

## One-Center Basis Set SCF MO's. III. H<sub>2</sub>O, H<sub>2</sub>S, and HCl

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One-Center Basis Set SCF MO's. III.  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{S}$ , and  $\text{HCl}$ 

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One-center expanded SCF MO wavefunctions are reported for  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{S}$ , and  $\text{HCl}$  in their ground states. The wavefunctions refer to the calculated equilibrium configurations which agree well with the experimental data. The corresponding computed molecular energies are  $-75.922436$ ,  $-397.58906$ , and  $-458.83776$  a.u., respectively, which are reasonably close to the experimental values. The energy obtained for  $\text{H}_2\text{O}$  is found to be near the estimated Hartree-Fock value.

The computed electric dipole moment of  $\text{H}_2\text{O}$  agrees well with the experimental value, while for  $\text{H}_2\text{S}$  and  $\text{HCl}$  larger discrepancies are found.

## INTRODUCTION

IN two previous papers,<sup>1,2</sup> to which we refer as I and II, the general characteristics of our approach have been discussed, and the results for  $\text{HF}$ ,  $\text{CH}_4$ ,  $\text{SiH}_4$  (Paper I), and  $\text{NH}_3$ ,  $\text{NH}_4^+$ ,  $\text{PH}_3$ ,  $\text{PH}_4^+$  (Paper II) in their calculated equilibrium geometries have been reported. Here we present the results for  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{S}$ , and  $\text{HCl}$ . As in previous investigations (I and II), the wavefunction is approximated by a single determinant. This is constructed with molecular orbitals which are the best possible linear combination available from a basis set consisting of functions all centered upon the heaviest nucleus. These wavefunctions are computed by a general program for several arbitrary positions of the nuclei employing different basis sets. The wavefunctions which give the minimum value of the total energy are those reported here together with the corresponding geometrical parameters.

We consider these geometrical parameters as those of the calculated equilibrium configurations, because it is believed that the basis sets presented are not capable of great improvement within the present limitations of the machine program. This is particularly reasonable for  $\text{H}_2\text{O}$  and less so for  $\text{H}_2\text{S}$  and  $\text{HCl}$ . In Papers I and II, the general features of the present approach have been discussed; therefore only the results are considered here. All symbols and definitions are as given in I and II.

 $\text{H}_2\text{O}$ 

Ellison and Shull<sup>3</sup> were the first to perform rather accurate calculations of the electronic wavefunction of this molecule. They used a minimal basis set of Slater orbitals to construct SCF LCAO MO's. Sub-

sequently, McWeeny and Ohno,<sup>4</sup> using the same basis set, performed additional calculations checking Ellison's results and testing other approaches.

As in the previous cases (Papers I and II), the calculations were carried out locating the expansion center upon the oxygen nucleus because of the favorable implications of this arrangement. Table I shows the results obtained.

Several basis sets were tried, testing different combinations of symmetries and values of the  $n$ 's. It appeared, as for  $\text{HF}$ , that high values of  $n$  are not required, indicating that within the present limitations the "peakedness" of the orbitals, closely connected to the cusp conditions at the protons (I), is not of primary importance. A second point which emerged was that it is not convenient to greatly increase the number of functions approximating the radial part of a given symmetry, and better results are achieved when the available functions are used to better approximate the radial parts of higher symmetries. This is so primarily because the radial behavior may be greatly improved by a careful selection of the orbital exponents  $\zeta$  of a reasonable number of functions. In addition, it is not wise to increase the number of functions too much because of the danger of redundancy.

From Table I, it appears that the basis functions characterized by the same values of  $n$  and  $l$  have the same value of  $\zeta$  regardless of the value of  $m$ . In principle this is not required because the components of these functions are not degenerate for the nonspherical molecular symmetry considered here. But only a limited optimization of the  $\zeta$ 's was possible, and their equality was retained to reduce the number of nonlinear variational parameters. This imposition is rather arbitrary, but it is partly justified by the slight dissimilarity existing between the radial parts associated with spherical harmonics with the same  $l$  value appearing in different orbitals. If we consider, for example, the radial parts associated with the spherical harmonic  $S_{1,m}$  in the three orbitals  $3a_1$ ,  $1b_2$ , and  $1b_1$  ( $m=0, -1, 1$ ,

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<sup>1</sup> R. Moccia, J. Chem. Phys. **40**, 2164 (1964).

<sup>2</sup> R. Moccia, J. Chem. Phys. **40**, 2176 (1964).

<sup>3</sup> F. O. Ellison, and H. Shull, J. Chem. Phys. **23**, 2348 (1955).

<sup>4</sup> R. K. McWeeny and K. A. Ohno, Proc. Roy. Soc. (London) **A255**, 367 (1960).

