set to converge to within 10^{-7}a.u. (except for calculations

Table I

Basis Functions[a] χ_p for $R = 5a_o$

${}^1\Sigma_g^+$ State	${}^3\Sigma_u^+$ State
1s	1s
2s	2s
3s	3s
4s	4s
2p	2p
3p	3p
4p	3d
3d	4d
4f	4f

---

[a] These are Slater-type orbitals as defined in Ref. (6). $m = 0$ and $\zeta = 1$ for all functions.

Table II. Basis Functions for small R and the United Atom

χ_p[a] for Separated Atoms		UA limit for σ_g basis	UA limit for σ_u basis
1s	0.350	1s	2p
1s	1.000	1s	2p
1s	1.900	1s	2p
2s	0.875	2s	3p
2s	1.220	2s	—
2s	7.600	2s	3p
2p	2.155	—	4p
2p	4.300	3s	4p
3s	3.870	3d	4f
3d	1.680	4d	5f
3d	3.400	4d	5f
4f	2.700	6s	—

[a] These are STO as defined in Ref. (6). m=o for all functions.

at $R = 10a_o$ where the threshold was 10^{-8}a.u.). Thus the integrals were calculated to an order of magnitude higher precision than the deviation from the Hartree-Fock energies.

IV. Results and Discussion

The results of the calculation are discussed from three perspectives: the various energies, the wavefunctions at the United Atom and Separated Atom limits, and a comparison of the orbitals from the singlet and triplet. The orbitals for H_2 are also compared with wavefunctions for H_2^+.

Energy

The total energy from the calculation are in Table III, along with the correlation energy[15], $E_{corr} = E_{H-F} - E_{exact}$. In Table IV, the energy is expressed as Coulomb energy, $E_{Coul} = \frac{1}{2} [E(^1\Sigma_g^+) + E(^3\Sigma_u^+)]$ and the exchange energy, $E_{exch} = [E(^1\Sigma_g^+) - E(^3\Sigma_u^+)]$. The accuracy of the Coulomb and exchange energy is also included in Table IV.

The Hartree-Fock potential curves are shown in Figure 1, and compared with the exact potential curve of Kolos and Wolniewicz. For small R, the triplet energies are closer to being exact than the singlet energies. To make this comparison for all R, the ratio $E_{corr}\ (^3\Sigma_u^+)/E_{corr}\ (^1\Sigma_g^+)$ is plotted in Figure 2. It ranges from around .15 at R = 0 to nearly 1.0 at R = 10.

Limiting Bahaviour

The mixing co-efficients and orbital energies are given in Table V. At R = 10 the values of these parameters are within 0.5%

Table III. Total Hartree-Fock Energy and Correlation Energy (in atomic units). The underlined numbers do not agree with the H-F energy as estimated by eq. (12).

R	$^1\Sigma_g^+$ State		$^3\Sigma_u^+$ State	
	-E	E_{corr}	-E	E_{corr}
0.0	(2.86866912)[a]	.0350553	(2.1282925)	.0048785
1.3	$1.14913\underline{320}$	$.02321\underline{27}$	$0.74866\underline{877}$	$.00573\underline{45}$
1.4	$1.15214\underline{823}$	$.02232\underline{62}$	$0.77844\underline{420}$	$.00570\underline{59}$
1.5	$1.15140\underline{136}$	$.02145\underline{23}$	$0.80403\underline{953}$	$.00557\underline{00}$
1.6	$1.14799\underline{196}$	$.02058\underline{79}$	$0.82636\underline{423}$	$.00535\underline{96}$
2.0	$1.12089\underline{613}$	$.01723\underline{51}$	$0.89288\underline{169}$	$.00418\underline{19}$
3.0	$1.04809\underline{155}$	$.00922\underline{03}$	$0.97003\underline{347}$	$.00197\underline{69}$
4.0	$1.01308\underline{762}$	$.00328\underline{13}$	$0.99245\underline{095}$	$.00092\underline{72}$
5.0	$1.0028465\underline{9}$	.0009160	$0.9982878\underline{6}$	.0003970
6.0	$1.0005554\underline{2}$	.0002596	$0.999641\underline{81}$	$.000170\underline{7}$
7.0	$1.0001026\underline{7}$	.0000862	$0.9999300\underline{0}$	.0000730
8.0	$1.0000183\underline{0}$	.0000352	$0.9999870\underline{2}$	.0000326
9.0	$1.0000031\underline{7}$	.0000153	$0.9999977\underline{0}$	.0000150
10.0	1.00000053	.0000081	0.99999960	.0000080

---

[a] The energies in parentheses are electronic energies, the total energy with 1/R subtracted off. The true Hartree-Fock energy was not estimated for the UA, so the significant figures could not be designated.

Table IV. Coulomb and Exchange Energies (in atomic units). The underlined figures are not the H-F values as estimated by eq. (12).

R	$-E_{Coul}$ H-F	E_{Coul} H-F $-E_{Coul}$ exact	$-E_{exch}$ H-F	E_{exch} H-F $-E_{exch}$ exact
0.0	———	———	0.3701883[a]	.0150884
1.3	0.94890099	.0144736	0.20023222	.0087391
1.4	0.96529622	.0140161	0.18685202	.0083102
1.5	0.97772045	.0135112	0.17368092	.0079412
1.6	0.98717809	.0129738	0.16081387	.0076142
2.0	1.00688891	.0107085	0.11400722	.0065266
3.0	1.00906251	.0055986	0.03902904	.0036217
4.0	1.00276929	.0021043	0.01031834	.0011771
5.0	1.00056723	.0006565	0.00227937	.0002595
6.0	1.00009862	.0002152	0.00045681	.0000445
7.0	1.00001634	.0000796	0.00008634	.0000066
8.0	1.00000266	.0000339	0.00001564	.0000013
9.0	1.00000044	.0000152	0.00000274	.0000002
10.0	1.00000007	.0000081	0.00000047	.00000007

[a] The true Hartree-Fock values were not estimated for the UA.

Table V. Mixing Co-efficients and Orbital Energies (in atomic units).

R	A_g	$-A_u$	$-{}^1\epsilon_g$	$-{}^1\epsilon_u$	$-{}^3\epsilon_g$	$-{}^3\epsilon_u$
0.0	0.99928	0.03798	0.92312	0.00489	1.7401	0.1283
1.3	0.99490	0.10084	0.62061	0.01472	0.9609	0.2009
1.4	0.99397	0.10968	0.60400	0.01633	0.9175	0.2144
1.5	0.99288	0.11913	0.58847	0.01813	0.8786	0.2287
1.6	0.99162	0.12922	0.57392	0.02012	0.8440	0.2432
2.0	0.98433	0.17634	0.52373	0.03043	0.7393	0.3002
3.0	0.94106	0.33824	0.42967	0.07794	0.6064	0.4024
4.0	0.86194	0.50702	0.35355	0.14596	0.5489	0.4539
5.0	0.78970	0.61350	0.30147	0.19800	0.5222	0.4786
6.0	0.74659	0.66528	0.27394	0.22592	0.5098	0.4904
7.0	0.72517	0.68857	0.26087	0.23910	0.5042	0.4958
8.0	0.71519	0.69893	0.25488	0.24511	0.5018	0.4982
9.0	0.71066	0.70353	0.25216	0.24784	0.5007	0.4993
10.0	0.70865	0.70556	0.25095	0.24905	0.5003	0.4997
∞	0.70711	0.70711	0.25000	0.25000	0.5000	0.5000

of the limits predicted for $R = \infty$.

