

Gaussian Basis Functions for Use in Molecular Calculations. III. Contraction of (10s6p) Atomic Basis Sets for the First-Row Atoms

THOM. H. DUNNING, JR.

Battelle Memorial Institute, Columbus, Ohio 43201

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Contracted [5s3p] and [5s4p] Gaussian basis sets for the first-row atoms are derived from the (10s6p) primitive basis sets of Huzinaga. Contracted [2s] and [3s] sets for the hydrogen atom obtained from primitive sets ranging in size from (4s) to (6s) are also examined. Calculations on the water and nitrogen molecules indicate that such basis sets when augmented with suitable polarization functions should yield wavefunctions near the Hartree-Fock limit.

I. INTRODUCTION

In a previous paper¹ contraction of the (9s5p) Gaussian basis sets of Huzinaga for the first-row atoms was examined in some detail. Although the contracted sets put forward at that time are capable of yielding molecular wavefunctions of rather high accuracy, larger, more flexible sets are required in order to closely approach the Hartree-Fock limit. In addition, functions must be added to the atomic (*sp*) sets to describe the polarization effects resulting from molecular formation. The representation of polarization functions for the first-row atoms and hydrogen is investigated in a subsequent paper in this series.² In the present paper, to further improve on the atomic (*sp*) basis, we consider the contraction of the (10s6p) primitive basis sets of Huzinaga³ for the first-row atoms lithium through neon as well as selected primitive sets for the hydrogen atom. As the results to be presented later indicate, the contracted basis sets derived from these primitive sets when augmented with suitable polarization functions should yield molecular wavefunctions of essentially Hartree-Fock accuracy. This conclusion is supported by the calculation of Moskowitz, Neumann, and co-workers⁴ with the corresponding uncontracted sets.

II. CONTRACTION OF THE ATOMIC (10s6p) GAUSSIAN BASIS SETS FOR THE FIRST-ROW ATOMS

In the first article¹ of this series it was argued that contracted Gaussian basis sets suitable for use in *molecular* calculations can be obtained from *atomic* calculations if the nature of the molecular environment is taken into account. For internuclear distances of ordinary chemical interest, only the valence orbitals of the atoms are modified to any appreciable extent by molecular formation; the inner-shell orbitals remain essentially atomic in character. In accordance with this observation it has been found^{1,5} that a basis set for use in molecular calculations must combine flexibility in the valence regions with an adequate description of the atomic inner shells.

First, let us consider the contraction of the *s* sets in the (10s6p) primitive sets of Huzinaga³ for the first-row atoms (the oxygen atom will be used as an example when appropriate). The two most diffuse *s* functions

are the principle components of the atomic 2s orbital and thus, their coefficients should be allowed to vary freely. Such flexibility in the valence region is necessary in order to be able to respond to the changes which will be brought about by molecular formation. The next function (in order of increasing orbital exponent) makes a positive contribution to both the 1s and 2s atomic orbitals (except for lithium; see Appendix A). Because of the partial valence character of this function, it should also be left uncontracted. This now leaves only the seven functions which describe the 1s core region to be contracted.

TABLE I. Contraction of the oxygen *s* set: Hartree-Fock calculations on the oxygen atom and the water molecule.^a

Contracted <i>s</i> set	<i>s</i> split ^b	Hartree-Fock energy	
		O(³ P)	H ₂ O(¹ A ₁)
[6s]	(5/1/1/1/1)	-74.8060 a.u.	-76.0207 a.u.
Hartree-Fock energy difference ^c			
[5s]	(6/1/1/1/1)	0.0053	0.0050
	(5/2/1/1/1)	0.0057	...
	(6/1/1/1/1) ^d	0.0235	...
	(6/2/1/1/1) ^e	0.0000	0.0000

^a The oxygen (6p) set has been contracted to [4p], split *p*(3/1/1/1), and the hydrogen (5s) has been contracted to [3s], split *h*(3/1/1), with an effective Slater exponent of 1.49.

^b In the contraction splitting (*P/Q/R/...*) indicates that the first *P* primitives are grouped together, the next *Q* together, and so on. The functions are ordered with the higher exponents to the left.

^c Energy differences are relative to those obtained with the [6s] set.

^d In this set *s*₇ has been grouped with (*s*₁, ..., *s*₅); *s*₆ is uncontracted.

^e One of the primitive functions has been included in two of the contracted functions.

On the basis of the previous studies,^{1,5} it was decided that two contracted functions should be sufficient to describe the 1s core region. To establish a reference point calculations were carried out on the oxygen atom and water molecule with three contracted core functions split *s*(5/1/1).⁶ The results of these calculations are given in Table I. Contracting the seven primitive core functions in this manner raises the energy by only 0.0003 a.u. for the oxygen atom. Comparing the ratios of the coefficients of the primitive functions in the

TABLE II. Contraction of the hydrogen primitive s sets: Hartree-Fock calculations on the water molecule.