TABLE I. Ground state of H<sub>2</sub>O.

| $R_1=1.8140$ |     |     | $\theta_1=53.27^\circ$ | $\phi_1=90.00^\circ$  | $\mu_{N_x}=0.0000$ | $\mu_{e_x}=0.0000$  | $\mu=0.8205$ | $F_{e1}=-85.086639$ |  |  |
|--------------|-----|-----|------------------------|-----------------------|--------------------|---------------------|--------------|---------------------|--|--|
| $R_2=1.8140$ |     |     | $\theta_2=53.27^\circ$ | $\phi_2=270.00^\circ$ | $\mu_{N_y}=0.0000$ | $\mu_{e_y}=0.0000$  |              | $E_N=9.164201$      |  |  |
|              |     |     |                        |                       | $\mu_{N_z}=2.1697$ | $\mu_{e_z}=-1.3492$ |              | $E_T=-75.922438$    |  |  |
| $n$          | $l$ | $m$ | $\zeta$                | $1A_1$                | $2A_1$             | $3A_1$              | $1B_2$       | $1B_1$              |  |  |
| 1            | 0   | 0   | 12.600                 | 0.05167               | 0.01889            | -0.00848            |              |                     |  |  |
| 1            | 0   | 0   | 7.450                  | 0.94656               | -0.25592           | 0.08241             |              |                     |  |  |
| 2            | 0   | 0   | 2.200                  | -0.01708              | 0.77745            | -0.30752            |              |                     |  |  |
| 2            | 0   | 0   | 3.240                  | 0.02497               | 0.09939            | -0.04132            |              |                     |  |  |
| 2            | 0   | 0   | 1.280                  | 0.00489               | 0.16359            | 0.14954             |              |                     |  |  |
| 2            | 1   | 0   | 1.510                  | 0.00107               | 0.18636            | 0.79979             |              |                     |  |  |
| 2            | 1   | 0   | 2.440                  | -0.00244              | -0.00835           | 0.00483             |              |                     |  |  |
| 2            | 1   | 0   | 3.920                  | 0.00275               | 0.02484            | 0.24413             |              |                     |  |  |
| 3            | 2   | 0   | 1.600                  | 0.00000               | 0.00695            | 0.05935             |              |                     |  |  |
| 3            | 2   | 0   | 2.400                  | 0.00000               | 0.00215            | 0.00396             |              |                     |  |  |
| 3            | 2   | 2   | 1.600                  | -0.00004              | -0.06403           | -0.09293            |              |                     |  |  |
| 3            | 2   | 2   | 2.400                  | 0.00003               | -0.00988           | 0.01706             |              |                     |  |  |
| 4            | 3   | 0   | 1.950                  | -0.00004              | -0.02628           | -0.01929            |              |                     |  |  |
| 4            | 3   | 2   | 1.950                  | -0.00008              | -0.05640           | -0.06593            |              |                     |  |  |
| 2            | 1   | -1  | 1.510                  | ...                   | ...                | ...                 | 0.88270      |                     |  |  |
| 2            | 1   | -1  | 2.440                  |                       |                    |                     | -0.07083     |                     |  |  |
| 2            | 1   | -1  | 3.920                  |                       |                    |                     | 0.23189      |                     |  |  |
| 3            | 2   | -1  | 1.600                  |                       |                    |                     | 0.25445      |                     |  |  |
| 3            | 2   | -1  | 2.400                  |                       |                    |                     | -0.01985     |                     |  |  |
| 4            | 3   | -1  | 1.950                  |                       |                    |                     | 0.04526      |                     |  |  |
| 4            | 3   | -3  | 1.950                  |                       |                    |                     | -0.06381     |                     |  |  |
| 2            | 1   | 1   | 1.510                  | ...                   | ...                | ...                 | ...          | 0.72081             |  |  |
| 2            | 1   | 1   | 2.440                  |                       |                    |                     |              | 0.11532             |  |  |
| 2            | 1   | 1   | 3.920                  |                       |                    |                     |              | 0.24859             |  |  |
| 3            | 2   | 1   | 1.600                  |                       |                    |                     |              | 0.05473             |  |  |
| 3            | 2   | 1   | 2.400                  |                       |                    |                     |              | 0.00403             |  |  |
| 4            | 3   | 1   | 1.950                  |                       |                    |                     |              | 0.00935             |  |  |
| 4            | 3   | 3   | 1.950                  |                       |                    |                     |              | -0.02691            |  |  |
| Eigenvalues  |     |     |                        | -20.5249              | -1.3261            | -0.5561             | -0.6814      | -0.4954             |  |  |

respectively), it is seen that the dissimilarities are small but not negligible, and probably a better result would have been obtained using different  $\zeta$ 's for different  $m$ 's. But at this stage it is not considered worthwhile to investigate this possibility since for a linear geometry, which is examined in our calculations, the  $3a_1$  and the  $1b_1$  orbitals become degenerate  $\pi_x$ ,  $\pi_y$  orbitals. In this situation a limited basis set comprised of functions with different values of  $\zeta$  for  $m=+1$  and  $-1$ , for the same values of  $n$  and  $l$ , would never lead to the expected degeneracy. At any rate the value obtained for the total energy supports the conclusion that the present basis set works remarkably well in spite of all its limitations.

