compounds (R is a rare-earth element), a value of $k_F a \sim 0.85 k_{F0} a$ used in conjunction with the above theory predicts the correct magnetic ordering. It is of interest to see if the above theory distinguishes between the $(\pi\pi 0)$ and the $(\pi\pi\pi)$ ordering observed for the present rare-earth tri-indium and tri-platinum compounds.

The tri-indium compounds have a value of $n=12$ for the number of valence electrons per magnetic atom; this gives $k_{F0}a = (3\pi^2 n)^{1/3} = 7.1$. The latter free-electron value, as well as a $k_F a$ value reduced by about 15%, both lie in the $k_F a$ region which predicts the observed $(\pi\pi 0)$ structure.[16] It should be mentioned that this theory is based upon a spherical Fermi surface and therefore its results would be expected to be less reliable at large values of n or $k_{F0}a$. In the case of the tri-platinum compounds, it is not clear what precise value of n should be used for platinum. However, as in the case of nickel, band structure information indicates that a small value between 0.1 and 0.4 is appropriate. Using values of n between 3 and 4 for the triplatinum compounds results in $k_{F0}a$ values between 4.9 and 4.5 which predict ferromagnetism. In order for this theory to agree with the observed $(\pi\pi\pi)$ ordering, values of $k_F a$ in the ranges 2.7–3.7 or 5.3–6.1 are necessary.[16] Therefore, in the case of the triplatinum compounds, this theory does not apparently predict the observed magnetic ordering. However, this discrepancy may be due to the uncertainty in assigning the proper electron concentration for platinum. Also, if platinum is a magnetic atom carrying a small moment in this compound, the present powder diffraction data would not detect the magnetic character of the atom.

ACKNOWLEDGMENTS

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Gaussian Basis Functions for Use in Molecular Calculations. I. Contraction of ($9s5p$) Atomic Basis Sets for the First-Row Atoms

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The contraction of Gaussian basis functions for use in molecular calculations is investigated by considering the effects of contraction on the energies and one-electron properties of the water and nitrogen molecules. The emphasis is on obtaining principles which can be used to predict optimal contraction schemes for other systems without the necessity of such exhaustive calculations. Using these principles, contractions are predicted for the first-row atoms.

I. INTRODUCTION

One of the most efficient means of solving the Hartree–Fock equations[1] for nonlinear polyatomic molecules is to expand the solutions in large sets of nuclear-centered Gaussian basis functions.[2] Such an approach has been used to compute (near) Hartree–Fock wavefunctions for water,[3] ethylene,[4] formaldehyde,[5] and many other molecules.[6] However, in such calculations, although the required integrals can be computed quite efficiently, the iterative solution of the matrix Hartree–Fock equations can be very time consuming. Numerous techniques have been devised to accelerate the convergence of the solutions, thus reducing the time requirement by reducing the number of iterations. On the other hand, a considerable savings in the time required per iteration would be affected if some of the bais functions could be grouped together, i.e., contracted, and manipulated as only one function.[4,7,8,9] As such a procedure must adversely affect the solution of the equations, the time saved per iteration

must be balanced against the loss in variational freedom.

We will define a *contracted basis function* by

$$\chi_i = \sum_j \chi_j' C_{ji},$$

where $\{\chi_j'\}$ denotes the original basis set, called the *primitive set*, and $\{\chi_i\}$ the *contracted set*. If there are n functions in the primitive set and m functions in the contracted set, then contraction reduces the number of integrals to be manipulated by $(m/n)^4$. In practice we shall see that little accuracy is lost if $m \approx n/2$, so that the contracted set contains $1/16$ the number of integrals and will require only $1/16$ of the time per iteration.

