Physical and Inorganic Chemistry

Ground State Self-Consistent-Field Wave Functions and Molecular Properties for the Isoelectronic Series SiH$_4$, PH$_3$, H$_2$S, and HCl

Stephen Rothenberg,[1a] Ralph H. Young,[1b] and Henry F. Schaefer III[1c]

Contribution from the University Computing Company, Palo Alto, California, the Department of Chemistry, Jackson State College, Jackson, Mississippi, and the Department of Chemistry, University of California, Berkeley, California. Received January 27, 1970

Abstract: After determining an improved contraction for Veillard's gaussian atomic basis sets for Si, P, S, and Cl, approximate Hartree–Fock wave functions were computed for the molecules SiH$_4$, PH$_3$, H$_2$S, and HCl. The calculations employ two contracted gaussian functions for each atomic orbital, plus additional d and p functions to describe molecular charge distortion. It is estimated that the calculated SCF energies lie no more than 0.04 hartree above the Hartree–Fock energies for these molecules. A large number of one-electron properties are reported. The calculated molecular properties for HCl are usually in excellent agreement with the accurate Hartree–Fock results of McLean and Yoshimine, and it is concluded that the computed properties for SiH$_4$, PH$_3$, and H$_2$S should also be very close to their true Hartree–Fock values. Population analyses indicate that d function participation in SiH$_4$, PH$_3$, and H$_2$S is less than that indicated by the calculations of Lipscomb and coworkers. This conclusion is also borne out by energy calculations with and without d functions on the central atom. Calculated dissociation energies, ionization potentials, and dipole moments are in good agreement with experiment. Molecular quadrupole and octupole moments are also predicted. Paramagnetic contributions χ^{hf} to the magnetic susceptibility are deduced from experiment. Calculated diamagnetic contributions to the proton chemical shifts are reported. Calculated electric field gradients are used to deduce the following reliable (to about 10%) nuclear electric quadrupole moments: $Q(^{33}S) = -0.065$, $Q(^{35}S) = +0.045$, $Q(^{35}Cl) = -0.080$, and $Q(^{37}Cl) = -0.063$ barn.

Perhaps the simplest isoelectronic series of molecules containing second-row atoms is the 18-electron series SiH$_4$, PH$_3$, H$_2$S, and HCl. Only for the diatomic HCl have accurate[2] self-consistent-field (SCF) functions been reported in the literature.

McLean and Yoshimine[3a] have calculated a very accurate SCF wave function for HCl, and they report

molecular properties which should be very close to their Hartree–Fock values. In their study of second-row diatomic hydrides, Cade and Huo[3b] obtained an SCF wave function for HCl only slightly less accurate than that of McLean and Yoshimine.[3a] Earlier SCF calculations involving Slater-type orbitals (STO's) on both centers were performed by Scrocco and Tomasi[4] and by Nesbet.[5]

In SiH$_4$, PH$_3$, H$_2$S, and HCl, the energy of the large atom Si, P, S, or Cl comprises over 99% of the total molecular energy. It is therefore not surprising to find that most of the *ab initio* calculations on these molecules

(1) (a) University Computing Co., supported by a grant from the Chemical Applications Department of the UCC Computer Utility Network; (b) Jackson State College; (c) University of California, supported in part by the Petroleum Research Fund, administered by the American Chemical Society.

(2) For a molecule containing one second-row atom, we use the word "accurate" to indicate that the calculated SCF energy is within 0.1 hartree of the Hartree–Fock energy.

(3) (a) A. D. McLean and M. Yoshimine, *J. Chem. Phys.*, **47**, 3256 (1967); (b) P. E. Cade and W. M. Huo, *ibid.*, **47**, 649 (1967).

(4) E. Scrocco and J. Tomasi in "Molecular Orbitals in Chemistry, Physics, and Biology: A Tribute to R. S. Mulliken," P. O. Löwdin and B. Pullman, Ed., Academic Press, New York, N. Y., 1964.

(5) R. K. Nesbet, *J. Chem. Phys.*, **41**, 100 (1964).

have utilized one-center approaches. Carter[6] performed an early one-center numerical Hartree calculation on SiH_4. Using a set of Slater-type orbitals centered on the large atom, Moccia[7] obtained one-center SCF functions for the entire series SiH_4, PH_3, H_2S, and HCl. Recently Moccia[8] has reported a more accurate one-center SCF wave function for HCl. Albasiny and Cooper[9] performed a one-center numerical Hartree–Fock computation on SiH_4. Finally Banyard and Hake[10] studied the 18-electron isoelectronic series using the united atom method.

The only SCF calculations for SiH_4, PH_3, and H_2S using STO's on different centers are those of Boyd and Lipscomb[11] for PH_3 and Boer and Lipscomb[12] for SiH_4 and H_2S. These calculations employed minimal sets of STO's plus d functions centered on the large atoms Si, P, and S.

Finally, Rauk and Csizmadia[13] have performed SCF calculations on H_2S using a small gaussian basis.

In the present work we first discuss the problem of obtaining a suitable basis of contracted gaussian functions for use in molecules containing second-row atoms. Then SCF wave functions and molecular properties are obtained for SiH_4, PH_3, H_2S, and HCl. To determine the reliability of our results, a comparison is made between the present SCF energies and properties and the accurate Hartree–Fock results of McLean and Yoshimine.[3a] Further comparison is made with experiment, and a large number of molecular properties are predicted.

Procedure

All calculations reported here were performed using the MOLE Quantum Chemistry System, which has been described elsewhere.[14] The UCC Univac 1108 computer was used, and total computation time for all calculations reported here was less than 6 hr.