Contracted s set ^a	Primitive s set	Scale ^b	h split ^c	Energy E_{HF}	Dipole moment μ
[2s]	(4s)	1.275	(3/1)	-76.0190 a.u.	1.0638 a.u.
	(5s)	1.325	(4/1)	-76.0185	1.0670
	(5s)	1.48	(3/2)	-76.0194	1.0725
[3s]	(5s)	1.49	(3/1/1)	-76.0203	1.0699
	(6s)	1.64	(4/1/1)	-76.0196	1.0743

^a The oxygen (10s6p) set has been contracted to [5s3p]; see text.^c See Footnote b of Table I.^b The scale is the effective Slater exponent for the s -set expansion. In each case it has been optimized.

atomic 1s and 2s orbitals,³ we see that the sixth s function (denoted as s_6) cannot be contracted with s_5 , ($c_6^{1s}/c_5^{1s}=1.94$ whereas $c_6^{2s}/c_5^{2s}=2.34$)⁷ or with s_7 ($c_7^{1s}/c_6^{1s}=0.87$ while $c_7^{2s}/c_6^{2s}=1.42$). Nor can s_7 be contracted with s_5 ($c_7^{1s}/c_5^{1s}=1.69$ compared to $c_7^{2s}/c_5^{2s}=3.32$). The increase in the Hartree-Fock energy of the oxygen atom over that obtained with the [3s] core set⁸ resulting from use of any of the above groupings is given in Table I. These results indicate that the seven primitive core functions cannot be contracted to two *disjoint* sets of functions without undue loss of energy. As illustrated for the chlorine atom,⁵ however, such a situation can often be satisfactorily resolved just by grouping s_6 with both s_5 and s_7 . Although duplication of one of the primitive functions effectively increases the size of the primitive set by one, the resulting increase in the time for calculation of the integrals can be more than offset by the decrease in the time required to solve the self-consistent-field equations.

If a primitive function is duplicated, two parameters must be specified—the contributions of this function to each of the two contracted functions. In the calculations on the second-row atoms⁵ these were determined by optimizing the ratio of the coefficients of the duplicated function in each contracted function under the constraint that the coefficient of the duplicated function in the atomic 1s orbital be that obtained from the calculation with the primitive set. In the present case, however, utilizing the results of the calculations with the [6s] sets (containing the three core functions), these parameters can be determined analytically. If d_j^{is} represents the coefficient of the j th contracted function in the atomic is orbital from a calculation with the [6s] set, then x and y , the contribution of the duplicated function to the two contracted functions replacing the three core functions, can be obtained by solving the following two equations:

$$\begin{aligned} d_1^{1s}x + d_3^{1s}y &= d_2^{1s}, \\ d_1^{2s}x + d_3^{2s}y &= d_2^{2s} \end{aligned} \quad (1)$$

(where the second function is the one duplicated). In this case, with two variables, the contributions of the duplicated function to each contracted function, and two conditions to be satisfied, the coefficients of the

duplicated function in the atomic 1s and 2s orbitals, redundant contraction of s_6 *completely* eliminates the loss in energy upon contracting the [6s] set to a [5s] set.⁹ Energies obtained for the oxygen atom and water molecule with the contracted [5s] oxygen set derived in this manner are listed in the last row of Table I.

The (6p) primitive set for the first-row atoms can be contracted to either a [3p] set, split $p(4/1/1)$, or a [4p] set, split $p(3/1/1/1)$. Contracting the (6p) set to fewer than three functions would be inconsistent with the flexibility inherent in the primitive set and would result in a significant deterioration in the over-all quality of the charge distribution. In fact, as we shall see in the fourth section, even the [3p] set is a *slight* overcontraction of the (6p) set.

Contracted [5s3p] and [5s4p] basis sets for the first-row atoms obtained from the (10s6p) sets of Huzinaga³ are given in Appendix A. Total energies, virial ratios, orbital energies, and expansion coefficients from matrix Hartree-Fock calculations on those states arising from the ground-state configuration, $1s^2 2s^2 2p^N$, are tabulated in Appendix B.

Huzinaga and Arnau¹⁰ have recently published contracted sets obtained from (11s6p) primitive sets. For the atoms they obtain Hartree-Fock energies essentially identical to those given here. However, their contracted s sets contain three core functions and only one valence function, a situation which would be far from optimal in a molecule. In addition, the flexibility of the primitive p set has been severely limited by grouping together those p functions most concentrated in the valence region. In conclusion, for molecular calculations their basis sets *as is* will be decidedly inferior to those put forward here. While accurate atomic energies are a necessary condition for a satisfactory molecular basis set, they alone are not sufficient.