The efficacy of such a contraction procedure was first noted by Shavitt,[7] Whitten,[8] Davis and Clementi,[9] and Schulman, Moskowitz, and Hollister.[4] In none of these papers, however, was the procedure investigated in sufficient detail. Whitten[8] tried only one type of single- and double-zeta basis set; Davis and Clementi[9] studied the effect of contraction on atoms, a procedure which cannot be expected to anticipate those changes which will result from molecular formation[10]; and Schulman, Moskowitz, and Hollister,[4] although they experimented with a somewhat larger number of contractions, chose such a large molecule (ethylene) that their investigation was, of necessity, severely limited. In all of these papers the approach to the problem tended to be mathematical, obscuring any physical basis for contraction. Nevertheless, these papers did bring into view a powerful means of increasing the efficiency of calculations with Gaussian basis functions.

More recently, contraction has been investigated by Ritchie and King,[11] Basch, Robin, and Kuebler,[12] and Neumann and Moskowitz.[3] Again, however, these studies were never pursued sufficiently far to allow a valid assessment of the potential of the technique: Ritchie and King[11] limited their investigation to just the inner-shell s basis functions and, although Basch *et al.*[12] and Neumann and Moskowitz[3] consider p-orbital contractions, their s set is both inferior to and larger than the one employed here. Further, in none of these works was an attempt made to thoroughly compare the various contracted sets or to compare corresponding contracted and uncontracted results. However, the contraction schemes they suggested closely parallel many of those put forward here and indicate an implicit, if not explicit, awareness of the basic nature of contraction (the same can be said of Whitten's double-zeta basis set[8]).

In the next section Hartree–Fock calculations on the water molecule are used to determine optimum contracted basis sets for the oxygen $(9s5p)$ and hydrogen $(4s)$ primitive sets obtained by Huzinaga.[13] The effect of contraction on the calculated charge distribution, as reflected in the total energy *and* one-electron properties, is carefully examined. These studies are used to develop general principles for contracting basis sets for other first-row atoms. In order to assess the generality of the contraction schemes so obtained, the contracted basis sets for the nitrogen atom are used for calculations on the nitrogen molecule. The accuracy of the contracted Gaussian basis sets is compared to that of Slater basis sets for the nitrogen molecule. In the following section these optimum contraction schemes are given a simple, physical interpretation and rules are formulated to allow their extension to other atoms. In the last section we discuss some additional aspects of the contraction problem and indicate further work which is presently being pursued.

The notation used is that suggested by Schulman, Moskowitz, and Hollister[4]: Parentheses are used to denote primitive basis sets and brackets are used to denote contracted basis sets.

II. CALCULATIONS

The best means of ascertaining the effect of contraction is through a series of calculations on a given molecule with various contracted basis sets obtained from the same primitive set. In order that the comparison be meaningful the way in which the primitive functions are grouped together, i.e., the contraction splitting, for a given size contracted set must be optimized. Of course, such a procedure would be quite useless if it had to be followed for each molecule of interest—it would be more efficient to just do the calculation with the uncontracted basis set and be done with it. On the other hand, it might be hoped that the contraction of a given primitive basis set is closely related to the physical problem at hand, rather than being a purely mathematical artifact. If this were the case, a careful study of a model system could be expected to lead to a set of rules of general applicability. The present work is predicated upon this assumption. The validity of this viewpoint is strongly supported by the success of the calculations reported here.

In order to be as economical and as general as possible a number of limitations must be placed on the contraction schemes. First, a given primitive function cannot appear in more than one contracted function, i.e., the contracted functions must be formed from disjoint sets. If the contracted sets were not so restricted, it would be necessary to compute many of the integrals more than once, thus increasing the integral computation time substantially. In addition, we shall take the contraction coefficients directly from the atomic calculations. This independence of the method from molecular information greatly enhances its generality. Fortunately, as we shall see, the combined effect of these restrictions is of no consequence.

A. The Water Molecule

In this section the optimum *contraction splittings* are determined for various sizes of oxygen and hydrogen contracted basis sets for the water molecule. In addition, we extensively compare the wavefunctions obtained

with the various optimum contracted sets and the uncontracted set. Finally, there is a brief discussion of the contraction schemes previously advanced by others.