The experimentally observed geometries were used in all calculations, and these geometries are given in Table I. For SiH_4, the tetrahedral geometry is based on an experimental Si–H bond distance[15] of 1.4798 Å and the cartesian coordinates in Table I are those given by Boer and Lipscomb.[12] The PH_3 geometry is determined by the experimental values[16] of the P–H bond distance, 2.680 bohrs, and the H–P–H angle, 93° 22′, and the coordinates of Table I are those given by Boyd and Lipscomb.[11] For H_2S, the coordinates of Table I are those of Boer and Lipscomb,[12] obtained from an experimental[17] H–S bond distance of 1.328 Å and H–S–H bond angle of 92.2°. The HCl coordinates are based

Table I. Geometries Used in the Present Calculations on SiH_4, PH_3, H_2S, and HCl[a]

	x	y	z
SiH_4			
Si	0.0	0.0	0.0
H_1	1.61453	1.61453	1.61453
H_2	1.61453	−1.61453	−1.61453
H_3	−1.61453	1.61453	−1.61453
H_4	−1.61453	−1.61453	1.61453
PH_3			
P	0.0	0.0	0.0
H_1	2.251535	0.0	1.453614
H_2	−1.125767	−1.949887	1.453614
H_3	−1.125767	−1.949887	1.453614
H_2S			
S	0.0	0.0	0.0
H_1	1.74015	1.80828	0.0
H_2	1.74015	−1.80828	0.0
HCl			
Cl	0.0	0.0	0.0
H_1	2.4087	0.0	0.0

[a] Distances are in atomic units (1 au = 0.529172 Å).

on an experimental equilibrium separation[18] of 1.2746 Å.

Atomic Calculations

Veillard[19] has recently reported optimized gaussian basis sets for the second-row atoms Na through Ar. From this basis set of 12 s-type and 9 p-type primitive gaussians, Veillard considered 9 possible contractions[20] to form 6 s-type and 4 p-type contracted functions. However, Veillard's three best contractions (i.e., the three that yield the lowest energy for the atom) all contract the last two 2p gaussians to form a single function. To the present authors, however, it seems that the valence region (where Veillard's last two 2p functions are located) is the area in which a molecular basis set should have the most flexibility. This contention has been verified for a smaller molecule, H_2O, in a definitive study by Dunning.[21] Thus the most logical contraction for molecular calculations appeared to be one in which the 12 s-type functions were grouped as 6 2 1 1 1 1 and the 9 p-type functions were grouped as 6 1 1 1. The above notation for p orbitals indicates that the first six functions are contracted to form a single orbital, and the last three primitive gaussians are used directly in the calculation.

Table II indicates the energies obtained from SCF calculations on the atoms Si, P, S, and Cl using the above-discussed contraction. For the purpose of comparison with later molecular calculations, Table II contains a number of energy quantities besides the total energy.

Table III contains a comparison of SCF energies obtained from a wide variety of calculations[19,22-28] on the

(6) C. Carter, *Proc. Roy. Soc., Ser. A*, **235**, 321 (1956).

(7) R. Moccia, *J. Chem. Phys.*, **37**, 910 (1962); **40**, 2164, 2176, 2186 (1964).

(8) R. Moccia, *Theor. Chim. Acta*, **8**, 8 (1967).

(9) E. L. Albasiny and J. R. A. Cooper, *Proc. Phys. Soc.*, **85**, 1133 (1965).

(10) K. E. Banyard and R. B. Hake, *J. Chem. Phys.*, **41**, 3221 (1964); **43**, 2684 (1965); **44**, 3523 (1966); **45**, 3199 (1966).

(11) D. B. Boyd and W. N. Lipscomb, *ibid.*, **46**, 910 (1967).

(12) F. P. Boer and W. N. Lipscomb, *ibid.*, **50**, 989 (1969).

(13) A. Rauk and I. G. Csizmadia, *Can. J. Chem.*, **46**, 910 (1967).

(14) S. Rothenberg, P. Kollman, M. E. Schwartz, E. F. Hayes, and L. C. Allen, *Int. J. Quantum. Chem.*, **3S**, 715 (1970).

(15) D. R. J. Boyd, *J. Chem. Phys.*, **23**, 922 (1955).

(16) M. H. Sirvetz and R. E. Weston, *ibid.*, **21**, 898 (1953).

(17) Geometry recalculated by L. E. Sutton and D. H. Whiffen in "Tables of Interatomic Distances and Configurations in Molecules and Ions," Special Publication No. 18, The Chemical Society, London, 1965, using moments of inertia from H. C. Allen and E. K. Plyer, *J. Chem. Phys.*, **25**, 1132 (1956).

(18) G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Company, Princeton, N. J., 1950.

(19) A. Veillard, *Theor. Chim. Acta*, **12**, 405 (1968).

(20) J. L. Whitten, *J. Chem. Phys.*, **44**, 359 (1966); E. Clementi and D. R. Davis, *J. Comput. Phys.*, **2**, 223 (1967).

(21) T. H. Dunning, "Optimum Contractions of Gaussian Basis Functions for Use in LCGO-MO SCF Calculations on Molecules," unpublished.

(22) S. Huzinaga and Y. Sakai, *J. Chem. Phys.*, **50**, 1371 (1969).

(23) J. D. Petke, J. L. Whitten, and A. W. Douglas, *ibid.*, **51**, 256 (1969).

(24) E. Clementi and D. L. Raimondi, *ibid.*, **38**, 2686 (1963).

(25) E. Clementi, *ibid.*, **40**, 1944 (1964).

(26) P. S. Bagus and T. L. Gilbert, Appendix E to Argonne National Laboratory Report ANL-7271.

Table II. Total and Orbital Energies for the Ground States of the Si, P, S, and Cl Atoms Using a Particular Contraction (6 2 1 1 1 1 on s and 6 1 1 1 on p) of Veillard's 12s 2p Results[a]

	³P Si	⁴S P	³P S	²P Cl
Total energy	−288.83306	−340.69545	−397.48137	−459.45495
Potential energy	−577.51248	−681.23382	−794.83208	−918.75854
One-electron potential	−689.19403	−811.97741	−946.67146	−1094.07829
Two-electron potential	111.68155	130.74359	151.83938	175.31975
Kinetic energy	288.67941	340.53836	397.35071	459.30359
$-V/T$	2.00053	2.00046	2.00033	2.00033
Orbital energies				
1s	−68.82402	−79.98248	−92.01611	−104.89874
2s	−6.14790	−7.50369	−8.99825	−10.60273
2p	−4.25603	−5.40238	−6.68478	−8.07659
3s	−0.53893	−0.69555	−0.87858	−1.07194
3p	−0.29683	−0.39140	−0.43688	−0.50577

[a] Reference 19.