Contraction of the (10s6p) sets of Huzinaga has also been considered by Basch and co-workers.¹¹

III. CONTRACTION OF HYDROGEN PRIMITIVE SETS

From the hydrogen atom a number of two- and three-term contracted sets obtained from primitive sets ranging in size from (4s) to (6s) were considered.¹² A brief

TABLE III. Calculations on the water molecule with the recommended contracted basis sets: total energies, orbital energies, and selected one-electron properties. All quantities are in atomic units.

Properties ^b	[4s3p/2s] ^c	Contracted set ^a	
		[5s3p/3s]	[5s4p/3s]
E_{HF}	-76.0109	-76.0203	-76.0207
$-V/T$	1.9998	2.0001	2.0001
$\epsilon(1a_1)$	-20.5629	-20.5667	-20.5667
$\epsilon(2a_1)$	-1.3616	-1.3656	-1.3653
$\epsilon(1b_1)$	-0.7158	-0.7196	-0.7194
$\epsilon(3a_1)$	-0.5668	-0.5702	-0.5704
$\epsilon(1b_2)$	-0.5060	-0.5087	-0.5087
μ^d	1.0554	1.0699	1.0678
$\langle x Q^2 \rangle^{e,f}$	7.2110	7.1963	7.2008
$\langle y Q^2 \rangle$	5.5020	5.5841	5.5791
$\langle z Q^2 \rangle$	6.5155	6.5637	6.5627
$\Theta_{yy}(Q)^g$	-1.7270	-1.7923	-1.7857
$\Theta_{zz}(Q)$	-0.1303	-0.1448	-0.1440
$\langle 1/r_H \rangle^e$	5.7414	5.7376	5.7382
$\langle 1/r_O \rangle$	23.4386	23.4354	23.4352
$E_x(H1)^h$	0.0919	0.0946	0.0941
$E_z(H1)$	0.0315	0.0340	0.0340
$E_z(O)$	-0.1927	-0.2094	-0.1529
$q_{\alpha\alpha}(D1)^{i,j}$	0.2421	0.2413	0.2390
$q_{\beta\beta}(D1)$	-0.5490	-0.5474	-0.5431
ϕ	2°44'	2°36'	2°36'
$q_{xx}(O)^i$	-1.9113	-1.8213	-1.8997
$q_{zz}(O)$	-0.2023	-0.2169	-0.2088
$\langle \delta(r-H) \rangle^k$	0.4273	0.4426	0.4430
$\langle \delta(r-O) \rangle$	295.0690	299.9973	299.9983

^a The effective Slater exponent for the hydrogen s functions ($\zeta=1.49$) was optimized.

^b For definitions of the properties see Ref. 1.

^c Taken from Ref. 2.

^d Dipole moment: 1 a.u. = 2.54158 D.

^e This property has only an electronic contribution.

^f Q is the point (0.0, 0.0, 0.1176). This point was mistakenly referred to as the center of mass in Ref. 1. For comparison we use this point here also.

^g Quadrupole moment: 1 a.u. = 1.34492 buckingham.

^h Electric fields: 1 a.u. = 1.71524×10^7 esu/cm².

ⁱ Electric field gradients: 1 a.u. = 3.24140×10^{18} esu/cm³.

^j The axes (α, β, γ) are the principle axes of the deuterium field gradient tensor. The β axis is tilted off the OH bond axis by an angle of φ (a positive value corresponding to a cant toward the other hydrogen).

^k Density (electrons/atomic units cubed).

summary of the calculations on the water molecule with these sets is given in Table II. For each hydrogen s set the scale has been optimized, i.e., all of the exponents in the set were multiplied by a common factor the value of which was optimized.

For the contracted sets containing two functions we see that the (5s) set split $s(3/2)$ yields a slightly lower energy (0.0004 a.u.) than the (4s) set split $s(3/1)$, whereas the same (5s) set split $s(4/1)$ actually yields

a worse energy. For the sets with three contracted functions, the (5s) set split $s(3/1/1)$ gives a somewhat lower energy than the (6s) set split $s(4/1/1)$. Finally, for water the best contracted [3s] set for the hydrogens yields an energy 0.0013 a.u. lower than the [2s] recommended in previous work.¹³ These results once again illustrate the interplay between the primitive and contracted sets. The advantages gained by use of a large, flexible primitive set are easily lost by too severe a contraction.

The [3s] contracted basis set for hydrogen obtained from the (5s) primitive set of Huzinaga³ is given in Appendix A.