The values of the energies obtained by Ellison<sup>3</sup> or by McWeeny<sup>4</sup> are higher by  $\sim 3$  eV although the latter author performed, in addition to the SCF LCAO MO calculation, a configuration mixing treatment. To better judge the value of the energy obtained, we should compare it to the Hartree-Fock value. Until now this quantity has not been evaluated, but it is possible to make some estimate of it. In the same manner as described in Paper II, we estimate a value of  $-76.088$  a.u. which means that our calculated value of the energy is only  $0.166$  a.u., inferior to the best obtainable with an infinite basis set.

Our Hartree-Fock estimate might be questionable, but it appears quite reasonable and there is no other simple way of obtaining it. Clementi<sup>5,6</sup> has suggested a more sophisticated method for computing this quantity, but in the present instance it leads to some ambiguities. Following his reasoning, we should add to the correlation energy of the O<sup>2+</sup> ion, a contribution of  $2 \times 0.073$  a.u. arising from the two pairs of electrons of the two O-H bonds to obtain the molecular correlation energy. To this should be added the relativistic molecular energy, quite well approximated by that of the oxygen, to obtain the difference between the known experimental energy and the desired Hartree-Fock value. But which state of the O<sup>2+</sup> ion has to be considered?

The available values refer to the  $^3P$ ,  $^1D$ , and  $^1S$  states<sup>7</sup> arising from the configuration  $(1s)^2(2s)^2(2p)^2$ , while the configuration to be considered is probably a  $(1s)^2(hy_1)^2(hy_2)^2$ , where by  $hy_1$  and  $hy_2$  two suitable equivalent  $2s-2p$  hybrids have been indicated. This configuration, similar to the well-known valency state, is expressible through a hybridization parameter as a

<sup>5</sup> E. Clementi, J. Chem. Phys. **38**, 2780 (1963).

<sup>6</sup> E. Clementi, "Correlation Energy in the CH<sub>4</sub> Molecule," IBM Research Note, NJ-35, 3/25/63.

<sup>7</sup> E. Clementi, J. Chem. Phys. **38**, 2248 (1963).

linear combination of several states arising from the following configurations:

$$\begin{aligned}(1s)^2(2s)^2(2p)^2 & \quad {}^3P, {}^1D, {}^1S; \\ (1s)^2(2s)(2p)^3 & \quad {}^5S, {}^3S, {}^3D, {}^1D, {}^3P, {}^1P; \\ (1s)^2(2p)^4 & \quad {}^3P, {}^1D, {}^1S.\end{aligned}$$

Once the correlation energies of these states are known, it would be easy to obtain the desired correlation energy. But these quantities are not known, and therefore we prefer to rely upon the very simple method used in Paper II. It is unfortunate that the correlation energies of the listed states are not known, because, by considering the hybridization parameter as a simple function of the bond angle, it would have helped in making some estimate of the variation of the molecular correlation energy with bond angle.

The geometrical parameters of the equilibrium configuration are found by a method similar to that explained in Papers I and II, and they agree well with the experimental values. The poor agreement found by Ellison<sup>3</sup> and McWeeny<sup>4</sup> for the bond angle, the only internal coordinate varied in their computations, is due essentially to the type of wavefunction used. The first of these authors used a single detor approximation, but owing to the very limited basis set employed, his wavefunction was not sufficiently near the Hartree-Fock solution which, as discussed in Paper II, is likely to give good results for the equilibrium geometrical parameters. McWeeny, in his most accurate approach, used a single detor similar to that of Ellison, mixed with 12 other detors corresponding to excited configuration. It is difficult to predict how good the expectation values for the operators of interest might be with such a wavefunction. The available results, in our opinion, emphasize the convenience of computing Hartree-Fock wavefunctions, which for several simple molecules is coming within the reach of present computational facilities. In addition, it is quite convenient as a favorable starting point for more advanced computations.

As in earlier studies, the expectation value of the electric dipole moment is evaluated with the reported wavefunction. Its value of 0.8205 a.u., with the oxygen nucleus at the negative end, is larger than the experimental value of 0.725 a.u. This, as discussed in Papers I and II, is related to the inability of the basis set in its limited form, to give a high electronic density far from the expansion center.