The primitive basis set for water is a $(9s5p/4s)$ Gaussian set with the oxygen orbital exponents and the contraction coefficients taken from Huzinaga's[13] atomic calculations and the hydrogen exponents and coefficients from Huzinaga's[13] four-term expansion of a $1s$ orbital with an exponent of 1.2. This particular basis set was chosen because it appears to be an ideal candidate for moderately accurate calculations on relatively large molecules containing as many as four or so first-row atoms.

The geometry used is that chosen by Aung, Pitzer, and Chan[14] and corresponds fairly closely to the experimental equilibrium geometry[15]: an OH bond distance of 1.8111 a.u. and an $\angle$ HOH bond angle of 104°27'. The molecule lies in the xz plane with the z axis being the symmetry axis. The coordinates of the nuclei are H1 (1.43153, 0.0, 1.10941), H2 (−1.43153, 0.0, 1.10941), and O (0.0, 0.0, 0.0), all in atomic units.

The optimization procedure used was quite simple. First a given type of contracted basis set was chosen, say the $[3s2p/2s]$. Then, starting from some base mode of contraction, the splittings of the various groups (hydrogen, oxygen p, and oxygen s) were optimized in turn. Using this information as a starting point, the set was further uncontracted and the contraction splitting again optimized. As an example of this procedure, the optimization of $[3s2p/2s]$ basis set is given in Table I.

Studying Table I in some detail, we see that the total energy is rather sensitive to the splittings of each of the basis function groups, i.e., the oxygen s, oxygen p and hydrogen groups. In order to obtain satisfactory results, the splittings of each of these groups must be optimized.

Table II lists the total energies, orbital energies and selected one-electron properties obtained for the water molecule for all of the (optimum) contracted basis sets (the basis sets are given in Table IV.A, Appendix A). In addition the table contains the corresponding information for the uncontracted $(9s5p/4s)$ basis. Examining Table II, one fact which we immediately note is that the energy is raised by only 0.0052 a.u. (or 0.007%) by the loss of variational freedom for the smallest basis set, $[3s2p/2s]$. Also, we see that in general the properties are accurate to within 1–5% for the same set. For the most flexible contracted set investigated, the energy error is reduced to only 0.0005 a.u. and the orbital energies and one-electron properties are accurate to $\frac{1}{2}$–1%. Even for this set there are just 20 basis functions as compared to 32 in the primitive set, which means there are less than $\frac{1}{6}$ the number of integrals to be processed. This clearly demonstrates the effectiveness of contraction and suggests that there is little reason to use completely uncontracted basis sets.

Studying Table II in further detail, we find that the $[4s3p/2s]$ set appears to be a good compromise between

TABLE I. Optimization of the contraction splitting for the $[3s2p/2s]$ basis set by Hartree–Fock calculations on the water molecule.

S split[a]	P split[a]	H split[a]	Hartree–Fock energy
Optimization on the hydrogen contraction			
4/3/2	3/2	2/2	−75.9718
4/3/2	3/2	3/1	−75.9864
Optimization of the oxygen $2p$ contraction			
4/3/2	4/1	3/1	−75.9984
Optimization of the oxygen $(1s, 2s)$ contraction			
7/1/1	4/1	3/1	−75.9553
5/2/2	4/1	3/1	−76.0073
6/1/2[b]	4/1	3/1	−76.0080

[a] In the contraction splitting $P/Q/R$ indicates that the first P primitives are contracted together, the next Q together, etc. Except as noted, the higher exponents are always to the left.