IV. CALCULATIONS ON THE WATER AND NITROGEN MOLECULES

In order to test the efficacy of the proposed [5s3p] and [5s4p] contracted basis sets for the first-row atoms, matrix Hartree-Fock calculations were carried out for the water and nitrogen molecules. The geometry for both systems is identical to that used previously,^{1,14} namely, for water the OH distance is 1.8111 a.u. and the HOH angle 104°27' while for nitrogen the internuclear distance is 2.068 a.u. For water the xz plane is the molecular plane, z being the symmetry axis, and for nitrogen the z axis is the internuclear axis. The results of these calculations are given in Tables III and IV.

TABLE IV. Calculations on the nitrogen molecule with the recommended contracted basis sets, total energies, orbital energies, and selected one-electron properties. All quantities are in atomic units.

Properties ^a	[4s3p] ^b	Contracted set	
		[5s3p]	[5s4p]
E_{HF}	-108.8877	-108.9008	-108.9038
$-V/T$	1.9998	2.0002	2.0006
$\epsilon(1\sigma_g)$	-15.7072	-15.7085	-15.7098
$\epsilon(1\sigma_u)$	-15.7036	-15.7049	-15.7062
$\epsilon(2\sigma_g)$	-1.5252	-1.5272	-1.5252
$\epsilon(2\sigma_u)$	-0.7723	-0.7741	-0.7747
$\epsilon(3\sigma_g)$	-0.6267	-0.6304	-0.6308
$\epsilon(1\pi_u)$	-0.6237	-0.6251	-0.6237
$\langle x^2 \rangle_{e.m.}^c$	7.5704	7.6016	7.5961
$\langle z^2 \rangle_{e.m.}$	24.3304	24.3579	24.3625
$\Theta_{zz}(\text{c.m.})^e$	-1.7918	-1.7881	-1.7982
$\langle 1/r_N \rangle$	21.6367	21.6339	21.6319
$E_z(N1)$	-0.2138	-0.2241	-0.1565
$q_{zz}(N1)$	1.2480	1.2532	1.1656
$\langle \delta(r-N) \rangle$	195.4258	198.7184	198.7409

^a For definitions of the operators see the footnotes to Table III.

^b Taken from Ref. 1.

^c The center of mass of the nitrogen molecule is at (0.0, 0.0, 1.034).

TABLE V. Contracted Gaussian basis sets for the first-row atoms lithium–neon derived from the (10s) and (10s6p) primitive sets.

Lithium ^a			Beryllium					
<i>s</i> exponents		Coefficients [4 <i>s</i>]	<i>s</i> exponents		Coefficients [5 <i>s</i>]			
1783.		0.000824	3630.		0.000839			
267.1		0.006403	532.3		0.006735			
60.07		0.033239	117.8		0.035726			
16.78		0.126621	32.66		0.138635			
5.403		0.337749	10.48		0.385399			
1.906		0.575669	3.668		0.547688			
0.2634		0.062311	3.668		0.213406			
					0.814692			
0.7179		1.000000	1.354		1.000000			
0.07716		1.000000	0.3890		1.000000			
0.02854		1.000000	0.1502		1.000000			
			0.05241		1.000000			
Boron			Carbon			Nitrogen		
<i>s</i> exponents		Coefficients [5 <i>s</i>]	<i>s</i> exponents		Coefficients [5 <i>s</i>]	<i>s</i> exponents		Coefficients [5 <i>s</i>]
6250.		0.000798	9471.		0.000776	13 520.		0.000760
916.1		0.006410	1398.		0.006218	1 999.		0.006076
202.2		0.034299	307.5		0.033575	440.0		0.032847
55.83		0.135487	84.54		0.134278	120.9		0.132396
17.86		0.388532	26.91		0.393668	38.47		0.393261
6.253		0.547758	9.409		0.544169	13.46		0.546339
6.253		0.232643	9.409		0.248075	13.46		0.252036
2.312		0.797219	3.500		0.782844	4.993		0.779385
0.6824		1.000000	1.068		1.000000	1.569		1.000000
0.2604		1.000000	0.4002		1.000000	0.5800		1.000000
0.08940		1.000000	0.1351		1.000000	0.1923		1.000000
Coefficients			Coefficients			Coefficients		
<i>p</i> exponents	[3 <i>p</i>]	[4 <i>p</i>]	<i>p</i> exponents	[3 <i>p</i>]	[4 <i>p</i>]	<i>p</i> exponents	[3 <i>p</i>]	[4 <i>p</i>]
15.46	0.016822	0.040494	25.37	0.016295	0.038802	35.91	0.016916	0.040319
3.483	0.100878	0.242838	5.776	0.102098	0.243118	8.480	0.102200	0.243602
1.066	0.336895	0.810987	1.787	0.340228	0.810162	2.706	0.338134	0.805968
0.3928	0.672317	1.000000	0.6577	0.668269	1.000000	0.9921	0.669281	1.000000
0.1503	1.000000	1.000000	0.2480	1.000000	1.000000	0.3727	1.000000	1.000000
0.05722	1.000000	1.000000	0.09106	1.000000	1.000000	0.1346	1.000000	1.000000