At the United Atom limit, the mixing co-efficient A_u is small, but not zero. Thus, the p-functions in the $({}^3\sigma_u)^2$ configuration slightly deform the ${}^1S$ spherical symmetry expected of the overall wavefunction for this atom.[16] In order for the Hartree-Fock wavefunction to have strictly ${}^1S$ symmetry, additional constraints would have to be imposed on the wavefunction.

The Orbitals

Using the BISON computer system, contour diagrams were made of the orbital densities, $|\sigma_\lambda|^2$.. In Figure 3, the triplet MO have dotted contour lines, and are super-imposed on the contours of the corresponding singlet orbital. The pictures compare the orbitals for these two states at $R = 5a_o$ (where the two hydrogen atoms have begun to overlap) and at $R = 1.5a_o$ (close to the equilibrium separation for the singlet).

A striking result of this calculation is the near identity of the singlet and triplet orbitals at $R = 5a_o$. Theory had predicted these states would have the same orbitals for infinite R. But this calculation shows this situation persists for internuclear separations as small as $5a_o$ and probably $4a_o$.

This coincidence breaks down as R gets smaller. Figure 3 shows how these two orbitals differ when $R = 1.5a_o$, and Figure 4 compares them when $R = 0$, the United Atom. The σ_g orbitals remain roughly the same size as they both converge to 1s orbitals for helium. On the otherhand, the σ_g orbitals diverge. As expected, ${}^3\sigma_u$ goes to a 2p orbital for He. However the ${}^1\sigma_u$

becomes a p-function with roughly the same dimensions as the ${}^1\sigma_g$ (or the 1s) orbital.

The size of the ${}^1\sigma_u$ is determined by optimizing the energy. However, it is apparent that the only way in which the $({}^1\sigma_u)^2$ configuration can lower the value of ${}^1\tilde{E}$ is by maximizing the exchange integral $< {}^1\sigma_g\, {}^1\sigma_g | r_{12}^{-1} | {}^1\sigma_u\, {}^1\sigma_u >$. This condition is roughly equivalent to maximizing the overlap between ${}^1\sigma_g$ with each lobe of the ${}^1\sigma_u$. Thus, the ${}^1\sigma_u$ remains small like the ${}^1\sigma_g$ (or 1s) orbital rather than becoming large like the ${}^3\sigma_u$ (or 2p) orbital.

H_2^+ <u>Wave Functions</u>.

In Figures 5 and 6, the H_2 orbitals at $R = 1.5a_o$ are compared with the exact H_2^+ wavefunctions.[17] Table IV gives the values of the orbitals at a nucleus. The H_2^+ orbitals become indestinguishable from the H_2 orbitals when R is greater than $5a_o$. At $R = 1.5a_o$, the value of σ_g at the nuclear cusp is greatest for the H_2^+ and least for the H_2 triplet. This is the result of the shielding by the second electron tending to make the H_2 orbitals more spread out. The shielding is greater for the singlet than for the triplet state.

For the σ_u at $R = 1.5\ a_o$, the value of the H_2^+ orbital cusp is greater than for the H_2 triplet , as we would expect on the basis of shielding. The large cusp value for the H_2 singlet corresponds to the fact (which we previously explained) that the ${}^1\sigma_u$ orbital is smaller than the ${}^3\sigma_u$.

For $R = 5\ a_o$, the differences between the H_2 and H_2^+ which were caused by shielding have become insignificant. However, there remains a difference between the cusp values of the σ_g and the σ_u orbitals which rapidly disappears for larger values of R.

Table VI. Values of H_2 and H_2^+ Orbitals at a Nucleus

		$R = 1.5a_o$	$R = 5.0a_o$
σ_g	H_2^+	0.528	0.379
	H_2, Singlet	0.464	0.383
	H_2, Triplet	0.506	0.389
σ_u	H_2^+	0.410	0.420
	H_2, Singlet	0.616	0.418
	H_2, Triplet	0.307	0.412

Acknowledgments

Peter Bertoncini, Peter Maldonado, Warren Zemke, and Paul Sutton deserve thanks for their help with the calculation.

The Illustrations

Fig. 1 The Hartree-Fock potential curves (energy is in a.u.) for the $^1\Sigma_g^+$ and $^3\Sigma_u^+$ states of H_2, compared with the exact curves of Kolos and Wolniewicz (ref. 6).

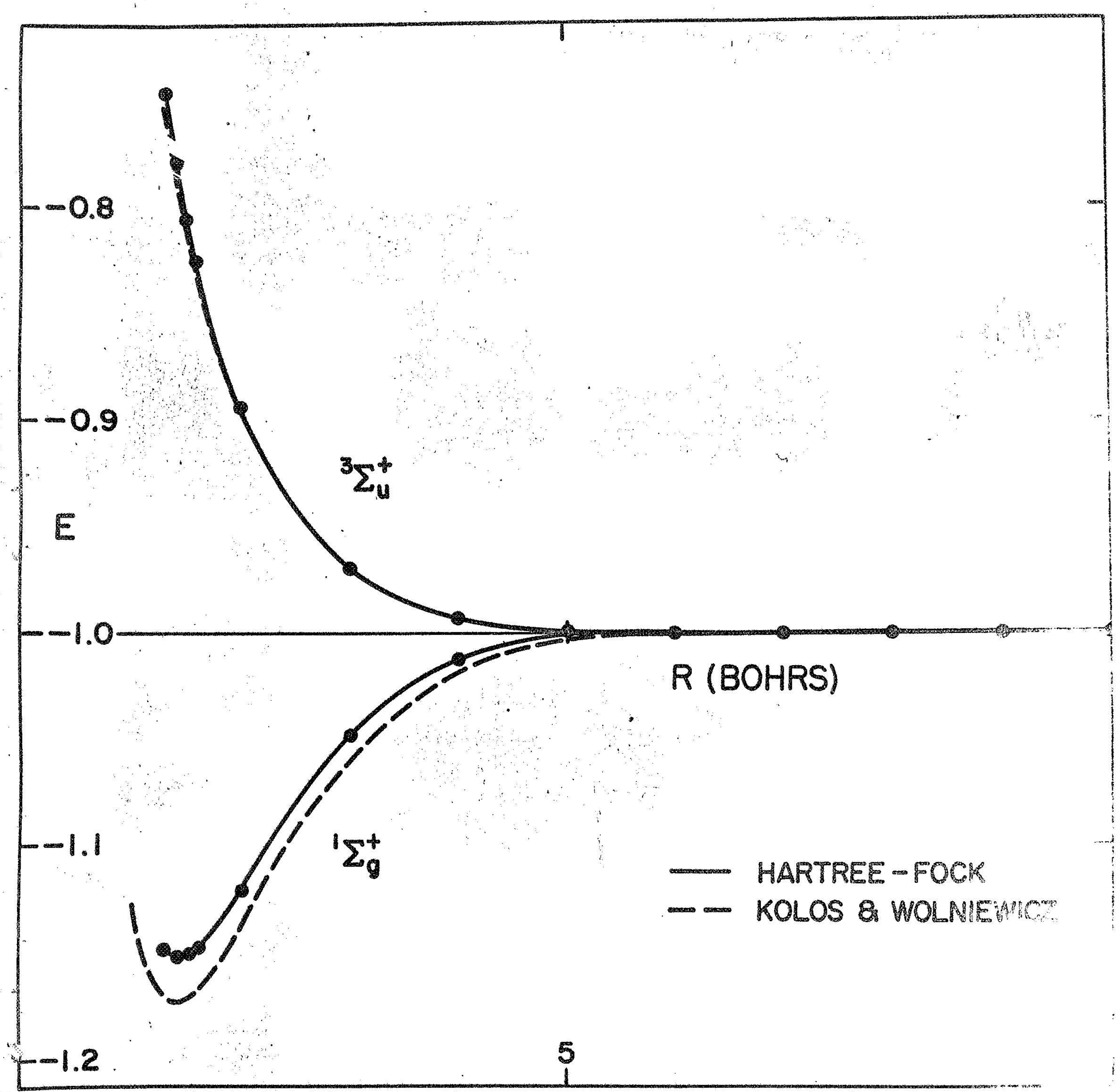
Fig. 2 The ratio $E_{corr}(^1\Sigma_g^+)/E_{corr}(^3\Sigma_u^+)$ plotted against the internuclear distance.