[b] In this contraction the function with $\zeta = 9.5322$ is the uncontracted function. The function with $\zeta = 3.4136$ has been included in the six function contraction. See the discussion in the text and Table IV.A, Appendix A.

accuracy and the desire to keep the basis set as small as possible. Comparison with the $[5s3p/2s]$ and $[5s3p/3s]$ sets show that the oxygen and hydrogen s sets are well approximated by the $[4s]$ and $[2s]$ contractions while comparison with the $[4s2p/2s]$ set reveals that the oxygen p set requires a $[3p]$ contraction [note especially $q_{ii}(0)$]. Further, we note that for this set the energy penalty is just 0.0028 a.u. and, with minor exceptions,[16] the properties have converged to within 1% of the uncontracted results. For all properties, this set yields results within 1% of the most flexible contracted set investigated, $[5s3p/3s]$. Augmentation of this basis set with suitable polarization functions should be far more important than increasing the flexibility of the (sp) set.[17]

Calculations were also carried out to compare the double zeta basis set, $[4s2p/2s]$, obtained here with that put forth by Basch et al.[12] They[12] use an oxygen $10s$ set obtained from Whitten's atomic calculations[8] and an oxygen $5p$ set and a hydrogen $4s$ set identical to that employed here. As might be expected from the similarity of the basis sets, the two wavefunctions are shown by the one-electron properties to be nearly identical in the important valence regions of the molecule. The lower energy (0.0057 a.u.) obtained in the present work, although substantial, is essentially due to a better description of the oxygen inner-shell region by Huzinaga's atomic set.[13] The principle advantage then of the $[4s2p/2s]$ basis set proposed here is that the primitive set of each first-row atom requires one less basis function.

A comparison with the contraction scheme proposed by Ritchie and King[11] can only be made indirectly since they would completely uncontract the oxygen p and hydrogen s components of the $[5s3p/3s]$ set.[18] The

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TABLE II. A comparison of the optimum contracted basis sets and the uncontracted basis set for the water molecule: total energies, orbtal energies, and selected one-electron properties. (All quantities are in atomic units.)

Properties[a]	Optimum contracted sets					(9s5p/4s)
	[3s2p/2s]	[4s2p/2s]	[4s3p/2s]	[5s3p/2s]	[5s3p/3s]	
E_{HF}	−76.0080	−76.0093	−76.0105	−76.0116	−76.0128	−76.0133
$\epsilon(1a_1)$	−20.5547	−20.5594	−20.5629	−20.5608	−20.5606	−20.5606
$\epsilon(2a_1)$	−1.3595	−1.3613	−1.3609	−1.3615	−1.3613	−1.3609
$\epsilon(1b_1)$	−0.7147	−0.7165	−0.7160	−0.7159	−0.7156	−0.7155
$\epsilon(3a_1)$	−0.5655	−0.5668	−0.5670	−0.5671	−0.5671	−0.5673
$\epsilon(1b_2)$	−0.5037	−0.5063	−0.5060	−0.5059	−0.5057	−0.5056
μ[b]	1.0701	1.0558	1.0519	1.0511	1.0432	1.0428
$\langle x^2 \rangle$ (c.m.)[c,d]	7.1954	7.2315	7.2180	7.2184	7.1922	7.1920
$\langle y^2 \rangle$ (a.m.)	5.4910	5.4916	5.4904	5.4908	5.4955	5.4914
$\langle z^2 \rangle$ (c.m.)	6.4989	6.5128	6.5093	6.5094	6.5059	6.5035
$\langle r^2 \rangle$ (c.m.)	19.1853	19.2358	19.2176	19.2186	19.1936	19.1869
Θ_{xx} (c.m.)[c,e]	1.8591	1.8302	1.8414	1.8413	1.8681	1.8650
Θ_{yy} (c.m.)	−1.7321	−1.7077	−1.7150	−1.7152	−1.7347	−1.7320
Θ_{zz} (c.m.)	−0.1270	−0.1225	−0.1264	−0.1261	−0.1334	−0.1330
$\langle 1/r_H \rangle$[d]	5.7386	5.7384	5.7389	5.7389	5.7399	5.7403
$\langle 1/r_O \rangle$	23.4488	23.4426	23.4387	23.4409	23.4412	23.4386
$E_x(H1)$[f]	0.0959	0.1000	0.0939	0.0940	0.0919	0.0903
$E_z(H1)$	0.0356	0.0366	0.0331	0.0332	0.0345	0.0332
$E_z(O)$	−0.2495	−0.2479	−0.1920	−0.1919	−0.1887	−0.1389
$q_{yy}(D)$[g]	0.3128	0.3114	0.3082	0.3083	0.3087	0.3071
$q_{\alpha\alpha}(D)$	0.2485	0.2467	0.2436	0.2437	0.2428	0.2412
$q_{\beta\beta}(D)$	−0.5612	−0.5581	−0.5518	−0.5519	−0.5516	−0.5483
ϕ	2°32′	2°43′	2°43′	2°43′	2°35′	2°35′
$q_{xx}(O)$	−1.8203	−1.8084	−1.9138	−1.9126	−1.9172	−1.9084
$q_{yy}(O)$	2.0366	2.0517	2.1147	2.1147	2.1168	2.1103
$q_{zz}(O)$	−0.2162	−0.2432	−0.2009	−0.2020	−0.1995	−0.2018
$\langle \delta(r\text{-}H) \rangle$[h]	0.4132	0.4147	0.4120	0.4121	0.4105	0.4083
$\langle \delta(r\text{-}O) \rangle$	295.1358	295.0512	295.0717	294.6061	294.6091	294.1736