TABLE V (Continued)

Oxygen			Fluorine			Neon		
<i>s</i> exponents	Coefficients [5 <i>s</i>]		<i>s</i> exponents	Coefficients [5 <i>s</i>]		<i>s</i> exponents	Coefficients [5 <i>s</i>]	
18 050.	0.000757		23 340.	0.000757		28 660.	0.000767	
2 660.	0.006066		3 431.	0.006081		4 263.	0.006068	
585.7	0.032782		757.7	0.032636		946.8	0.032474	
160.9	0.132609		209.2	0.131704		261.5	0.131468	
51.16	0.396839		66.73	0.396240		83.34	0.397723	
17.90	0.542572		23.37	0.543672		29.17	0.542491	
17.90	0.262490		23.37	0.264893		29.17	0.269065	
6.639	0.769828		8.624	0.767925		10.76	0.764121	
2.077	1.000000		2.692	1.000000		3.343	1.000000	
0.7736	1.000000		1.009	1.000000		1.241	1.000000	
0.2558	1.000000		0.3312	1.000000		0.4063	1.000000	
Coefficients			Coefficients			Coefficients		
<i>p</i> exponents	[3 <i>p</i>]	[4 <i>p</i>]	<i>p</i> exponents	[3 <i>p</i>]	[4 <i>p</i>]	<i>p</i> exponents	[3 <i>p</i>]	[4 <i>p</i>]
49.83	0.016358	0.037778	65.66	0.016037	0.037012	84.84	0.015550	0.036154
11.49	0.106453	0.245844	15.22	0.105697	0.243943	19.71	0.103011	0.239503
3.609	0.349302	0.806685	4.788	0.350227	0.808302	6.219	0.349215	0.811934
1.321	0.657183	1.000000	1.732	0.658195	1.000000	2.211	0.662839	1.000000
0.4821	1.000000	1.000000	0.6206	1.000000	1.000000	0.7853	1.000000	1.000000
0.1651	1.000000	1.000000	0.2070	1.000000	1.000000	0.2566	1.000000	1.000000

^a For lithium the set contains only four *s* functions.

Comparing the [5*s*3*p*] and [5*s*4*p*] sets with the [4*s*3*p*] sets put forward earlier,¹ we see that for the present sets the total energies of the water and nitrogen molecules are lower by ~ 0.01 and ~ 0.015 a.u., respectively. Part of the decrease in the molecular energy can, of course, be attributed to an improved description of the nitrogen and oxygen atoms. To some extent this can be taken into account by comparing the calculated binding energies rather than the total energies. For the water molecule the binding energy increases by 0.0020 and 0.0024 a.u. for the [5*s*3*p*/3*s*] and [5*s*4*p*/3*s*] sets, respectively; for nitrogen the corresponding figures are 0.0045 and 0.0075 a.u. These increases are a measure of the ability of the basis set to respond to those changes brought about by molecular formation.

Differences in the one-electron properties obtained with the present sets and the [4*s*3*p*] sets proposed earlier are typically 1%–5%. The exceptions are the quadrupole moment (in water only) and the electric fields and field gradients at the oxygen and nitrogen nuclei; the changes in these properties range 5%–15%.

Comparing the [5*s*3*p*] and [5*s*4*p*] sets, we find that the differences in the energies of the two sets is insignificant for water (0.0004 a.u.), although of some consequence for nitrogen (0.0030 a.u.). For the most part

TABLE VI. Contracted [3*s*] Gaussian basis set for the (5*s*) hydrogen primitive set. The scale factor is unity.

Exponents ^a	Coefficients [3 <i>s</i>]
33.64	0.025374
5.058	0.189684
1.147	0.852933
0.3211	1.000000
0.1013	1.000000

^a Exponents for the scale factor of 1.49, which is optimum for water, are (74.69, 11.23, 2.546, 0.7130, 0.2249); the contracted functions are normalized for this scale factor.

TABLE VII. Hartree-Fock energies, virial ratios, and orbital energies and expansion coefficients for those states of the first-row atoms lithium-neon derived from the ground-state configuration. Basis set: [5s3p].