Fig. 3 A comparison of the orbital density from the $^1\Sigma_g^+$ state (solid controus) with those from the $^3\Sigma_u^+$ (dotted contours). In all contour diagrams, the outermost line corresponds to a density of 3×10^{-5} e^-/a_o. Each successive inner contour then increases by a factor of 2.

Fig. 4 Orbital density contours for the United Atom.

Fig. 5 The σ_g orbitals for H_2 and H_2^+ plotted along the internuclear axis with the origin midway between the nuclei. $R = 1.5a_o$.

Fig. 6 The σ_u orbitals for H_2 and H_2^+ at $R = 1.5a_o$.



-0.8
-0.9
-1.0
-1.1
-1.2
E
5
R (BOHRS)
$^3\Sigma_u^+$
$^1\Sigma_g^+$
HARTREE - FOCK
KOLOS & WOLNIEWICZ

Figure 1

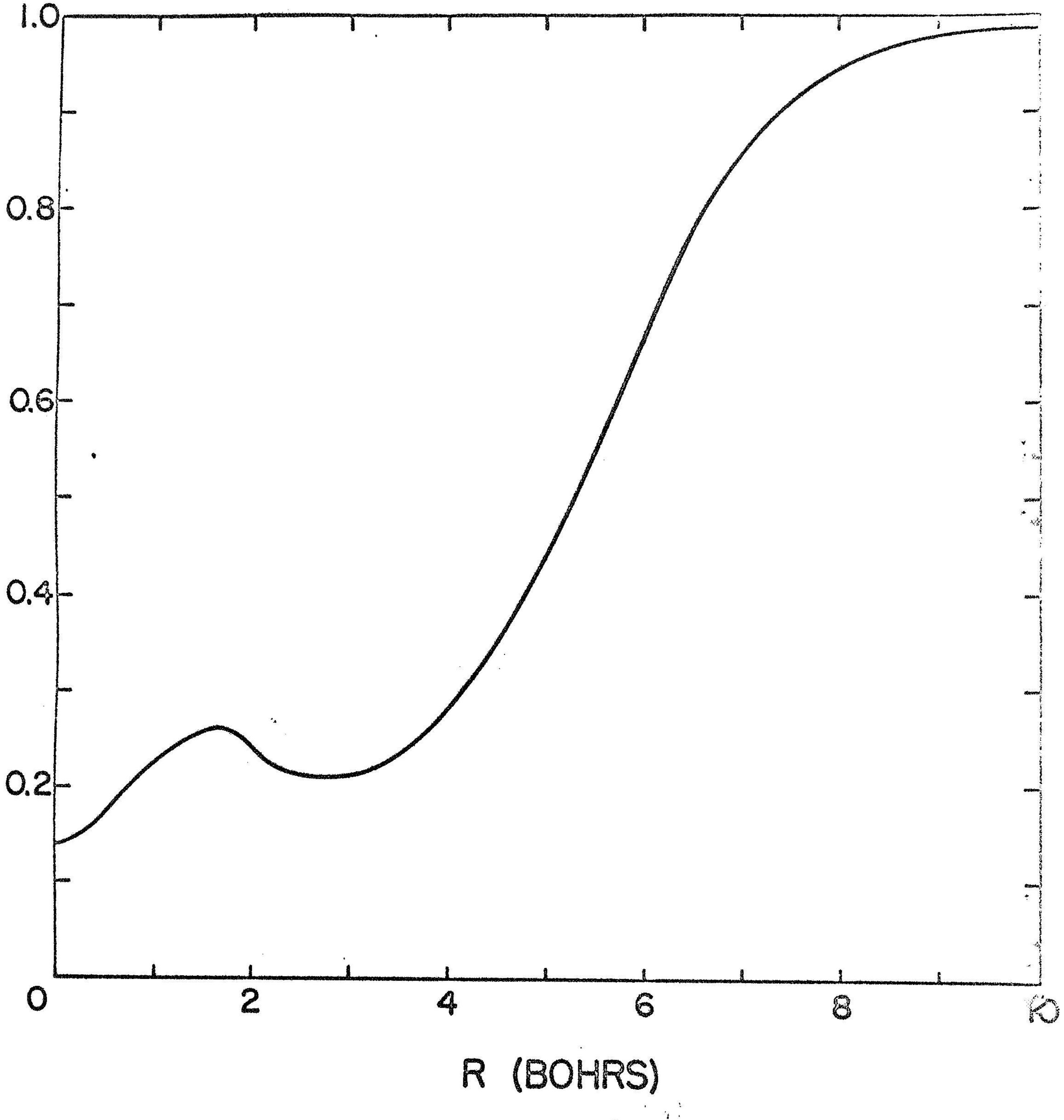
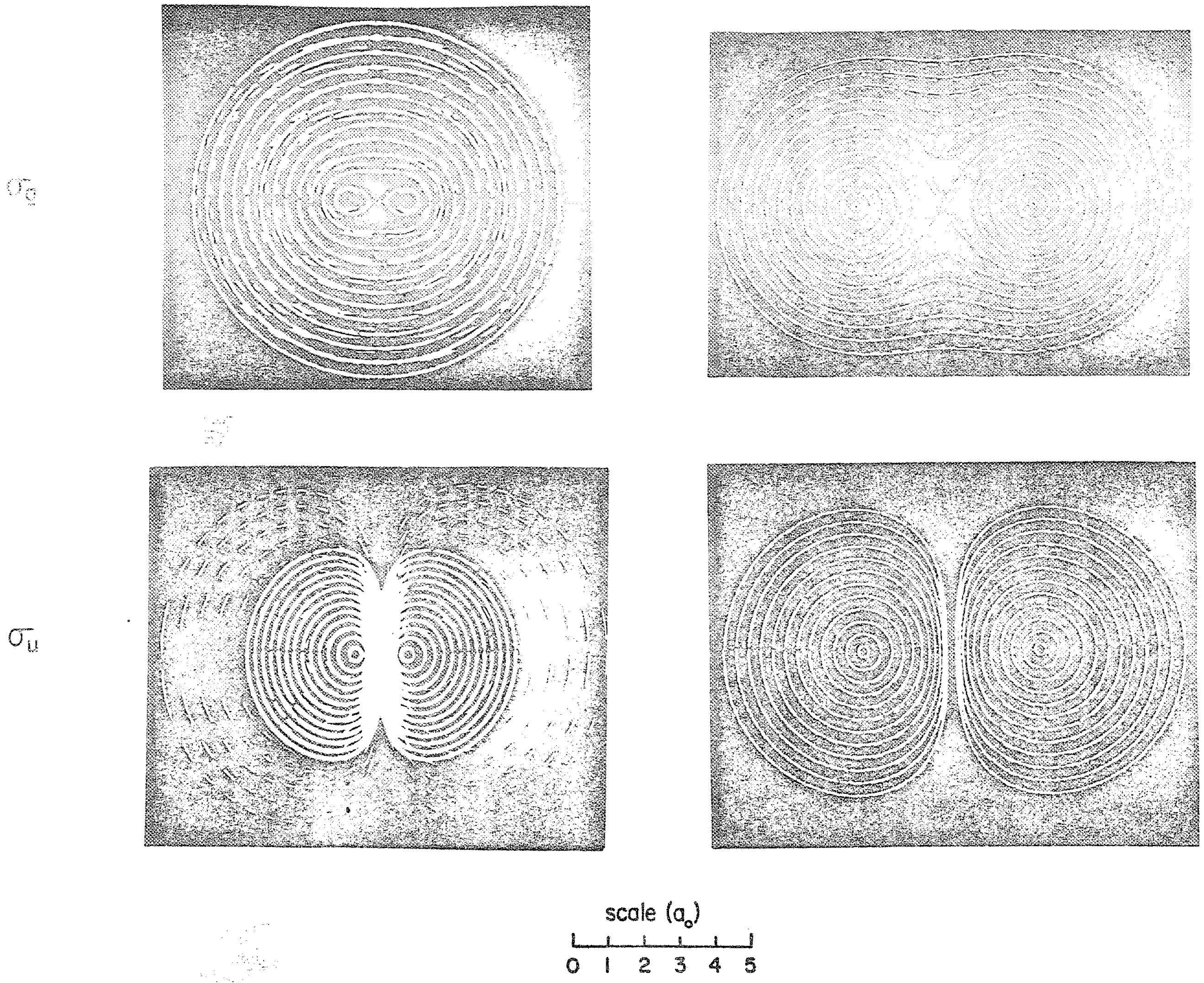