Using the Koopmans theorem, we find that the lowest ionization potential is approximated by the orbital energy of the  $1b_1$  orbital, and its value of 0.4954 agrees well with the experimental value of 0.465 a.u.

### H<sub>2</sub>S

As far as we know, there are no examples in the literature of fairly accurate calculations of the electronic

wavefunction of this molecule. Walsh<sup>8</sup> made some conjectures about the shapes and energies of the molecular orbitals, but his speculations were qualitative and not useful for helping to make a selection of the trial basis set. The basis set choice for this molecule is made by considering the first five orbitals as quite similar to the first five atomic Hartree-Fock orbitals of the sulfur atom. To approximate the remaining four of more "molecular" character, functions whose orbital exponent,  $\zeta$ , is such as to give an average value of  $r$  close to the experimental S-H distance are included. Afterwards, the  $\zeta$ 's are varied by trial to minimize the energy. For this molecule, not many basis sets were tried, and a more thorough selection of the basis function would surely bring some improvement in the energy, but we are confident that the general features are correctly described by the wavefunction reported in Table II.

It is seen that the ground state is described in the one-electron approximation by

$$(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2(1b_1)^2(4a_1)^2(2b_2)^2(5a_1)^2(2b_1)^2, \\ {}^1A_1,$$

which, as expected, from the results of Table II can be fairly well approximated by

$$(1s)^2(2s)^2(2p)^6(4a_1)^2(2b_2)^2(5a_1)^2(2b_1)^2, \quad {}^1A_1,$$

where  $(1s)$ ,  $(2s)$ , and  $(2p)$  refer to the sulfur. From Table II it is seen that the basis set is of the same dimension as that used for H<sub>2</sub>O.

This restriction, due to the program, is rather serious because now we are dealing with a system containing eight more electrons than H<sub>2</sub>O. This decreases the possibility of the basis set satisfying the augmented requirements of the molecular orbitals because of their very different shapes. To this must be added the additional orthogonality conditions which decrease the number of truly independent linear variational parameters. For this molecule as in the case of H<sub>2</sub>O, the radial functions associated with different components of a spherical harmonic are kept equal. For the orbitals of atomic character this is satisfactory, but for the more "molecular" orbitals the situation is worse than for H<sub>2</sub>O, as may be seen from the results of Table II. In this same table appear the geometrical parameters which, according to what has been said for the other molecules treated, are considered as those for the calculated equilibrium configuration. They are obtained similarly to the other cases and also agree well with the experimental values.

A gratifying feature is the correct variation for the equilibrium bond angle in going from H<sub>2</sub>O to H<sub>2</sub>S, resembling the behavior found for NH<sub>3</sub> and PH<sub>3</sub> (Paper II). This variation is found, for the molecules

<sup>8</sup> A. D. Walsh, J. Chem. Soc. **1963**, 2260.

TABLE II. Ground state of H<sub>2</sub>S.