Table III. Comparison of Computed SCF Energies for the Ground States of the Si, P, S, and C Atoms[a]

Author	Type of calculation	³P Si	⁴S P	³P S	²P Cl
Veillard[19]	12s, 9p	−288.8486	−340.7121	−397.4978	−459.4741
Veillard[19]	Best 6s,[12] 4p[9] contraction	−288.8333	−340.6958	−397.4818	−459.4556
This work	6s,[12] 4p[9] contraction	−288.8331	−340.6955	−397.4814	−459.4550
Huzinaga and Sakai[22]	4s,[17] 3p[12] contraction	−288.8442	−340.7036	−397.4893	−459.4644
Petke, Whitten, and Douglas[23]	6s,[19] 3p[12] contraction	−288.8427	−340.7092	−397.4887	−459.4638
Clementi and Raimondi[24]	Minimal STO	−288.0900	−339.9099	−396.6276	−458.5237
Clementi[25]	Double ζ STO	−288.8503	−340.7140	−397.4990	−459.4738
Bagus and Gilbert[26]	6s, 5p, STO	−288.8542	−340.7185	−397.5045	−459.4816
Clementi[27]	Extended STO	−288.8543	−340.7187	−397.5048	−459.4819
Malli[28]	Extended STO	−288.8543	−340.7187	−397.5047	−459.4820

[a] The first five rows list calculations done with gaussian orbitals and the last five rows refer to calculations done with Slater-type orbitals.

Si, P, S, and Cl atoms. The present SCF calculations are no more than 0.0006 hartree higher in energy than the best contracted results of Veillard.[19] The gaussian lobe computations of Petke, et al.,[23] are comparable in energy to the cartesian gaussian results of Huzinaga and Sakai.[22] Both of these sets of calculations give about 0.01 hartree improvement over our energies, but they require a considerably larger number of primitive gaussian functions. Inspection of the atomic STO results indicates that the present results are almost 1 hartree below the minimal basis set energies,[24] and are roughly 0.02 hartree above the double ζ energies.[25] The most accurate SCF results are the STO functions of Clementi[27] and Malli,[28] and their results should be within 0.0001 hartree of the Hartree–Fock energies. Comparison with Malli's energies indicates that the present contracted gaussian results lie 0.0212, 0.0232, 0.0233, and 0.0270 hartree above the Hartree–Fock energies for Si, P, S, and Cl.

In order to test the hypothesis that our contracted gaussian basis was more suitable to molecular calculations than the best contraction of Veillard,[19] we performed SCF computations on HCl using both basis sets. In these and all following calculations, for hydrogen we used the five-term gaussian fit[29] to the exact 1s function, with a scale factor of 1.4. The first four hydrogen gaussians are contracted and the last is split off for added flexibility. Using Veillard's best contraction for the Cl atom, the HCl molecular SCF energy was −460.04487. Using our contraction for the Cl atom, an energy of −460.04851 was obtained. The energy improvement of 0.00364 seems to warrant the

use of the present contracted gaussian basis set in molecular SCF calculations involving second-row atoms.

Molecular Basis Set

We have discussed the s and p basis sets used for Si, P, S, and Cl and the s basis set used for H. However, it is now accepted[30] that in order to obtain accurate approximations to Hartree–Fock energies and molecular properties it is necessary to use additional functions to describe molecular charge distortion. The most commonly used procedure to describe this type of distortion or polarization is to include in the basis set functions of higher orbital angular momentum centered on each atom. In particular, for molecules containing Si, P, and S the use of d functions on the big atom has long been considered[31] an important contribution to bonding, since the 3d atomic orbital is nearly degenerate to the 3s and 3p orbitals.

In the present calculations we describe molecular distortion using a set of six d functions (d_{xx}, d_{yy}, d_{zz}, d_{xy}, d_{xz}, and d_{yz}) on the second-row atom and a set of three p functions on each hydrogen. Determining reasonable values of the exponents for these polarization functions is a fairly ambiguous task, in light of the fact that it was not economically feasible to optimize the exponents directly. In previous work[32] we had determined optimum exponents in the methane molecule for a set of d functions on the carbon (0.75) and a set of p functions on the hydrogen (1.08). We also made several trial

(27) E. Clementi, *IBM J. Res. Develop.*, **9**, 1 (1965).

(28) G. Malli, *Can. J. Phys.*, **44**, 3121 (1966).

(29) J. L. Whitten (unpublished), reported by W. H. Fink and L. C. Allen, *J. Chem. Phys.*, **46**, 2261 (1967).

(30) R. K. Nesbet, *Advan. Quantum Chem.*, **3**, 1 (1965).

(31) (a) L. Pauling, *J. Amer. Chem. Soc.*, **53**, 1367 (1931); (b) H. C. Longuet-Higgens, *Trans. Faraday Soc.*, **45**, 173 (1949); (c) R. S. Mulliken, *J. Amer. Chem. Soc.*, **72**, 4493 (1950); (d) W. Moffitt, *Proc. Roy. Soc., Ser., A*, **200**, 409 (1950); (e) D. P. Craig, A. Moccoll, R. S. Nyholm, L. E. Orgel, and L. E. Sutton, *J. Chem. Soc.*, 332 (1954); (f) D. P. Santry and G. A. Segal, *J. Chem. Phys.*, **47**, 158 (1967).

(32) S. Rothenberg, R. H. Young, and H. F. Schaefer, unpublished.