Atom state	Lithium ^a $2S$	Beryllium $1S$	Boron $2P$	Carbon $3P$	Carbon $1D$	Carbon $1S$	Nitrogen $4S$
E_{HF}	-7.43237	-14.57253	-24.52818	-37.68716	-37.62982	-37.54781	-54.39869
$-V/T$	1.99967	1.99995	1.99996	1.99997	2.00004	2.00006	1.99998
Orbital	1s	1s	1s	1s	1s	1s	1s
ϵ_{1s}	-2.47718	-4.73240	-7.69512	-11.32530	-11.35161	-11.39076	-15.62858
1s	0.72946	0.62674	0.59418	0.57611	0.57618	0.57626	0.55813
1s'	0.33030	0.41659	0.44374	0.45720	0.45728	0.45739	0.47106
2s	-0.00169	0.03703	0.04400	0.04876	0.04852	0.04821	0.05351
2s'	0.00091	-0.00788	-0.00807	-0.00755	-0.00754	-0.00754	-0.00661
2s''		0.00182	0.00208	0.00213	0.00212	0.00212	0.00201
Orbital	2s	2s	2s	2s	2s	2s	2s
ϵ_{2s}	-0.19617	-0.30917	-0.49458	-0.70542	-0.71824	-0.73815	-0.94488
1s	-0.12636	-0.12118	-0.12750	-0.13065	-0.13130	-0.13229	-0.13091
1s'	-0.15792	-0.18853	-0.20861	-0.21913	-0.22059	-0.22280	-0.22637
2s	0.52998	0.04503	0.07109	0.08155	0.08387	0.08732	0.07876
2s'	0.56225	0.59342	0.60651	0.60949	0.61528	0.62410	0.60621
2s''		0.47097	0.44399	0.43716	0.42989	0.41882	0.44586
Orbital			2p	2p	2p	2p	2p
ϵ_{2p}			-0.30965	-0.43306	-0.38088	-0.30869	-0.56708
2p			0.53189	0.53682	0.52436	0.50785	0.53615
2p'			0.43631	0.43282	0.41448	0.38115	0.42652
2p''			0.19787	0.20335	0.24381	0.30676	0.21523
Atom state	Nitrogen $2D$	Nitrogen $2P$	Oxygen $3P$	Oxygen $1D$	Oxygen $1S$	Fluorine $2P$	Neon $1S$
E_{HF}	-54.29382	-54.22558	-74.80599	-74.72580	-74.60738	-99.40449	-128.54045
$-V/T$	2.00007	2.00011	1.99999	2.00005	2.00013	1.99999	1.99999
Orbital	1s	1s	1s	1s	1s	1s	1s
ϵ_{1s}	-15.66625	-15.69126	-20.66812	-20.69291	-20.73000	-26.38184	-32.77129
1s	0.55820	0.55824	0.54944	0.54948	0.54953	0.53756	0.53333
1s'	0.47115	0.47121	0.47885	0.47889	0.47895	0.48913	0.49288
2s	0.05327	0.05311	0.05436	0.05424	0.05407	0.05672	0.05720
2s'	-0.00661	-0.00661	-0.00670	-0.00670	-0.00670	-0.00673	-0.00673
2s''	0.00201	0.00201	0.00212	0.00212	0.00212	0.00218	0.00226
Orbital	2s	2s	2s	2s	2s	2s	2s
ϵ_{2s}	-0.96280	-0.97498	-1.24370	-1.25557	-1.27361	-1.57155	-1.92913
1s	-0.13155	-0.13198	-0.13279	-0.13310	-0.13357	-0.13249	-0.13346
1s'	-0.22785	-0.22883	-0.23338	-0.23410	-0.23519	-0.23857	-0.24229
2s	0.08096	0.08243	0.09173	0.09285	0.09452	0.09368	0.10488
2s'	0.61199	0.61585	0.61066	0.61339	0.61748	0.60989	0.61668
2s''	0.43875	0.43398	0.43296	0.42952	0.42435	0.43344	0.41852
Orbital	2p	2p	2p	2p	2p	2p	2p
ϵ_{2p}	-0.50780	-0.46999	-0.63118	-0.59971	-0.55393	-0.72891	-0.84904
2p	0.52730	0.52180	0.54463	0.54111	0.53606	0.54868	0.55100
2p'	0.41135	0.40020	0.42494	0.41875	0.40887	0.42272	0.42040
2p''	0.24689	0.26839	0.21969	0.23285	0.25279	0.22396	0.22772

^a For lithium the set contains only four s functions.

TABLE VIII. Hartree-Fock energies, virial ratios, and orbital energies and expansion coefficients for those states of the first-row atoms boron-neon derived from the ground-state configuration. Basis set: $[5s4p]$.