| $R_1 = 2.5090$ |     |     |        | $\theta_1 = 44.70^\circ$ | $\phi_1 = 90.00^\circ$  | $\mu_{Nx} = 0.0000$ | $\mu_{xz} = 0.0000$  | $\mu = 0.6789$ | $E_{el} = -410.62646$ |          |          |          |
|----------------|-----|-----|--------|--------------------------|-------------------------|---------------------|----------------------|----------------|-----------------------|----------|----------|----------|
| $R_2 = 2.5090$ |     |     |        | $\theta_2 = 44.70^\circ$ | $\phi_2 = 270.00^\circ$ | $\mu_{Ny} = 0.0000$ | $\mu_{xy} = 0.0000$  |                | $E_N = 13.03740$      |          |          |          |
|                |     |     |        |                          |                         | $\mu_{Nz} = 3.5668$ | $\mu_{xz} = -2.8878$ |                | $E_T = -397.58906$    |          |          |          |
| $n$            | $l$ | $m$ | I      | $1A_1$                   | $2A_1$                  | $3A_1$              | $4A_1$               | $5A_1$         | $1B_1$                | $2B_1$   | $1B_2$   | $2B_2$   |
| 1              | 0   | 0   | 22.000 | 0.19212                  | 0.03530                 | -0.00008            | -0.00883             | 0.00376        |                       |          |          |          |
| 1              | 0   | 0   | 14.000 | 0.82420                  | -0.40135                | 0.00115             | 0.08887              | -0.03557       |                       |          |          |          |
| 2              | 0   | 0   | 5.800  | -0.01418                 | 1.07921                 | -0.00327            | -0.25742             | 0.10334        |                       |          |          |          |
| 3              | 0   | 0   | 1.570  | 0.00866                  | 0.06903                 | 0.00323             | 1.68263              | -0.77626       |                       |          |          |          |
| 4              | 0   | 0   | 1.570  | -0.00748                 | -0.05535                | -0.00202            | -0.79082             | 0.58199        |                       |          |          |          |
| 3              | 2   | 0   | 1.400  | 0.00000                  | 0.00042                 | 0.00132             | 0.05284              | 0.07191        |                       |          |          |          |
| 4              | 2   | 0   | 1.400  | 0.00000                  | -0.00029                | -0.00103            | 0.00296              | 0.04363        |                       |          |          |          |
| 3              | 2   | 2   | 1.400  | 0.00000                  | -0.00116                | -0.00083            | -0.08534             | -0.06688       |                       |          |          |          |
| 4              | 2   | 2   | 1.400  | 0.00000                  | 0.00093                 | 0.00045             | -0.00059             | -0.04804       |                       |          |          |          |
| 2              | 1   | 0   | 5.770  | 0.00003                  | 0.00234                 | 0.98724             | -0.04530             | -0.18020       |                       |          |          |          |
| 3              | 1   | 0   | 1.560  | -0.00002                 | 0.00190                 | 0.11344             | 0.25711              | 1.12623        |                       |          |          |          |
| 4              | 1   | 0   | 1.560  | 0.00002                  | -0.00122                | -0.08881            | -0.00487             | -0.19336       |                       |          |          |          |
| 4              | 3   | 0   | 1.250  | 0.00000                  | -0.00006                | -0.00003            | -0.01735             | -0.00382       |                       |          |          |          |
| 4              | 3   | 2   | 1.250  | 0.00000                  | -0.00021                | -0.00035            | -0.07711             | -0.09829       |                       |          |          |          |
| 3              | 2   | 1   | 1.400  | ...                      | ...                     | ...                 | ...                  | ...            | 0.00068               | 0.04089  |          |          |
| 4              | 2   | 1   | 1.400  |                          |                         |                     |                      |                | -0.00060              | 0.02367  |          |          |
| 2              | 1   | 1   | 5.770  |                          |                         |                     |                      |                | 0.98770               | -0.20468 |          |          |
| 3              | 1   | 1   | 1.560  |                          |                         |                     |                      |                | 0.10984               | 1.33720  |          |          |
| 4              | 1   | 1   | 1.560  |                          |                         |                     |                      |                | -0.08637              | -0.35642 |          |          |
| 4              | 3   | 1   | 1.250  |                          |                         |                     |                      |                | 0.00006               | 0.02383  |          |          |
| 4              | 3   | 3   | 1.250  |                          |                         |                     |                      |                | -0.00010              | -0.03296 |          |          |
| 3              | 2   | -1  | 1.400  | ...                      | ...                     | ...                 | ...                  | ...            | ...                   | ...      | 0.00225  | -0.26447 |
| 4              | 2   | -1  | 1.400  |                          |                         |                     |                      |                |                       |          | -0.00142 | -0.11659 |
| 2              | 1   | -1  | 5.770  |                          |                         |                     |                      |                |                       |          | 0.98711  | 0.17206  |
| 3              | 1   | -1  | 1.560  |                          |                         |                     |                      |                |                       |          | 0.11456  | -1.05167 |
| 4              | 1   | -1  | 1.560  |                          |                         |                     |                      |                |                       |          | -0.08972 | 0.13665  |
| 4              | 3   | -1  | 1.250  |                          |                         |                     |                      |                |                       |          | 0.00027  | -0.13359 |
| 4              | 3   | -3  | 1.250  |                          |                         |                     |                      |                |                       |          | -0.00020 | 0.06997  |
| Eigenvalues    |     |     |        | -92.4785                 | -9.0798                 | -6.6350             | -0.9403              | -0.4543        | -6.6318               | -0.3506  | -6.6362  | -0.5307  |

mentioned, with all trial sets which gave energies comparable in quality to those reported here and in Paper II. The variation of the equilibrium bond angle, in going from H<sub>2</sub>O to H<sub>2</sub>S, can be interpreted along the same lines followed for NH<sub>3</sub> and PH<sub>3</sub>. Since the electronic energies of H<sub>2</sub>O and H<sub>2</sub>S are quite similar functions of the bond angle, the difference in the equilibrium value will be set almost solely by the difference in the bond lengths.

Concerning the variation of the orbital energies with the bond angle, we observe a behavior similar to that presented by H<sub>2</sub>O. The energies of the more "molecular" orbitals, belonging to the same irreducible representation, all displayed the same trend when varying the bond angle. Specifically, the energies of the  $a_1$ 's and  $b_1$  increase while that of  $b_2$  decreases on increasing the angle. This characteristic was shown by NH<sub>3</sub> and PH<sub>3</sub> as well, where the  $a_1$  orbital energies increase while the  $e_{x,y}$  values decrease on increasing the bond angles. The explanation of this behavior which was given in Paper II for NH<sub>3</sub> and PH<sub>3</sub> can be applied in the present case as well.