Figure 2

Figure 3



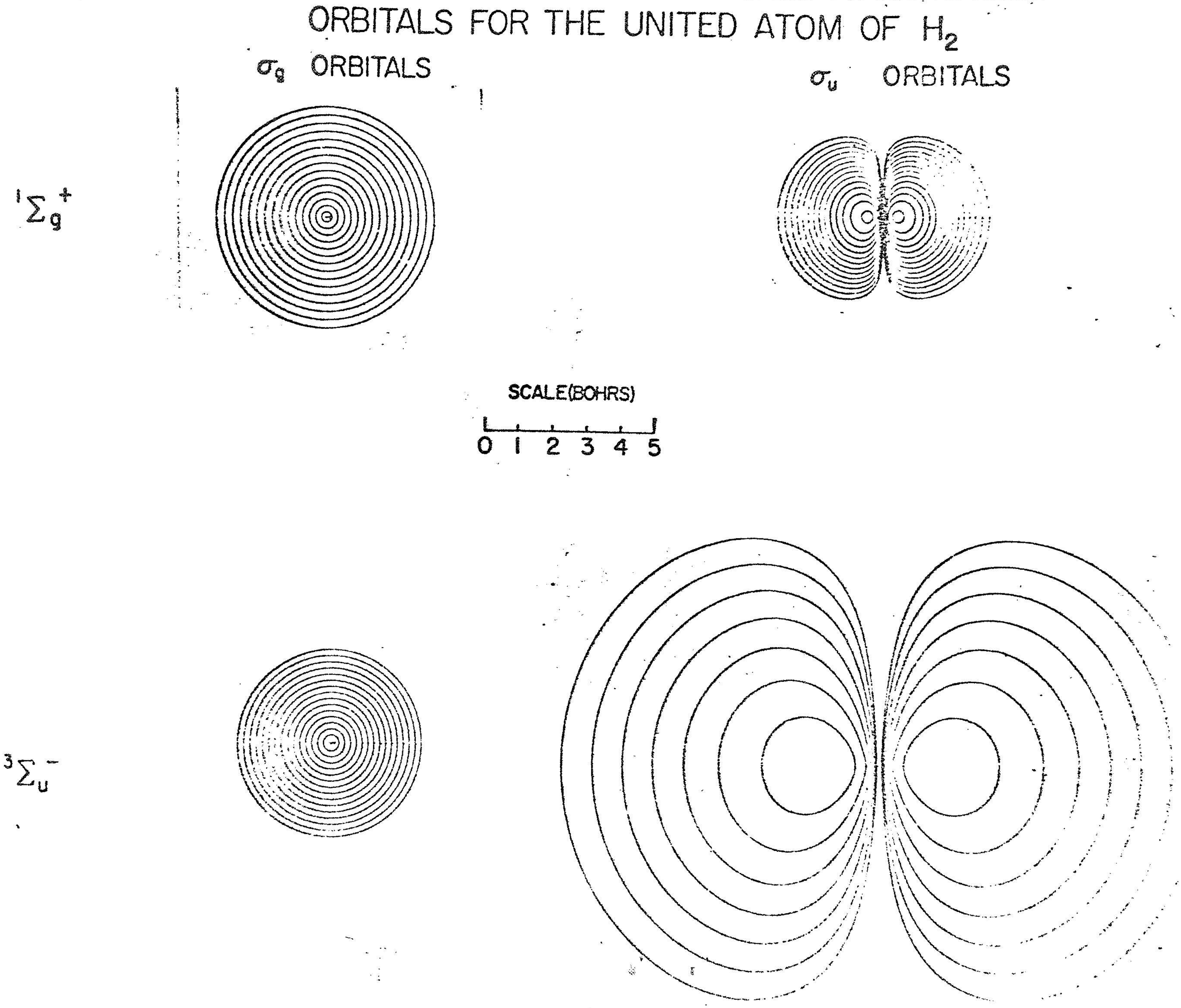

ORBITALS FOR THE UNITED ATOM OF H_2
σ_g ORBITALS
σ_u ORBITALS
${}^1\Sigma_g^+$
SCALE(BOHRS)
0 1 2 3 4 5
${}^3\Sigma_u^-$