Table IV. Comparison between Properties Computed from the Present SCF Function and the Accurate Hartree–Fock Functions of Cade and Huo and McLean and Yoshimine for HCl[a]

Property	This SCF	Cade–Huo[b]	McLean–Yoshimine[c]	Experiment
E	−460.0785	−460.1103	−460.1119	−462.184[b]
Dissociation energy, eV	3.37	3.49	3.53	4.62[b]
Ionization potential, eV	12.94	12.96	12.96	12.74[d]
$\langle 1/r_{Cl} \rangle$	64.8060	64.8209	64.8218	
$\langle 1/r_H \rangle$	7.9929	7.9976	8.0007	
μ, D	1.381	1.196	1.215	1.12[e]
Quadrupole moment, 10^{-26} esu cm^2	3.85	3.80	3.74	3.75[f]
$\langle y^2 + z^2 \rangle$	20.9129	20.9017	20.8710	
$\langle x_{Cl}/r_{Cl}{}^3 \rangle$	0.1344	0.1617	0.1684	
$\langle x_H/r_H{}^3 \rangle$	−2.9119	−2.9406	−2.9393	
Force on Cl nucleus	−0.6456	−0.1821	−0.0682	0.0
Force on H nucleus	0.0182	−0.0105	−0.0092	0.0
$\langle (3x_{Cl}{}^2 - r_{Cl}{}^2)/r_{Cl}{}^5 \rangle$	−3.3561	−3.4694	−3.4192	
$\langle (3x_H{}^2 - r_H{}^2)/r_H{}^5 \rangle$	2.1169	2.1192	2.1527	
q_{Cl}	3.4992	3.6125	3.5623	
q_H	0.3160	0.3137	0.2802	

[a] Unless indicated, all entries are in atomic units as defined in following tables. [b] Reference 3b. [c] Reference 3a. [d] K. Watanabe, *J. Chem. Phys.*, **26**, 542 (1957). [e] C. A. Burrus, *ibid.*, **31**, 1270 (1959). [f] W. S. Benedict and R. Herman, *J. Quant. Spectrosc., Radiat. Transfer*, **3**, 265 (1963).

Table V. Total and Orbital Energies for Silane, Phosphine, Hydrogen Sulfide, and Hydrogen Chloride

	SiH$_4$	PH$_3$	H$_2$S	HCl
Total energy	−291.23550	−342.46030	−398.68624	−460.07852
Potential energy	−582.36053	−684.78081	−797.29530	−920.02492
One-electron potential	−736.73138	−850.61093	−975.33194	−1109.69245
Two-electron potential	133.03156	148.26981	165.00900	182.60978
Nuclear repulsion	21.22930	17.56032	13.02764	7.05775
Kinetic energy	291.12501	342.32051	398.60906	459.94642
$-V/T$	2.00038	2.00041	2.00019	2.00029
Orbital energies				
	$1a_1$, 68.78264	$1a_1$ 79.95660	$1a_1$ 91.97446	1σ, 104.86269
	$2a_1$, 6.11412	$2a_1$, 7.48150	$2a_1$, 8.96175	2σ, 10.57029
	$1t_x$, 4.22897	$1e_x$, 5.38410	$1b_2$, 6.65205	3σ, 8.04764
	$1t_y$, 4.22897	$1e_y$, 5.38410	$3a_1$, 6.65108	$1\pi_+$, 8.04416
	$1t_z$, 4.22897	$3a_1$, 5.38276	$1b_1$, 6.64879	$1\pi_-$, 8.04416
	$3a_1$, 0.73088	$4a_1$, 0.85618	$4a_1$, 0.98597	4σ, 1.11807
	$2t_x$, 0.48561	$2e_x$, 0.52158	$2b_2$ 0.59408	5σ, 0.62546
	$2t_y$, 0.48561	$2e_y$, 0.52158	$5a_1$, 0.50086	$2\pi_+$, 0.47543
	$2t_z$, 0.48561	$5a_1$, 0.38711	$2b_1$, 0.38342	$2\pi_-$, 0.47543

computations on the HCl molecule. Finally, we considered the results of Petke and Whitten,[33] who have optimized exponents in several molecules containing second-row atoms. On the basis of the above, we decided to use an exponent of 0.6 for the d functions on the Si, P, S, and Cl and an exponent of 0.75 for the hydrogen p functions.

Comparison with Accurate Hartree–Fock Results for HCl

We are fortunate to have the accurate Hartree–Fock results of McLean and Yoshimine[3a] and Cade and Huo[3b] with which to compare our SCF energies and molecular properties. Such a comparison can indicate the degree to which our results for SiH$_4$, PH$_3$, H$_2$S, and HCl approach the Hartree–Fock limit. This comparison is made in Table IV. The properties reported in Table IV are defined either by McLean and Yoshimine[3a] or by Neumann and Moskowitz.[34,35] Table IV is presented without discussion at this point, and its contents are referred to throughout the rest of the paper.

(33) J. D. Petke and J. L. Whitten, unpublished.
(34) D. B. Neumann and J. W. Moskowitz, *J. Chem. Phys.*, **49**, 2056 (1968).
(35) D. B. Neumann and J. W. Moskowitz, *ibid.*, **50**, 2216 (1969).

Molecular Energy Quantities

The calculated energies are given in Table V. It is seen from Table IV that the present SCF energy lies 0.0334 hartree above the Hartree–Fock energy of McLean and Yoshimine.[3a] Since our atomic SCF calculation proved 0.0270 above the HF energy, only about 0.0064 hartree of our deviation from the HF energy is due to an inadequate description of molecule formation. Although this error due to molecule formation will doubtless increase as the number of hydrogens in the molecule is increased from one in HCl to four in SiH$_4$, the error in the atom description *decreases* in going from Cl to Si by 0.0058. It thus seems reasonable to estimate that our SCF energies for SiH$_4$, PH$_3$, and H$_2$S are no more than 0.04 hartree above the corresponding Hartree–Fock energies. More information on this point is provided by an additional calculation on SiH$_4$ in which two d functions (exponents 0.4 and 0.9) were centered on the Si atom. The calculated SCF energy was −291.23714 hartrees, only 0.00164 hartree below the energy reported in Table V. Since the lack of a second d function is the most likely (other than the incomplete s and p atomic basis for Si) deficiency in our wave function, it indeed seems reasonable to assume that our first wave function for SiH$_4$ is within 0.04 hartree of the HF limit.