This behavior contrasts with some conclusions reached by Walsh<sup>8</sup> for molecules of the same type. Probably his very dubious assumption that for a bond

angle of 90° there is no  $s$ - $p$  hybridization is responsible for the difference.

The electric dipole moment value of 0.6789 calculated here, with the sulfur nucleus at the negative end, is much larger than the experimental value of 0.362 a.u. This is not strange because of the particular approximations of our approach, but in this case a supplementary reason can be found in the lower-than-experimental bond angle. This brings the center of gravity of the positive charges farther away from the expansion center and adds to the limitation of the one-center expansion. The first ionization potential approximated by the energy of the  $2b_1$  orbital is 0.351 a.u. This value agrees well with the experimental value of 0.386 a.u. The calculated molecular energy of -397.58906 a.u. represents 99.18% of the experimental value of -400.81 a.u. This experimental value was obtained by summing a dissociation energy of 0.2584 a.u. and a zero-point energy of 0.01499 (anharmonicity neglected) with the energies of the separated atoms. The energy of the sulfur atom in its <sup>3</sup>P ground state was obtained from the work of Clementi.<sup>9,10</sup>

<sup>9</sup> E. Clementi, J. Chem. Phys. **38**, 1001 (1963).

<sup>10</sup> E. Clementi (private communication).

TABLE III. Ground state of HCl.

|             |     |     |         | $R=2.4040$ | $\mu_N=2.4040$ | $\mu_o=-1.5516$ | $\mu=0.8524$ | $E_{el}=-465.90930$<br>$E_N=7.07154$<br>$E_T=458.83776$ |          |          |          |          |
|-------------|-----|-----|---------|------------|----------------|-----------------|--------------|---|----------|----------|----------|----------|
| $n$         | $l$ | $m$ | $\zeta$ | $1\sigma$  | $2\sigma$      | $3\sigma$       | $4\sigma$    | $5\sigma$   | $1\pi_x$ | $2\pi_x$ | $1\pi_y$ | $2\pi_y$ |
| 1           | 0   | 0   | 24.000  | 0.14379    | 0.05323        | -0.00004        | -0.01076     | 0.00312   |          |          |          |          |
| 1           | 0   | 0   | 15.300  | 0.86823    | -0.42957       | 0.00036         | 0.08611      | -0.02520  |          |          |          |          |
| 2           | 0   | 0   | 6.300   | 0.00863    | 1.08412        | -0.00095        | -0.23607     | 0.06943   |          |          |          |          |
| 3           | 0   | 0   | 1.800   | 0.00255    | 0.03721        | 0.00122         | 1.24070      | -0.40315  |          |          |          |          |
| 3           | 0   | 0   | 1.100   | -0.00170   | -0.02222       | -0.00045        | -0.33876     | 0.21076   |          |          |          |          |
| 2           | 1   | 0   | 6.300   | 0.00001    | 0.00056        | 0.99242         | -0.04135     | -0.17738  |          |          |          |          |
| 3           | 1   | 0   | 1.750   | -0.00001   | 0.00067        | 0.05753         | 0.22725      | 1.02242   |          |          |          |          |
| 3           | 1   | 0   | 1.100   | 0.00000    | -0.00025       | -0.03478        | -0.00559     | -0.09448  |          |          |          |          |
| 3           | 2   | 0   | 1.000   | 0.00000    | -0.00019       | -0.00022        | -0.05969     | -0.06197  |          |          |          |          |
| 3           | 2   | 0   | 1.500   | -0.00000   | 0.00051        | 0.00029         | 0.21813      | 0.37266   |          |          |          |          |
| 3           | 2   | 0   | 2.250   | 0.00000    | -0.00039       | 0.00091         | -0.07248     | -0.13894  |          |          |          |          |
| 3           | 2   | 0   | 3.500   | -0.00000   | 0.00052        | -0.00051        | 0.01719      | 0.04501   |          |          |          |          |
| 4           | 3   | 0   | 1.500   | 0.00000    | -0.00004       | -0.00024        | 0.04634      | 0.10117   |          |          |          |          |
| 4           | 3   | 0   | 2.250   | -0.00000   | 0.00025        | 0.00075         | 0.01833      | 0.00895   |          |          |          |          |
| 2           | 1   | 1   | 6.300   | ...        | ...            | ...             | ...          | ...   | 0.99267  | -0.19583 |          |          |
| 3           | 1   | 1   | 1.750   |            |                |                 |              |   | 0.05592  | 1.16378  |          |          |
| 3           | 1   | 1   | 1.100   |            |                |                 |              |   | -0.03408 | -0.18951 |          |          |
| 3           | 2   | 1   | 1.500   |            |                |                 |              |   | -0.00007 | 0.04886  |          |          |
| 3           | 2   | 1   | 2.250   |            |                |                 |              |   | 0.00013  | -0.00569 |          |          |
| 4           | 3   | 1   | 1.500   |            |                |                 |              |   | -0.00015 | 0.02284  |          |          |
| 4           | 3   | 1   | 2.250   |            |                |                 |              |   | 0.00029  | 0.00496  |          |          |
| 2           | 1   | -1  | 6.300   | ...        | ...            | ...             | ...          | ...   |          |          | 0.99267  | -0.19583 |
| 3           | 1   | -1  | 1.750   |            |                |                 |              |   |          |          | 0.05592  | 1.16378  |
| 3           | 1   | -1  | 1.100   |            |                |                 |              |   |          |          | -0.03408 | -0.18951 |
| 3           | 2   | -1  | 1.500   |            |                |                 |              |   |          |          | -0.00007 | 0.04886  |
| 3           | 2   | -1  | 2.250   |            |                |                 |              |   |          |          | 0.00013  | -0.00569 |
| 4           | 3   | -1  | 1.500   |            |                |                 |              |   |          |          | -0.00015 | 0.02284  |
| 4           | 3   | -1  | 2.250   |            |                |                 |              |   |          |          | 0.00029  | 0.00496  |
| Eigenvalues |     |     |         | -105.5328  | -10.8868       | -8.2483         | -1.0832      | -0.6203   | -8.2456  | -0.4850  | -8.2456  | -0.4850  |