Figure 4

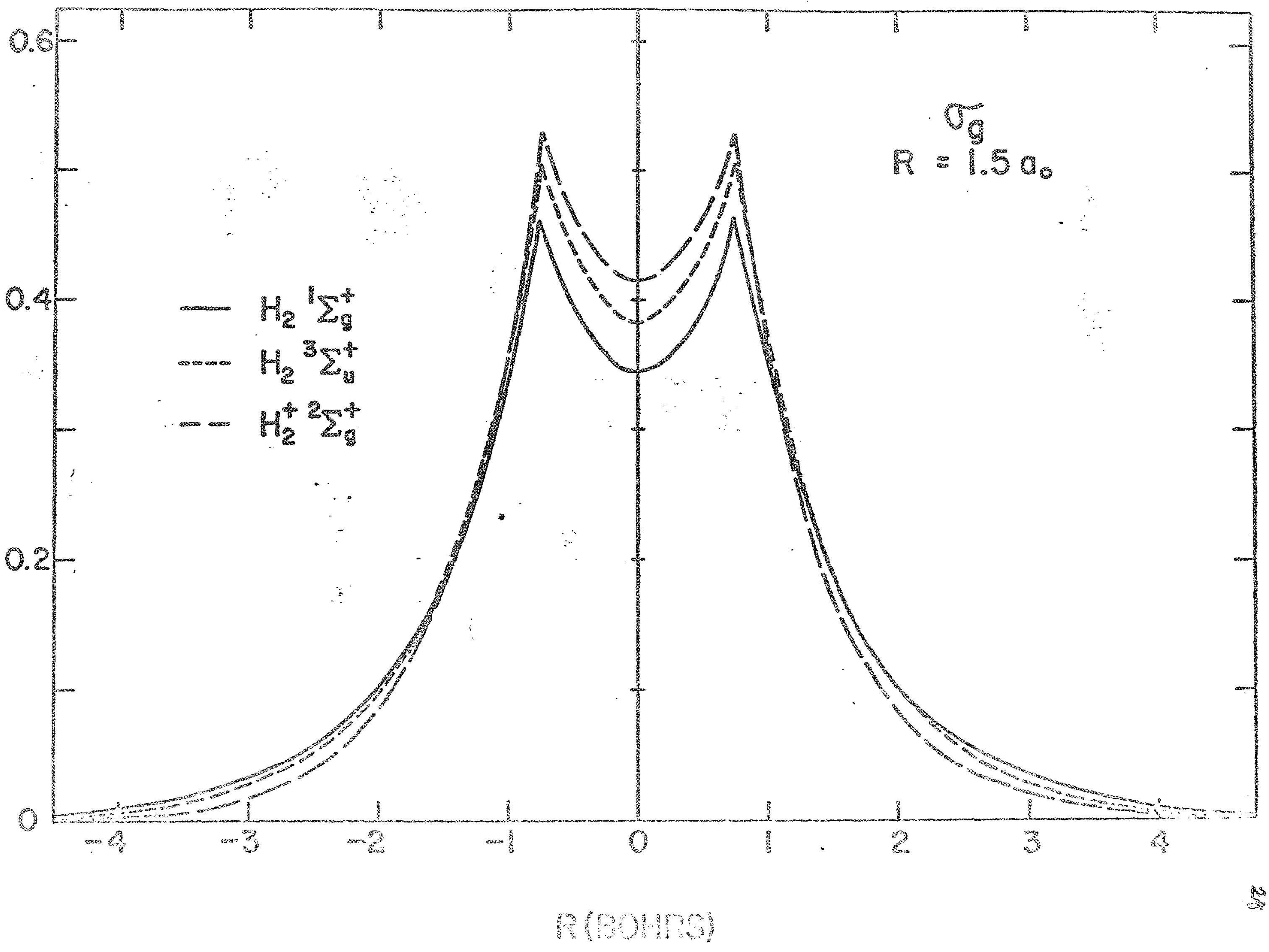

0.6
0.4
0.2
0
-4
-3
-2
-1
0
1
2
3
4
R (BOHRS)
σ_g
$R = 1.5\,a_0$
$H_2\ {}^1\Sigma_g^+$
$H_2\ {}^3\Sigma_u^+$
$H_2^+\ {}^2\Sigma_g^+$