Table VI. Energies Obtained from Different *Ab Initio* Calculations on SiH_4, PH_3, H_2S, and HCl

Calculation	Reference	SiH_4	PH_3	H_2S	HCl
Numerical one-center	6	−290.02			
STO one-center	7	−290.1024	−341.3960	−397.5891	−458.8378
STO two-center	4				−459.421
STO two-center	5				−459.8037
Numerical one-center	9	−290.792			
United atom	10	−288.9797	−340.1048	−396.3672	−457.8014
STO one-center	8				−460.0581
STO two-center	3b				−460.1103
STO two-center	3a				−460.1119
STO multicenter	11, 12	−290.5197	−341.3094	−397.8415	
Gaussian multicenter	13			−381.0389	
This work gaussian					
$6s^{12} 4p^9/2s^6$					−460.0485
$6s^{12} 4p^9/2s^6 1p^1$		−291.2050			
$6s^{12} 4p^9 1d^1/2s^6 1p^1$		−291.2355	−342.4603	−398.6862	−460.0785
$6s^{12} 4p^9 2d^2/2s^6 1p^1$		−291.2371			

For comparison with the results of Boer and Lipscomb,[12] we also computed an SCF wave function using no d functions on the Si atom and obtained an energy of −291.20495 hartrees. Therefore it can be stated that the contribution of two d functions on Si is 0.03219 hartree, much less than the 0.0947 obtained by a similar process in the minimal basis set calculations of Boer and Lipscomb.[12] We hasten to point out, however, that the contribution of the d functions, 20.2 kcal/mol, is certainly large enough to be of chemical significance.

Table VI compares the present SCF energies with those obtained by previous authors.[2-13] It is seen that the one-center calculations generally lie at least 1 hartree above the energies obtained in this work. Exceptions are the more accurate calculations of Albasiny and Cooper[9] on SiH_4 and Moccia[8] on HCl. The calculations of Boyd and Lipscomb[11] and Boer and Lipscomb[12] roughly parallel the atomic minimal basis set calculations[24] in that they lie about 1 hartree above the Hartree–Fock results.

Calculated dissociation energies have been determined by subtracting the molecular SCF energy from the sum of the atomic SCF energies. Reference to Table IV shows that for HCl our SCF dissociation energy is 95% of the Hartree–Fock dissociation energy,[3a] and that the present calculated value differs by only 0.16 eV from the HF value. It therefore seems reasonable to assume that calculated dissociation energies for SiH_4, PH_3, and H_2S will also be quite close to the Hartree–Fock values. Table VII compares the SCF dissociation energies with the experimental values. The calculated values are, respectively, 82.5, 72.3, 80.2, and 72.9% of experiment for SiH_4, PH_3, H_2S, and HCl. Both the absolute agreement with experiment and the percentage consistency with respect to experiment are encouraging.

As indicated in Table IV, the HCl ionization potential predicted by Koopmans' theorem[36] from the present SCF computations is nearly identical with the Hartree–Fock value. This agreement can also be expected for SiH_4, PH_3, and H_2S. Table VIII compares calculated ionization potentials with experimental values. Agreement is quite good, the calculated values being 108, 104, 100, and 102% of experiment.

Table VIII. Calculated and Experimental Ionization Potentials, eV^a

Molecule	Calculated	Experimental
SiH_4	13.21	12.2^b
PH_3	10.53	$10.0,^c 10.2^d$
H_2S	10.43	10.42^e
HCl	12.94	12.74^f

^{a} Calculated values were obtained using Koopmans' theorem. ^{b} H. Neuert and H. Clasen, *Z. Naturforsch. A*, 7, 410 (1952). ^{c} F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press, New York, N. Y., 1957, p 115. ^{d} Y. Wada and R. W. Kiser, *Inorg. Chem.*, 3, 174 (1964). ^{e} W. C. Price, *J. Chem. Phys.*, 4, 147 (1936). ^{f} K. Watanabe, *ibid.*, 26, 542 (1957).

Population Analysis

We have performed a variety of Mulliken population analyses[37] on the SCF wave functions obtained, and some of the more interesting results are given in Table IX. As expected, the total atomic population on hydrogen decreases (rather uniformly) in going from Si to the more electronegative Cl. It is also seen that the big atom–H total overlap population decreases monotonically in going from SiH_4 to HCl. A serious difference between Table IX and the minimal basis set population analysis of Boyd and Lipscomb[11] and Boer and Lipscomb[12] concerns the amount of charge contained in 3d orbitals. For SiH_4, PH_3, and H_2S, they[11,12] obtained d orbital populations of 0.447, 0.290, and 0.147,

Table VII. Calculated and Experimental Dissociation Energies, eV^a

Molecule	Calculated	Experimental
SiH_4	10.97	13.3^b
PH_3	7.22	9.99^b
H_2S	5.58	6.96^c
HCl	3.37	4.62^d

^{a} The calculated dissociation energies were obtained by subtracting the molecular SCF energy from the sum of the big atom SCF plus the SCF energy of one, two, three, or four isolated hydrogen atoms. ^{b} S. R. Gunn and L. C. Green, *J. Phys. Chem.*, 65, 779 (1961). ^{c} Obtained by adding the H–SH dissociation energy (3.26 eV) to the dissociation energy of SH (3.70 eV). The H–SH dissociation energy is given by G. Herzberg, "Electronic Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., Princeton, N. J., 1966. The SH dissociation energy is that obtained by P. E. Cade and W. M. Huo, *J. Chem. Phys.*, 47, 649 (1967), using experimental data given by P. G. Wilkinson, *Astrophys. J.*, 138, 778 (1963). ^{d} Given by Cade and Huo; see footnote c above.

(36) T. Koopmans, *Physica*, 1, 104 (1933).
(37) R. S. Mulliken, *J. Chem. Phys.*, 23, 1833, 1841 (1955).

Table IX. Population Analyses from SCF Wave Functions for Si_4H, PH_3, H_2S, and HCl

	Total Atomic Populations			
SiH_4	Si	13.1975	H	1.2006
PH_3	P	14.7563	H	1.0812
H_2S	S	16.0975	H	0.9512
HCl	Cl	17.1774	H	0.8226

	Total Overlap Populations			
SiH_4	Si–H	0.7606	H–H	−0.0226
PH_3	P–H	0.7305	H–H	−0.0375
H_2S	S–H	0.6749	H–H	−0.0324
HCl	Cl–H	0.6400		

	Total d Orbital Populations
SiH_4	0.1080
PH_3	0.0819
H_2S	0.0627
HCl	0.0299

Molecular Properties

In reporting molecular properties, we use the symbols and definitions given by Neumann and Moskowitz.[34,35] Atomic units are used in most tables, with conversion factors to conventional units given in footnotes.