## HCl

This is another molecule for which reasonably accurate wavefunctions are just becoming available.<sup>11</sup> The selection of the basis set is thus made along the lines described for H<sub>2</sub>S. In the basis set are included functions capable of approximating the  $1s$ ,  $2s$ , and  $2p$  Hartree-Fock orbitals of the chlorine atom. In fact the  $1\sigma$  and  $2\sigma$ , and the  $4\sigma$ ,  $1\pi_x$ , and  $1\pi_y$  molecular orbitals are very nearly identical to the above atomic orbitals. The other basis functions are chosen in order to describe a charge distribution mainly localized around the proton at  $\sim 2.5$  a.u. from the expansion center coinciding with the chlorine nucleus. The proton was located on the  $z$  axis to facilitate the selection of the basis functions. Not many basis sets were tried and those tested differed only for the  $\zeta$ 's. The number and type of the functions in the basis set are similar to the best found for HF in Paper I.

Probably this was not a wise selection and surely for the molecule there is the possibility of great improvement within the present limitations imposed by

the machine program. In spite of this, we think we have obtained some useful results with very little effort to optimize the basis set.

The determination of the bond length was very simple for this case because of the presence of only one internal coordinate. The results obtained are presented in Table III. The ground state which has the configuration,

$$(1\sigma)^2(2\sigma)^2(3\sigma)^2(1\pi)^4(4\sigma)^2(5\sigma)^2(2\pi)^4, \quad {}^1\Sigma^+$$

can be fairly well described as:

$$(1s)^2(2s)^2(2p)^6(4\sigma)^2(5\sigma)^2(2\pi)^4, \quad {}^1\Sigma^+,$$

as is clear from the results obtained.

Even here the radial functions associated with different components of a spherical harmonic are kept equal although, in view of the great difference between the  $4\sigma$  and  $5\sigma$ , and the  $2\pi$  orbitals, it would have been much better to use different values of the  $\zeta$ . But as said previously, the optimization of the basis set was carried out in a very limited fashion, and great im-

<sup>11</sup> R. K. Nesbet, Bull. Am. Phys. Soc. 7, 611 (1962).

TABLE IV. Summary.