Figure 5

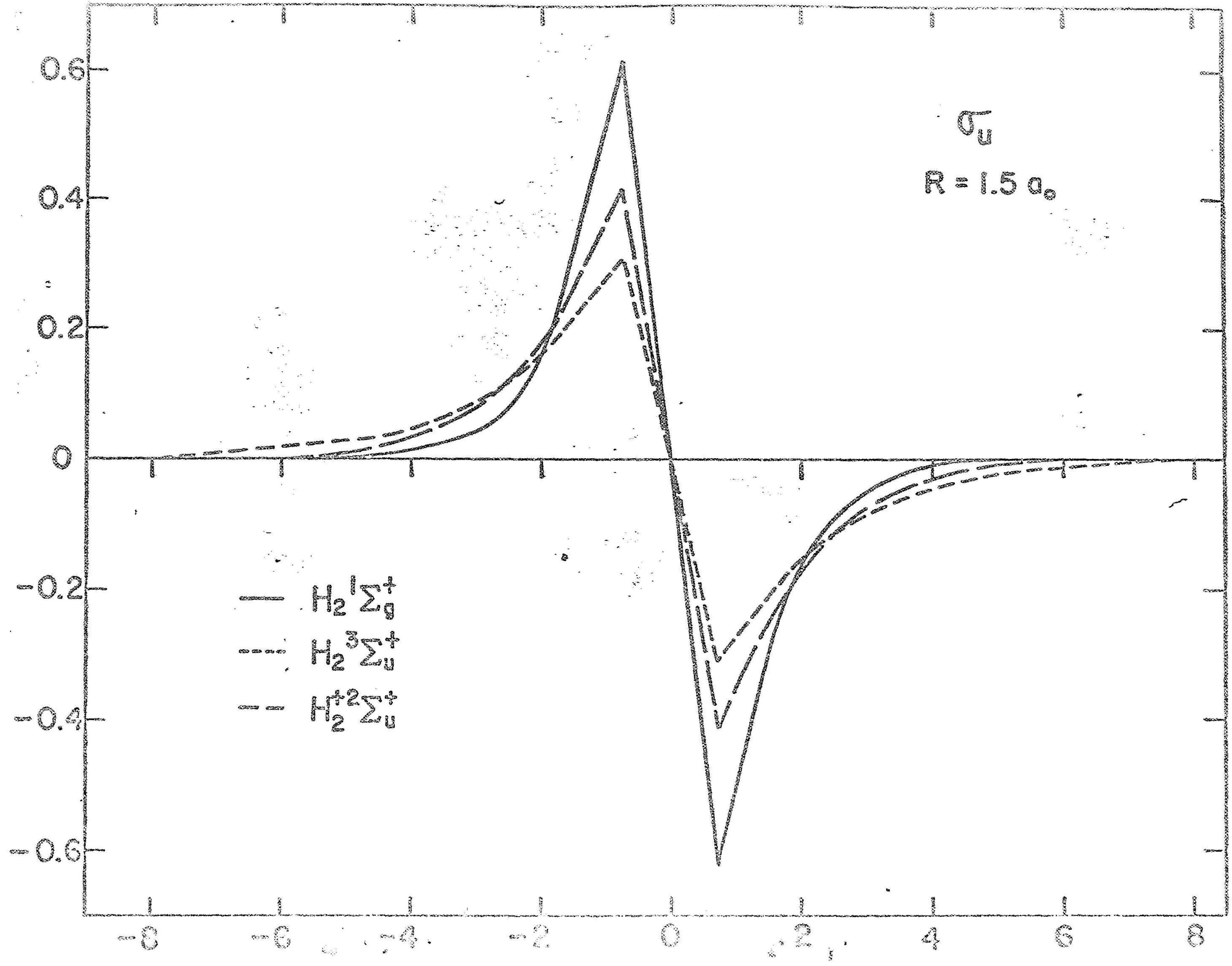

σ_u
R = 1.5 a₀
H₂ ¹Σ_g⁺
H₂ ³Σ_u⁺
H₂⁺ ²Σ_u⁺
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-8
-6
-4
-2
0
2
4
6
8
R(BOHRS)

Figure [illegible]

Appendix

Tables of the Complete Wavefunctions.

These tables present the complete results of calculations: the basis sets used, the co-efficients $C_{\lambda p}$, the mixing co-efficients A_{λ}, the orbital energies and total energies. These parameters are listed for both the ${}^1\Sigma_g^+$ and ${}^3\Sigma_u^+$ states over the range of internuclear separations from 0 to $10a_o$. The tables for the triplet also lists -V/T, the ratio of potential to kinetic energy, which occurs in the Virial Theorem.

$'\Sigma_g^+$ State of H_2: Wavefunction Coefficients

Basis	Set			Mixing and Orbital Coefficients						
		R (in Bohrs)		1.3	1.4	1.5	1.6	2.0	3.0	4.0
		-E (Hartree-Fock)		1.14913320	1.15214823	1.15140136	1.14799196	1.12089613	1.04809155	1.01308762
nl	ζ_p	-E (exact)		1.1723459	1.1744744	1.1728537	1.1685799	1.1381312	1.0573118	1.0163689
		A	σ_g	0.99490	0.99397	0.99288	0.99162	0.98433	0.94106	0.86194
1s	1.000	C	σ_g	-0.72520	-0.73405	-0.74260	-0.75064	-0.76856	0.57418	0.58138
1s	1.900			0.00104	0.00968	0.01762	0.02484	0.04397	0.02069	0.02547
2s	0.875			0.04784	0.04516	0.04205	0.03861	0.02386	-0.00283	0.01346
2p	2.155			-0.01988	-0.01974	-0.01970	-0.01973	-0.01989	0.01286	0.00435
3d	1.680			0.00266	0.00332	0.00394	0.00449	0.00535	0.00084	0.00158
2s	1.220			0.17283	0.16992	0.16766	0.16581	0.15418	0.01910	0.03346
2p	4.300			0.00083	0.00113	0.00144	0.00176	0.00302	-0.00303	-0.00107
3s	3.870			-0.00418	-0.00357	-0.00279	-0.00188	0.00220	-0.00017	0.00173
1s	0.350			-0.00276	-0.00242	-0.00203	-0.00163	-0.00015	0.00047	-0.00135
2s	7.600			-0.00032	-0.00018	-0.00005	0.00007	0.00039	0.00004	0.00018
3d	3.400			-0.00230	-0.00233	-0.00240	-0.00251	-0.00285	0.00069	-0.00019
4f	2.700			0.00000	0.00024	0.00047	0.00067	0.00114	-0.00002	0.00020
		ϵ	σ_g	-0.62061	-0.60400	-0.58847	-0.57392	-0.52373	-0.42967	-0.35355
		A	σ_u	-0.10084	-0.10968	-0.11913	-0.12922	-0.17634	-0.33824	-0.50702
1s	1.000	C	σ_u	4.04724	3.75012	3.48659	3.24931	2.42084	1.26819	0.88605
1s	1.900			-0.98456	-0.89921	-0.82287	-0.75363	-0.50275	-0.14788	-0.03785
2s	0.875			-0.06340	-0.08523	-0.10520	-0.11836	-0.13840	-0.09045	-0.03953
2p	2.155			-0.00448	-0.00301	-0.00078	0.00113	0.00415	0.00306	0.00157
3d	1.680			-0.01111	-0.01100	-0.01031	-0.00949	-0.00683	-0.00227	-0.00056

nl	p	R =		1.3	1.4	1.5	1.6	2.0	3.0	4.0
2s	3.870			-2.12238	-1.90384	-1.71000	-1.53885	-0.96368	-0.23880	-0.04724
2p	4.300			-0.00245	-0.00215	-0.00215	-0.00218	-0.00193	-0.00107	-0.00057
3s	3.870			0.02307	0.01288	0.00512	-0.00087	-0.01091	-0.00730	-0.00258
1s	0.350	C	σ_u	-0.03558	-0.02602	-0.01566	-0.00840	0.00627	0.00813	0.00395
2s	7.600			0.00040	-0.00035	-0.00094	-0.00136	-0.00179	-0.00083	-0.00026
3d	3.400			-0.00328	-0.00279	-0.00220	-0.00167	-0.00031	0.00023	0.00011
4f	2.700			-0.00180	-0.00217	-0.00222	-0.00215	-0.00155	-0.00059	-0.00020
				-0.01472	-0.01633	-0.01813	-0.02012	-0.03043	-0.07794	-0.14596

All energies are in Hartrees. Exact energies are from Kolos and Wolniewicz.