(A) Multipole Moments. For HCl, our calculated dipole and quadrupole moments are 114 and 103% of the Hartree–Fock values of McLean and Yoshimine[3a] (see Table IV). It seems likely that the calculated dipole and quadrupole moments of PH_3 and H_2S are within 20% of the Hartree–Fock values. The calculated molecular dipole moments μ, quadrupole moments θ, and octupole moments Ω are given in Table X. The calculated dipole moments are all larger than the experimental values, being 145, 131, and 123% of ex-

Table X. Calculated Multipole Moments, in Atomic Units, for the Ground States of SiH_4, PH_3, H_2S, and HCl. Experimental Moments Are Given in Parentheses[a]

Property	SiH_4	PH_3	H_2S	HCl
μ^a	0.0 (0.0)	0.3298 (0.227)[d]	0.5251 (0.401[e])	0.5433 (0.441[f])
$\theta_{\alpha\alpha}{}^b$	0.0	0.9297	2.1503	2.8626 (2.79[g])
$\theta_{\beta\beta}$	0.0	0.9297	0.7363	−1.4313 (1.39[g])
$\theta_{\gamma\gamma}$	0.0	−1.8593	−2.8866	−1.4313 (1.39[g])
Octupole moment[c]	Ω_{xyz} −5.3327	Ω_{xxx} −0.6342	Ω_{xxx} −0.9510	Ω_{xxx} −3.2361
Components Ω		Ω_{zzz} 1.2830	Ω_{xyy} 1.7990	Ω_{xyy} −1.6181
		Ω_{xxz} −0.6414	Ω_{xzz} −0.8480	Ω_{xzz} −1.6181
		Ω_{xyy} 0.6342		
		Ω_{yyz} −0.6416		

[a] For the dipole moment μ, 1 au = 2.54154 D. [b] For the quadrupole moment θ, 1 au = 1.344911 × 10⁻²⁶ esuc m². [c] For the octupole moment Ω, 1 au = 0.711688 × 10⁻³⁴ esu cm³. [d] C. A. Burrus, *J. Chem. Phys.*, **28**, 427 (1958). [e] R. E. Hillger and M. W. P. Strandberg, *Phys. Rev.*, **83**, 575 (1951). [f] C. A. Burrus, *J. Chem. Phys.*, **31**, 1270 (1959). [g] W. S. Benedict and R. Herman, *J. Quant. Spectrosc. Radiat. Transfer*, **3**, 265 (1963).

Table XI. Calculated and Experimental Magnetic Susceptibilities. $\chi_{\alpha\alpha}$, $\chi_{\beta\beta}$, $\chi_{\gamma\gamma}$ Are the Components of the Diamagnetic Susceptibility Tensor in the Principal Axis System[a]

	SiH_4	PH_3	H_2S	HCl
$\chi_{\alpha\alpha}$	−45.6941	−36.9566	−28.0951	−20.9129
$\chi_{\beta\beta}$	−45.6941	−36.9566	−28.0285	−23.6111
$\chi_{\gamma\gamma}$	−45.6941	−37.1892	−31.2103	−23.6111
$\langle r^2 \rangle_{cm}$	−68.5411	−55.5512	−43.6669	−34.0675
χ^d, 10⁻⁶ emu/mol				
Moccia[b]	−57.03	−46.23	−33.85	−27.28
Banyard and Hake[c]	−52.89	−40.93	−30.40	−22.46
Albasiny and Cooper[d]	−54.9			
Cade and Huo[e]				−27.0
McLean and Yoshimine[f]				−27.0
This work	−54.28	−44.00	−34.58	−26.98
χ_{TOT}, 10⁻⁶ emu/mol experimental[g]	−20.4	−26.2	−25.5	−22.1
χ^{hf}, 10⁻⁶ emu/mol predicted, this work	+33.9	+17.8	+9.1	+4.9

[a] Unless specified, all entries are in atomic units, 1 au = 0.280023 × 10⁻¹⁶ cm². [b] Reference 7. [c] Reference 10. [d] Reference 9. [e] Reference 3b. [f] Reference 3a. [g] Reference 41.

compared to our populations of 0.108, 0.082, and 0.063. One motivation for performing the previously discussed calculation on SiH_4 using two d functions was to see if a drastic increase occurred in the SiH_4 3d population. The new calculated SiH_4 3d population was 0.139, again far from the value given by Boer and Lipscomb.[12] We conclude that minimal basis set calculations on molecules containing second-row atoms give unrealistically large atomic populations in the 3d orbital. In other words, the 3d STO is being used to repair defects in the inadequate s and p basis.

periment. Only for HCl is the molecular quadrupole moment known from experiment, and our SCF quadruple moment is only 3% greater than experiment. In light of the expected difficulty[38] in calculating molecular quadrupole moments, this excellent agreement may be somewhat fortuitous. For SiH_4, PH_3, H_2S, and HCl, no octupole moments Ω have been determined experimentally, but we anticipate that the calculated values in Table X are correct in sign and order of magnitude.

(38) D. E. Stogryn and A. P. Stogryn, *Mol. Phys.*, **11**, 371 (1966); Krishnaji and V. Prakash, *Rev. Mod. Phys.*, **38**, 690 (1966).

(B) Diamagnetic Susceptibility. Elements of the diamagnetic susceptibility tensor x are calculated quantum mechanically from expectation values such as $\langle x^2 + y^2 \rangle$ relative to the center of mass. From Table IV it is seen that for HCl, the present SCF calculations give a value of $\langle x^2 + y^2 \rangle$ equal to 100.2% of McLean and Yoshimine's[3a] near-Hartree–Fock value. We conclude that the diamagnetic susceptibilities given in Table XI for SiH_4, PH_3, and H_2S are also very close to their Hartree–Fock values. It can be shown[39] that the average magnetic susceptibility of a molecule is a sum of a diamagnetic contribution and a paramagnetic contribution (called the high-frequency term)

$$\chi_{TOT} = \chi^d + \chi^{hf} \tag{1}$$

where χ^d is simply proportional to $\langle r^2 \rangle_{cm}$. We have computed values of χ^d from our SCF functions and these values are compared with previous calculations[3,7,9,10] in Table XI. It is obvious from eq 1 that, given an experimental value of χ_{TOT} and a calculated value of χ^d, one can predict the value of the paramagnetic term χ^{hf}. Such predictions are given for SiH_4, PH_3, H_2S, and HCl in Table XI. For H_2S, our predicted value of χ^{hf}, 9.1×10^{-6} emu/mol, can be compared to an experimental value[40] of $7.18 \pm 0.07 \times 10^{-6}$ emu/mol. Considering that the experimental values[41] of χ_{TOT} can be subject to uncertainties of 1×10^{-6} emu/mol, this seems to be rather good agreement.