Atom state	Boron 2P	Carbon 3P	Carbon 1D	Carbon 1S	Nitrogen 4S	Nitrogen 2D
E_{HF}	-24.52818	-37.68716	-37.62985	-37.54790	-54.39869	-54.29385
$-V/T$	1.99996	1.99997	1.99995	1.99987	1.99998	1.99995
Orbital	1s	1s	1s	1s	1s	1s
ϵ_{1s}	-7.69512	-11.32530	-11.35086	-11.38903	-15.62858	-15.66518
1s	0.59418	0.57611	0.57617	0.57624	0.55813	0.55819
1s'	0.44374	0.45720	0.45728	0.45738	0.47106	0.47115
2s	0.04400	0.04876	0.04855	0.04827	0.05351	0.05330
2s'	-0.00807	-0.00755	-0.00756	-0.00756	-0.00661	-0.00662
2s''	0.00208	0.00213	0.00213	0.00213	0.00201	0.00202
Orbital	2s	2s	2s	2s	2s	2s
ϵ_{2s}	-0.49458	-0.70542	-0.71816	-0.73781	-0.94488	-0.96270
1s	-0.12750	-0.13065	-0.13130	-0.13227	-0.13091	-0.13155
1s'	-0.20861	-0.21913	-0.22057	-0.22274	-0.22637	-0.22782
2s	0.07109	0.08155	0.08381	0.08719	0.07876	0.08090
2s'	0.60651	0.60949	0.61521	0.62389	0.60621	0.61193
2s''	0.44399	0.43716	0.42999	0.41911	0.44586	0.43884
Orbital	2p	2p	2p	2p	2p	2p
ϵ_{2p}	-0.30965	-0.43306	-0.38091	-0.30871	-0.56708	-0.50781
2p	0.22096	0.22544	0.22236	0.21750	0.22494	0.22294
2p'	0.35760	0.35873	0.34584	0.33053	0.35883	0.34925
2p''	0.43631	0.43283	0.41941	0.39106	0.42652	0.41527
2p'''	0.19787	0.20334	0.24123	0.30132	0.21523	0.24486
Atom state	Nitrogen 2P	Oxygen 3P	Oxygen 1D	Oxygen 1S	Fluorine 2P	Neon 1S
E_{HF}	-54.22567	-74.80599	-74.72581	-74.60745	-99.40449	-128.54045
$-V/T$	1.99992	1.99999	1.99997	1.99994	1.99999	1.99999
Orbital	1s	1s	1s	1s	1s	1s
ϵ_{1s}	-15.68951	-20.66812	-20.69217	-20.72820	-26.38184	-32.77129
1s	0.55822	0.54944	0.54947	0.54951	0.53756	0.53333
1s'	0.47120	0.47885	0.47889	0.47895	0.48913	0.49288
2s	0.05316	0.05435	0.05425	0.05410	0.05672	0.05720
2s'	-0.00663	-0.00670	-0.00671	-0.00672	-0.00673	-0.00673
2s''	0.00202	0.00212	0.00212	0.00213	0.00218	0.00226
Orbital	2s	2s	2s	2s	2s	2s
ϵ_{2s}	-0.97476	-1.24370	-1.25551	-1.27341	-1.57155	-1.92913
1s	-0.13197	-0.13278	-0.13309	-0.13356	-0.13249	-0.13346
1s'	-0.22880	-0.23338	-0.23409	-0.23516	-0.23857	-0.24229
2s	0.08233	0.09173	0.09282	0.09445	0.09368	0.10488
2s'	0.61574	0.61066	0.61336	0.61740	0.60989	0.61668
2s''	0.43415	0.43296	0.42957	0.42448	0.43344	0.41852
Orbital	2p	2p	2p	2p	2p	2p
ϵ_{2p}	-0.46999	-0.63118	-0.59971	-0.55391	-0.72891	-0.84904
2p	0.22156	0.23583	0.23506	0.23386	0.23774	0.23699
2p'	0.34361	0.35792	0.35404	0.34866	0.36113	0.36522
2p''	0.40630	0.42494	0.42038	0.41269	0.42273	0.42040
2p'''	0.26518	0.21969	0.23201	0.25079	0.22396	0.22771

variations in the one-electron properties are less than 1%. Only for the electric fields and electric field gradients at the oxygen and nitrogen nuclei are the differences substantial, reflecting the sensitivity of these properties to the form of the wavefunction near the first-row nuclei—just that region in which the $[3p]$ sets are least flexible.

V. CONCLUSIONS

As the results presented here indicate, the $[5s3p]$ and $[5s4p]$ contracted sets for the first-row atoms when augmented with suitable polarization functions should be capable of yielding wavefunctions near the Hartree-Fock limit. Although additional improvements in the energy can be obtained using larger primitive sets, changes in the over-all charge distribution, as reflected in the one-electron properties, have been found to be of little importance.¹⁵ Further support of this conclusion is contained in the work of Moskowitz, Neumann, and co-workers⁴ and in unpublished calculations by the author.

The results given here also support the contention that the contracted basis sets suggested earlier¹ are capable of yielding molecular Hartree-Fock wavefunctions of high accuracy. Changes in the one-electron properties brought about by expansion of the (sp) set, although not negligible, were nevertheless small, typically 1%–5%.