|                             |        | CH <sub>4</sub> <sup>a</sup> | NH <sub>4</sub> <sup>++b</sup> | NH <sub>3</sub> <sup>b</sup> | H <sub>2</sub> O | HF <sup>a</sup> | SiH <sub>4</sub> <sup>a</sup> | PH <sub>4</sub> <sup>++b</sup> | PH <sub>3</sub> <sup>b</sup> | H <sub>2</sub> S | HCl       |
|-----------------------------|--------|------------------------------|--------------------------------|------------------------------|------------------|-----------------|-------------------------------|--------------------------------|------------------------------|------------------|-----------|
| $R_e(X-H)$                  | Calc.  | 2.08                         | 1.990                          | 1.928                        | 1.814            | 1.728           | 2.787                         | 2.750                          | 2.672                        | 2.509            | 2.404     |
|                             | Exptl. | 2.067                        | 1.96                           | 1.912                        | 1.810            | 1.7328          | 2.76                          | 2.68                           | 2.678                        | 2.525            | 2.409     |
| H-X-H                       | Calc.  | Tetr.                        | Tetr.                          | 108°54'                      | 106°32'          | ...             | Tetr.                         | Tetr.                          | 89°48'                       | 89°24'           | ...       |
|                             | Exptl. | Tetr.                        | Tetr.                          | 106°48'                      | 105°3'           | ...             | Tetr.                         | Tetr.                          | 93°10'                       | 92°13'           | ...       |
| $R_e(H-H)$                  | Calc.  | 2.402                        | 2.298                          | 3.137                        | 2.907            | ...             | 3.218                         | 3.175                          | 3.772                        | 3.530            | ...       |
|                             | Exptl. | 2.379                        | 2.26                           | 3.070                        | 2.873            | ...             | 3.187                         | 3.09                           | 3.890                        | 3.639            | ...       |
| $\mu$ (a.u.) <sup>c</sup>   | Calc.  | ...                          | ...                            | 0.5949                       | 0.8205           | 0.825           | ...                           | ...                            | 0.4610                       | 0.6789           | 0.8524    |
|                             | Exptl. | ...                          | ...                            | 0.583                        | 0.728            | 0.716           | ...                           | ...                            | 0.217                        | 0.362            | 0.413     |
| 1st I.P.                    | Calc.  | 0.5042                       | 0.9412                         | 0.4147                       | 0.4954           | 0.6429          | 0.4391                        | 0.7551                         | 0.3671                       | 0.3506           | 0.4850    |
|                             | Exptl. | 0.4774                       | ?                              | 0.386                        | 0.463            | 0.5795          | 0.448                         | ?                              | 0.371                        | 0.384            | 0.462     |
| $E_{Total}$                 | Calc.  | -39.86597                    | -56.21769                      | -55.97482                    | -75.92244        | -100.0053       | -290.1024                     | -341.5493                      | -341.3960                    | -397.5891        | -458.8378 |
|                             | Exptl. | -40.522                      | -56.86                         | -56.578                      | -76.46           | -100.48         | -292.141                      | ?                              | -343.42                      | -400.81          | -462.81   |
| $\%E_{Exptl.}$ <sup>d</sup> |        | 98.38                        | 98.87                          | 98.93                        | 99.30            | 99.53           | 99.30                         |                                | 99.38                        | 99.19            | 99.14     |

<sup>a</sup> Results obtained in I.<sup>b</sup> Results obtained in II.<sup>c</sup>  $\mu$  = electric dipole moment in atomic units.<sup>d</sup> Percentage of total experimental energy given by calculated energy.

provements can be expected by a more thorough optimization.

The calculated molecular energy of  $-458.8377$  a.u. represents 99.14% of the experimental value of  $-462.81$  a.u. This value was obtained by adding a dissociation energy of  $0.1626$  a.u. and a zero-point energy of  $0.00681$  a.u. to the energies of the separated atoms. The energy of the chlorine atom in its  $^2P$  ground state was obtained similarly to that of the sulfur.

As expected, the calculated value of the electric dipole moment is far larger than the experimental for the same reasons which were indicated for the other heavy hydrides treated. The first ionization potential approximated by the value of  $0.4850$  a.u. for the  $2\pi$  orbital energy compares well with the experimental value of  $0.462$  a.u.

To give an extended view of the possibilities of our approach, the most salient results obtained so far are collected in Table IV. They include all molecules considered in Papers I, II, and presently. Atomic units are used throughout. The results reported in Table IV have already been discussed, but we wish to call attention to the trend of the percentage of the experimental energy accounted for. This trend, which for the first-row hydrides agrees with the general characteristics of our approach discussed in Paper I, appears different for the second-row hydrides. As a matter of fact, we would expect an increasingly better result in going from  $\text{SiH}_4$  to  $\text{HCl}$ . The contradictory behavior could be explained by considering that for  $\text{H}_2\text{S}$  and  $\text{HCl}$  the basis sets were not optimized as well as for  $\text{SiH}_4$  and  $\text{PH}_3$ . But another important reason could be the uncertainty in the energy of the heavy atoms.

The experimental energies of Si and P were computed by summing all the successive ionization potentials

given by Moore<sup>12</sup> and Finkelnburg,<sup>13</sup> while for S and Cl we have used the values of the total energies as computed by Clementi.<sup>9,10</sup> The uncertainty in both the ionization potentials and the values extrapolated could reasonably be the cause of the unexpected behavior. An additional reason could be the fact that the computed energies refer to geometrical configurations which do not coincide with the experimental.

But in the present instance this is of no importance because of the smallness of the differences between the computed values and the experimental values of the geometrical parameters of equilibrium and the negligible energies connected with these differences.

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<sup>12</sup> C. E. Moore, Natl. Bur. Std. (U.S.) Circ. No. 467 (1958).

<sup>13</sup> W. Finkelnburg, Phys. Rev. **77**, 304 (1950).