(C) Potential. The potential at a nucleus is proportional to the expectation value $\langle 1/r \rangle$, where r is the distance from the nucleus. For HCl it can be seen in Table IV that the present SCF values of $\langle 1/r_H \rangle$ and $\langle 1/r_{Cl} \rangle$ are virtually identical (less than 0.1% difference) with the accurate Hartree–Fock results of McLean and Yoshimine.[3a] We conclude that the other calculated potentials, given in Table XII, are very close to their Hartree–Fock values.

Table XII. Potentials at the Big Atom A (A = Si, P, S, or Cl) and at Hydrogen[a]

	$\langle 1/r_A \rangle$	$\Phi(A)$	$\langle 1/r_H \rangle$	$\Phi(H)$
SiH_4	−50.6848	−49.2544	−6.7862	−1.1229
PH_3	−55.2691	−54.1497	−7.1913	−1.0815
H_2S	−60.0000	−59.2030	−7.6668	−1.0147
HCl	−64.8060	−64.3908	−7.9929	−0.9351

[a] All potentials are in atomic units and 1 au = 9.07618 esu/cm (or statvolts).

(D) Electric Fields and Forces. The force on a nucleus is given by the product of the nuclear charge and the electric field at the nucleus. For a molecule at its equilibrium geometry, the forces on all nuclei are zero. Table IV shows that for HCl the accurate SCF wave functions of Cade and Huo[3b] and McLean and Yoshimine[3a] predict substantially smaller forces at H and Cl than does our SCF wave function. This is not surprising since the force at a nucleus is an extremely sensitive measure of the accuracy of a wave function near the nucleus, where gaussian functions have their worst behavior. Calculated electric fields

Table XIII. Electric Fields and Forces at the Nuclei of the Big Atom A and the Hydrogen for SiH_4, PH_3, H_2S, and HCl[a]

	SiH_4	PH_3	H_2S	HCl
$E_x(A)$	0.0	0.0	−0.0422	−0.0380
$E_y(A)$	0.0	0.0	0.0	0.0
$E_z(A)$	0.0	−0.0361	0.0	0.0
$E_x(H)$	0.0031	0.0071	0.0093	0.0182
$E_y(H)$	0.0031	0.0	0.0157	0.0
$E_z(H)$	0.0031	0.0003	0.0	0.0
$F_x(A)$	0.0	0.0	−0.6746	−0.6456
$F_y(A)$	0.0	0.0	0.0	0.0
$F_z(A)$	0.0	−0.5416	0.0	0.0

[a] For hydrogen, the forces are identical with the electric fields. All quantities are in atomic units. For the electric field, 1 au = 0.171524×10^8 dyn/esu. For the force, 1 au = 0.823827×10^{-2} dyn.

and forces are given for all four molecules in Table XIII.

(E) Diamagnetic Shielding. The diamagnetic shielding, like the potential, is related to $\langle 1/r \rangle$, and thus from Table IV, our calculated elements of the diamagnetic shielding tensor σ should be very close to the Hartree–Fock values. Calculated elements of σ are given in Table XIV. Like the magnetic susceptibility, the average magnetic shielding is the sum of a diamagnetic term σ^d and a paramagnetic term.[42] Values in parts per million of σ^d are also given in Table XIV. Table XIV indicates that the average diamagnetic shielding at the proton increases monotonically in going from SiH_4 to HCl. From the average diamagnetic shielding for SiH_4, PH_3, H_2S, and HCl we have calculated the diamagnetic contribution to the proton chemical shifts relative to SiH_4. These results are given in Table XIV and compared with the experimental gas-phase chemical shifts.[43] It can be seen from the comparison that the paramagnetic contributions to the chemical shifts must be negative and nearly as large as the diamagnetic contributions.

(F) Electric Field Gradient at a Nucleus. The comparison in Table IV with the results of McLean and Yoshimine[3a] indicates that for HCl, our SCF field gradients at Cl and at H are 2 and 13% from the Hartree–Fock values. Work by others[44] seems to indicate that Hartree–Fock field gradients are within 10% of the exact field gradients. Table XV gives the calculated field gradients, charge densities at the nuclei, and values of the asymmetry parameter $\eta(x)$ at atom X

$$\eta(x) = [q_{\gamma\gamma}(x) - q_{\beta\beta}(x)]/q_{\alpha\alpha}(x) \tag{2}$$

where $|q_{\alpha\alpha}| \geq |q_{\beta\beta}| \geq |q_{\gamma\gamma}|$, the q's being the components of the electric field gradient tensor in the principal axis system.

The experimentally determined quantity related to the electric field gradient q is the quadrupole coupling constant eqQ. So we must multiply out computed values of q times an appropriate nuclear electric quadrupole moment Q in order to make a comparison with experiment. Unfortunately there is no accurate experimental method known for the direct determination of Q. In fact the most reliably known nuclear quad-

(39) J. H. Van Vleck, "Theory of Electric and Magnetic Susceptibilities," Oxford University Press, London, 1932.
(40) K. E. Banyard, *J. Chem. Phys.*, **36**, 1855 (1962).
(41) C. Barter, R. G. Meisensheimer, and D. P. Stevenson, *J. Phys. Chem.*, **64**, 1312 (1960).

(42) N. F. Ramsay, *Phys. Rev.*, **78**, 699 (1950).
(43) W. G. Schneider, H. J. Bernstein, and J. A. Pople, *J. Chem. Phys.*, **28**, 601 (1958).
(44) A. D. McLean and M. Yoshimine, *Bull. Amer. Phys. Soc.*, **13**, 373 (1968); C. T. O'Konski and T.-K. Ha, *J. Chem. Phys.*, **49**, 5354 (1968).