$^1\Sigma_g^+$ State of H_2: Wavefunction Coefficients

asis	Set			Mixing and Orbital Coefficients					
		R (in Bohrs) =		5.0	6.0	7.0	8.0	9.0	10.0
		-E (Hartree-Fock)		1.00284659	1.00055542	1.00010267	1.00001830	1.00000317	1.00000053
$n_p l_p$	ζ_p	-E (exact)		1.0037626	1.0008150	1.0001889	1.0000535	1.0000185	1.00000864
		A	σ_g	0.78970	0.74659	0.72517	0.71519	0.71066	0.70865
1s	1.00			-0.67315	-0.69024	-0.69908	-0.70345	-0.70546	-0.70640
2s	1.00			0.00807	0.00304	0.00079	0.00039	0.00011	0.00005
3s	1.00			-0.01315	-0.00554	-0.00144	-0.00072	-0.00021	-0.00006
4s	1.00			0.00277	0.00113	- - -	0.00010	- - -	- - -
2p	1.00	C	σ_g	-0.00174	0.00003	0.00014	0.00011	0.00006	0.00003
3p	1.00			0.00091	-0.00022	- - -	- - -	- - -	- - -
4p	1.00			-0.00145	- - -	- - -	- - -	- - -	- - -
3d	1.00			-0.00072	-0.00008	0.00001	0.00002	0.00001	0.00001
4f	1.00			-0.00022	- - -	0.00001	- - -	0.00000	0.00000
		ϵ	σ_g	-0.30147	-0.27394	-0.26087	-0.25488	-0.25216	-0.25095
		A	σ_u	-0.61350	-0.66528	-0.68857	-0.69893	-0.70353	-0.70556
1s	1.00			0.74502	0.72473	0.71526	0.71079	0.70875	0.70783
2s	1.00			0.00751	0.00313	0.00077	0.00038	0.00011	0.00005
3s	1.00			-0.01574	-0.00594	-0.00142	-0.00069	-0.00019	-0.00009
4s	1.00			0.00333	0.00185	- - -	0.00011	- - -	- - -
2p	1.00	C	σ_u	0.00049	0.00043	0.00035	0.00016	0.00007	0.00003
3p	1.00			0.00399	0.00083	- - -	- - -	- - -	- - -
4p	1.00			-0.00261	- - -	- - -	- - -	- - -	- - -
3d	1.00			0.00049	0.00028	0.00007	0.00004	0.00002	0.00001
4f	1.00			0.00011	- - -	0.00001	- - -	0.00000	0.00000
		ϵ	σ_u	-0.19800	-0.22592	-0.23910	-0.24511	-0.24784	-0.24905

All energies are in Hartrees. Exact energies are from Kolos and Wolniewicz, except at R = 10 where the 1/R expansion is used.

${}^3\Sigma_u^+$ State of H_2: Wavefunction Coefficients

Basis	Set			Orbital Coefficients						
		R (in Bohrs) =		1.3	1.4	1.5	1.6	2.0	3.0	4.0
		-E (Hartree-Fock)		0.74866877	0.77844420	0.80403953	0.82636423	0.89288169	0.97003347	0.99245095
		-E (exact)		0.7544033	0.7841501	0.8096095	0.8317238	0.8970636	0.9720104	0.9933781
$n_p l_p$	ζ_p	-V/T		1.6406930	1.6687873	1.6918728	1.7113950	1.7732846	1.8902524	1.9581930
1s	1.000			-1.07147	-1.13307	-1.14856	-1.13811	-1.06549	-0.84987	-0.70749
1s	1.900			-0.10455	0.13568	0.14828	0.15011	0.13804	0.06807	0.01269
2s	0.875			0.05317	0.05061	0.05174	0.05451	0.05935	0.04927	0.03045
2p	2.155			-0.03984	-0.03702	-0.03410	-0.03124	-0.02161	-0.01047	-0.00533
3d	1.680			-0.01162	-0.01194	-0.01205	-0.01198	-0.01001	-0.00445	-0.00230
2s	1.220	C		0.45954	0.48489	0.47804	0.45395	0.35311	0.14272	0.02196
2p	4.300		σ_g	0.00380	0.00385	0.00381	0.00370	0.00304	0.00202	0.00121
3s	3.870			-0.00797	-0.00287	0.00016	0.00196	0.00600	0.00554	0.00138
1s	0.350			-0.00350	-0.00199	-0.00173	-0.00211	-0.00303	-0.00328	-0.00217
2s	7.600			-0.00047	0.00005	0.00032	0.00049	0.00079	0.00055	0.00013
3d	3.400			-0.00097	-0.00076	-0.00053	-0.00031	0.00020	0.00024	0.00029
4f	2.700			-0.00103	-0.00116	-0.00124	-0.00129	-0.00132	-0.00076	-0.00042
		ϵ	σ_g	-0.9609	-0.9175	-0.8786	-0.8440	-0.7393	-0.6064	-0.5489
1s	1.000			-1.71723	-1.64715	-1.49956	-1.32116	-0.87543	-0.63468	0.67761
1s	1.900			0.34509	0.30329	0.23898	0.16751	0.00055	-0.06547	0.03181
2s	0.875			-1.59242	-1.43080	-1.24289	-1.05339	-0.52514	-0.11301	0.04079
2p	2.155			0.01753	0.01680	0.01656	0.01656	0.01568	0.01080	-0.00623
3d	1.680			-0.00672	-0.00720	-0.00740	-0.00737	-0.00661	-0.00361	0.00101
2s	1.220	C		0.97289	0.83743	0.65325	0.45835	0.01291	-0.13951	0.05930
2p	4.300		σ_u	-0.00042	-0.00035	-0.00040	-0.00053	-0.00104	-0.00162	0.00130
3s	3.870			0.02315	0.02158	0.01827	0.01416	0.00362	-0.00404	0.00322
1s	0.350			-0.67781	-0.42209	-0.26258	-0.16640	-0.02256	0.00214	-0.00312
2s	7.600			0.00237	0.00218	0.00180	0.00135	0.00018	-0.00048	0.00030
3d	3.400			0.00129	0.00124	0.00123	0.00125	0.00139	0.00128	-0.00059
4f	2.700			-0.00029	-0.00043	-0.00055	-0.00064	-0.00082	-0.00064	0.00020
		ϵ	σ_u	-0.2009	-0.2144	-0.2287	-0.2432	-0.3002	-0.4024	-0.4539

All energies are in Hartrees. The exact energies are from Kolos and Wolniewicz.