VI. COMPUTER PROGRAMS

All of the molecular calculations described here were carried out with the revised POLYATOM system written by D. Neumann, H. Basch, C. Hornback, C. Hollister, and J. W. Moskowitz.

The atomic calculations were carried out with the atomic Hartree-Fock program ATOM written by B. Roos, C. Salez, A. Veillard, and E. Clementi as modified by W. J. Hunt for use with contracted basis sets.

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APPENDIX A: CONTRACTED BASIS SETS FOR THE FIRST-ROW ATOMS LITHIUM THROUGH NEON AND FOR HYDROGEN

In Table V, the $[5s3p]$ and $[5s4p]$ contracted basis sets for the first-row atoms beryllium through neon are given. For the lithium atom only a $[4s]$ set is necessary. The primitive sets are the $(10s)$ or $(10s6p)$ sets of Huzinaga (the exponents have been rounded to four significant figures). Table VI contains the contracted $[3s]$ set for hydrogen obtained from the $(5s)$ set of Huzinaga (again the exponents have been rounded). The Gaussian exponents for the hydrogen set are those appropriate for a Slater orbital with an exponent of 1.0.

To adjust the exponents to fit a Slater orbital with an exponent of ζ , just multiply each of the Gaussian exponents by ζ^2 (the contraction coefficients need not be changed except for renormalization resulting from truncation of the exponents if so desired). The contracted functions are separated by lines and have been normalized.

APPENDIX B: ATOMIC HARTREE-FOCK CALCULATIONS ON THE ATOMS LITHIUM THROUGH NEON WITH THE CONTRACTED GAUSSIAN BASIS SETS

In order to facilitate the calculation of those properties which are differences of molecular and atomic quantities (e.g., dissociation energies, rearrangement of charge upon molecular formation, etc.), Tables VII and VIII give the total energies, virial ratios, orbital energies, and expansion coefficients obtained from matrix Hartree-Fock calculations on the atoms lithium through neon with the basis sets given in Appendix A. All states arising from the $1s^2 2s^2 2p^N$ ground-state configuration have been considered. The loss in energy upon contraction is quite small for the ground states of the atoms, never exceeding 0.0005 a.u. even for neon. Also, for the 1S excited state of the oxygen atom the error is small, only 0.0005 a.u.

¹ T. H. Dunning, Jr., *J. Chem. Phys.* **53**, 2823 (1970).

² T. H. Dunning, Jr., "Gaussian Basis Functions for Use in Molecular Calculations. IV. The Representation of Polarization Functions for the First-Row Atoms and Hydrogen," *J. Chem. Phys.* (to be published).

³ S. Huzinaga, *J. Chem. Phys.* **42**, 1293 (1965).

⁴ J. W. Moskowitz, D. B. Neumann, and M. C. Harrison, in *Quantum Theory of Atoms, Molecules and the Solid State*, edited by P.-O. Löwdin (Academic, New York, 1966); D. Neumann and J. W. Moskowitz, *J. Chem. Phys.* **49**, 2056 (1968).

⁵ See also T. H. Dunning, Jr., *Chem. Phys. Letters* **7**, 423 (1970).

⁶ In the contraction splitting $m(P/Q/\dots)$ indicates that for the m functions the first P primitives are contracted together, the next Q together, etc. Unless otherwise noted the functions are arranged in order of decreasing orbital exponents. The contraction coefficients are taken directly from the atomic calculations.

⁷ C_n^m is the coefficient of the primitive function n in the atomic m orbital. Primitive functions are ordered according to decreasing orbital exponent.

⁸ Following the established convention, primitive sets will be denoted by parentheses while brackets indicate that the set has been contracted.

⁹ Even for the second-row atoms, where there are two parameters and three conditions to be satisfied (because of the $3s$ orbital), it has been found that obtaining x and y from Eq. (1) leads to quite satisfactory results, e.g., for the chlorine atom the resulting increase in the energy is only 3×10^{-6} a.u.

¹⁰ S. Huzinaga and C. Arnau, *J. Chem. Phys.* **52**, 2224 (1970).

¹¹ H. Basch (private communication).

¹² The primitive sets were obtained from Ref. 3.

¹³ Note, however, that the difference in the energy for water obtained with the $[5s3p/2s]$ and $[5s3p/3s]$ sets of Ref. 1 is nearly as large, 0.0012 a.u.

¹⁴ W. S. Benedict, N. Gailar, and E. K. Plyler, *J. Chem. Phys.* **24**, 1139 (1956). G. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand, New York, 1950).

¹⁵ For example, with a $[6s5p/3s]$ set derived from an $(11s7p/5s)$ primitive set we obtain for the water molecule (all in atomic units): $E_{\text{HF}} = -76.0242$, $\mu = 1.0697$, $O_{zz} = -0.1427$, $E_z(0) = -0.1348$, and $q_{zz}(0) = -1.8755$.