Table XIV. Quantities Related to the Diamagnetic Shielding[a]

	SiH$_4$	PH$_3$	H$_2$S	HCl
σ_{xx}(A)	−16.8949	−18.4039	−20.0632	−21.6549
σ_{yy}(A)	−16.8949	−18.4039	−20.0088	−21.5755
σ_{zz}(A)	−16.8949	−18.4614	−19.9279	−21.5755
σ^{d}(A), ppm	899.64	981.01	1064.98	1150.29
σ_{xx}(H)	−2.2621	4.2153	3.1983	6.2880
σ_{yy}(H)	−2.2621	−0.8821	−3.6007	−0.8524
σ_{zz}(H)	−2.2621	−2.0939	−0.8678	−0.8524
σ_{xy}(H)	−1.4222	0.0	−2.4801	0.0
σ_{xz}(H)	−1.4222	−1.9988	0.0	0.0
σ_{yz}(H)	−1.4222	0.0	0.0	0.0
σ^{d}(H), ppm	120.45	127.64	136.08	141.87
Diamagnetic contribution (ppm) to the proton chemical shift relative to SiH$_4$	0.0	7.19	15.63	21.42
Observed[b] proton chemical shift (ppm) relative to SiH$_4$	0.0	1.52	2.92	3.45

[a] Components are given with respect to both the big atom nucleus A and the hydrogen nucleus H. Unless indicated, entries are in atomic units; 1 au = 17.7497 ppm. [b] Reference 43.

Table XV. Electric Field Gradients and Charge Densities at the Nucleus and Asymmetry Parameters[a]

	SiH$_4$	PH$_3$	H$_2$S	HCl
$q_{\alpha\alpha}$(A)	0.0	1.2581	−0.3890	−3.4992
$q_{\beta\beta}$(A)	0.0	−0.6288	−2.1684	1.7499
$q_{\gamma\gamma}$(A)	0.0	−0.6288	2.5578	1.7499
$q_{\alpha\alpha}$(H)	0.0786	0.1026	0.1106	−0.3160
$q_{\beta\beta}$(H)	0.0786	0.0868	−0.2655	0.1580
$q_{\gamma\gamma}$(H)	−0.1571	−0.1893	0.1549	0.1580
$\delta\,(r - r_\text{A})$	1716.0379	2124.2673	2598.5013	3133.1535
$\delta\,(r - r_\text{H})$	0.4355	0.4320	0.4267	0.4023
η(A)		0.0	0.6959	0.0
η(H)	0.0	0.0834	0.1670	0.0

[a] All entries are in atomic units; 1 au (electric field gradient) = 0.324140 × 10^{16} esu/cm^3 (or statvolts/cm^2) and 1 au (charge density) = 4.80298 × 10^{-10} esu. The asymmetry parameter is dimensionless.

rupole moments Q are those deduced from experimental values of eqQ and accurate configuration-interaction wave functions[45] for atoms. However, accurate values of Q are not available for second-row atom nuclei.

For H$_2$^{33}S, the elements of the quadrupole coupling tensor at the sulfur atom have been measured by Burrus and Gordy[46] to be $eq_{\alpha\alpha}Q(^{33}\text{S}) = -8$, $eq_{\beta\beta}Q(^{33}\text{S}) = -32$, and $eq_{\gamma\gamma}Q(^{33}\text{S}) = 40$ MHz. From the calculated field gradients in Table XV, we deduce the quadrupole moment of ^{33}S to be −0.088, −0.063, and −0.067 barn, respectively. Since a small change in $q_{\alpha\alpha}$ would produce a large change in the predicted quadrupole moment, we take the average of the other two values and predict the nuclear electric quadrupole moment to be −0.065 barn. From the ratio[47] $Q(^{35}\text{S})/Q(^{33}\text{S}) = -0.695$, we also predict $Q(^{35}\text{S}) = +0.045$. These quadrupole moments are probably correct within 10% and can be compared with the values, $Q(^{33}\text{S}) = -0.06$ and $Q(^{35}\text{S}) = 0.04$ barn, predicted by Burrus and Gordy[46] using somewhat naive notions about spd hydridization.

The nuclear electric quadrupole moments of ^{35}Cl and ^{37}Cl can also be deduced, using the experimental quad-

rupole coupling constants[48] $eqQ(^{35}\text{Cl}) = -67.0$ and $eqQ(\text{Cl}^{37}) = 53.0$ MHz. However, rather than using our own SCF field gradient, we use the more accurate Hartree–Fock field gradient computed by McLean and Yoshimine.[3a] It seems unfortunate that McLean and Yoshimine[3a] did not make this simple prediction themselves. Nevertheless, we deduce $Q(^{35}\text{Cl}) = -0.080$ and $Q(^{37}\text{Cl}) = -0.063$ barn. These quadrupole moments have previously been predicted by a number of less reliable procedures, and it is interesting to note that the previously accepted average values,[49] $Q(^{35}\text{Cl}) = -0.079$ and $Q(^{37}\text{Cl}) = -0.062$, are in close agreement with those predicted on sound theoretical grounds here.

Conclusions

We have presented an accurate self-consistent-field study of the electronic structure of the isoelectronic series SiH$_4$, PH$_3$, H$_2$S, and HCl. This study provides qualitative and quantitative indications of the participation of d orbitals in these molecules. A large number of molecular properties have been reported: many of these properties are in good agreement with experiment, and it is hoped that this work will stimulate new experiments to test the other predicted properties given here. It has been possible to predict the most reliable values to date for the nuclear electric quadrupole moments of ^{33}S, ^{35}S, ^{35}Cl, and ^{37}Cl. Finally, this study sets the foundation for and demonstrates the accuracy and feasibility of SCF studies of larger molecules containing second-row atoms.

(45) H. F. Schaefer, R. A. Klemm, and F. E. Harris, *Phys. Rev.*, **176**, 49 (1968); **181**, 137 (1969).

(46) C. A. Burrus and W. Gordy, *ibid.*, **92**, 274 (1953).

(47) T. Wentink, W. S. Koski, and V. W. Cohen, *ibid.*, **81**, 948 (1951).

(48) C. A. Burrus, W. Gordy, B. Benjamin, and R. Livingston, *ibid.*, **97**, 1661 (1955).

(49) G. H. Fuller and V. W. Cohen, *Nuclear Data, Sect. A*, **5**, 433 (1969).