$^3\Sigma_u^+$ State of H_2: Wavefunction Coefficients

Basis	Set			Orbital Coefficients					
		R (in Bohrs) =		5.0	6.0	7.0	8.0	9.0	10.0
		-E (Hartree-Fock)		0.99828786	0.99964181	0.99993000	0.99998702	0.99999770	0.99999960
		-E (exact)		0.9986849	0.9998125	1.0000030	1.0000196	1.0000127	1.00000758
$n_p l_p$	ζ_p	-V/T		1.9870967	1.99658032	1.99919871	1.99982283	1.99997551	1.99999477
1s	1.00			-0.68491	-0.69454	-0.70064	-0.70399	-0.70566	-0.70645
2s	1.00			0.00587	0.00220	0.00083	0.00033	0.00010	0.00004
3s	1.00			0.00665	0.00235	0.00087	0.00025	0.00012	0.00004
4s	1.00			-0.00108	-0.00011	- - -	0.00005	- - -	- - -
2p	1.00	C	σ_g	-0.00556	-0.00243	-0.00079	-0.00035	-0.00015	-0.00006
3p	1.00			0.00284	0.00091	- - -	- - -	- - -	- - -
3d	1.00			-0.00204	-0.00049	-0.00020	-0.00008	-0.00004	-0.00001
4d	1.00			0.00129	- - -	- - -	- - -	- - -	- - -
4f	1.00			-0.00046	- - -	-0.00009	-0.00003	-0.00001	0.00000
		ϵ	σ_g	-0.5222	-0.5098	-0.5042	-0.5018	-0.5007	-0.5003
1s	1.00			0.73444	0.72103	0.71385	0.71028	0.70856	0.70776
2s	1.00			0.00749	0.00252	0.00096	0.00034	0.00012	0.00004
3s	1.00			0.00270	0.00174	0.00052	0.00023	0.00009	0.00004
4s	1.00			-0.00008	-0.00030	- - -	0.00000	- - -	- - -
2p	1.00	C	σ_u	-0.00624	-0.00246	-0.00100	-0.00040	-0.00016	-0.00006
3p	1.00			-0.00041	0.00001	- - -	- - -	- - -	- - -
3d	1.00			-0.00209	-0.00063	-0.00029	-0.00011	-0.00004	-0.00002
4d	1.00			0.00034	- - -	- - -	- - -	- - -	- - -
4f	1.00			-0.00050	- - -	-0.00009	-0.00004	-0.00001	-0.00001
		ϵ	σ_u	-0.4786	-0.4904	-0.4958	-0.4982	-0.4993	-0.4997

All energies are in Hartrees. The exact energies are from Kolos and Wolniewicz, except at R = 10 where the 1/R expansion is used.

United Atom Wavefunctions for H_2

(All energies are in Hartrees.)

Basis Set					Wavefunction Coefficients	
Separated Atom	United Atom	ζ	State*		$^1\Sigma_g^+$	$^3\Sigma_u^+$
			-E (Hartree-Fock)		2.86866912	2.128293
			-E (exact)		2.90372438	2.133171
			A	σ_g	0.99928	- - - -
$1s\sigma_g$	1s	1.000	C	σ_g	0.51847	0.51398
$1s\sigma_g$	1s	1.900			0.71200	-1.27395
$2s\sigma_g$	2s	0.875			-0.04607	-0.02501
$2s\sigma_g$	2s	1.220			-0.14722	-0.25687
$2p\sigma_g$	3s	4.300			-0.05781	0.00846
$1s\sigma_g$	1s	0.350			0.00321	0.00053
$2s\sigma_g$	2s	7.600			-0.00859	0.00105
$4f\sigma_g$	6s	2.700			0.01715	-0.00896
$3s\sigma_g$	3d	3.870			0.00028	-0.00025
$3d\sigma_g$	4d	1.680			0.00028	-0.00096
$3d\sigma_g$	4d	3.400			0.00118	0.00135
			ϵ	σ_g	-0.92312	-1.7401
			A	σ_u	0.03798	- - - -
$1s\sigma_u$	2p	1.000	C	σ_u	0.45880	0.54092
$1s\sigma_u$	2p	1.900			0.64641	-0.11013
$2s\sigma_u$	3p	0.875			-0.19131	-0.91120
$2p\sigma_u$	4p	2.155			-0.45683	-0.26223
$2p\sigma_u$	4p	4.300			0.36631	-0.04804
$1s\sigma_u$	2p	0.350			0.02599	-0.35876
$2s\sigma_u$	3p	7.600			0.11355	-0.00887
$3s\sigma_u$	4f	3.870			-0.00657	0.00000
$3d\sigma_u$	5f	1.680			0.00010	-0.00001
$3d\sigma_u$	5f	3.400			0.00006	0.00000
			ϵ	σ_u	-0.00489	-0.1283

---

[*] Since the same wavefunctions were used for the united atoms as for H_2, these states have cylindrical rather than spherica symmetry. However, the calculated $^1\Sigma_g^+$ wavefunction has roughly ^1S symmetry; the $^3\Sigma_u^+$ wavefunction is close to ^3P symmetry. The exact energies above are the experimental energies for the lowest states of helium with these symmetries.

References

1. W. Heitler and F. London, Z. Physik 44, 455 (1927).
2. S. Weinbaum, J. Chem. Phys. 1, 593 (1933).
3. E. Callen, J. Chem. Phys. 23, 360 (1955).
4. A. D. McLean, A. Weiss and M. Yoshimine, Rev. Mod. Phys. 32, 211 (1960).
5. G. Das and A. C. Wahl, J. Chem. Phys. 44, 87 (1966).
6. W. Kolos and H. Wolniewicz, J. Chem. Phys. 43, 2429 (1965). This is also the best $^1\Sigma_g^+$ calculation for the most part. They have lowered the energy by $3\text{x}10^{-7}$ a.u. at the equilibrium separation (Phys. Rev. Letters 20, 243 (1968)), and by $7\text{x}10^{-7}$ a.u. at $R = 8a_o$ (J. Chem. Phys. 49, 24 (1968).
7. Arnold C. Wahl, J. Chem. Phys. 41, 2600 (1964).
8. C. C. J. Roothaan, Rev. Mod. Phys. 32, 179 (1960).
9. F. L. Pilar, Elementary Quantum Chemistry (Mc Graw-Hill, N.Y., 1968), p. 461.
10. Arnold C. Wahl, P. J. Bertoncini, K. Kaiser, and R. H. Land, Argonne National Laboratory Report ANL-7271.
11. G. Das and Arnold C. Wahl, J. Chem. Phys. 47, 2934 (1967).
12. T. L. Gilbert and Arnold C. Wahl, J. Chem. Phys. 47, 3425 (1967).
13. J. O. Hirschfelder and P. O. Löwdin, Molecular Physics 2, 229 (1959).
14. See the Appendix for the basis sets at all separations.

15. For $R = 0$, E_{exact} is the experimental energies for the lowest ^1S and ^3P states of He . For $R = 10a_o$, E_{exact} was calculated from the $1/R$ expansion of the H_2 energy (p. 6 of Intermolecular Forces (J. O. Hirschfelder, Ed.) which is Vol. 12 of Adv. in Chem. Phys. (John Wiley, New York, 1967). In all other cases, the source is Kolos and Wolniewicz, Ref. 6.

16. In the Appendix the co-efficients $C_{\lambda p}$ are given for all separations. For the two UA states, the $C_{\lambda p}$ for the d- and f-STO are very small, leaving the $^3\Sigma_u^+$ with essential ^3P symmetry and the $(^1\sigma_g)^2$ configuration with ^1S symmetry.

17. D. R. Bates, K. Ledsham, and A. L. Stewart, Phil. Trans. Roy. Soc. (London) 246, 215 (1953).