[a] For the definition of the operators see Refs. 3 and 5.
[b] Dipole moment. 1 a.u. =2.54158 D.
[c] c.m. denotes the center of mass, which is at (0.0, 0.0, 0.1176).
[d] This property is composed of only an electronic contribution.
[e] Quadrupole moment. 1 a.u. =1.34492 Buckinghams.
[f] Electric field.
[g] Electric field gradients. 1 a.u. =3.24140 ×10¹⁵ esu/cm³.
[h] Density at the nucleus.

results presented in Table II for the [5s3p/3s] set should, however, be a bound on the results obtainable with their scheme. The agreement between their basis set and the uncontracted basis set is expected to be excellent. However, their approach does not go far enough, completely neglecting any contraction of the oxygen p and hydrogen s functions. As the results presented here illustrate, this extra contraction can be done quite efficiently.

Finally, in order to test the sensitivity of the wavefunction to the hydrogen scale factor, this parameter was optimized for the [4s3p/2s] basis set. The optimum scale factor is 1.275, which is remarkably close to the optimum hydrogen exponent in a minimum basis set

calculation on water.[14] The total decrease in the energy was slight (just 0.0004 a.u.) and the one-electron properties were little affected (changes on the order of a 1–5% for the most sensitive properties).

B. The Nitrogen Molecule

In order to test the generality of the contraction schemes obtained for the oxygen $(9s5p)$ set in the preceding section, a limited number of calculations were carried out on the nitrogen molecule using the corresponding contracted nitrogen basis sets (obtained using the rules to be discussed in the next section). The nitrogen basis sets are given in Appendix A, Table III.A. Because of the more intense electric fields

TABLE III. Total energies, orbital energies, and selected one-electron properties for the nitrogen molecule obtained with the recommended contracted Gaussian basis sets. (All quantities are in atomic units.)

Properties[a]	Contracted basis set[b]			
	[3s2p]	[4s2p]	[4s3p]	[5s3p]
E_{HF}	−108.8153	−108.8782	−108.8877	−108.8890
$\epsilon_{1\sigma_g}$	−15.7156	−15.7191	−15.7072	−15.7055
$\epsilon_{2\sigma_g}$	−1.5077	−1.5282	−1.5252	−1.5254
$\epsilon_{3\sigma_g}$	−0.6138	−0.6246	−0.6267	−0.6267
$\epsilon_{1\sigma_u}$	−15.7120	−15.7156	−15.7036	−15.7019
$\epsilon_{2\sigma_u}$	−0.7671	−0.7723	−0.7723	−0.7726
$\epsilon_{1\pi_u}$	−0.6268	−0.6264	−0.6237	−0.6236
$\langle x^2 \rangle$ (c.m.)	7.5423	7.5658	7.5704	7.5706
$\langle z^2 \rangle$ (c.m.)	24.2281	24.3480	24.3304	24.3287
Θ_{zz} (c.m.)	−1.7175	−1.8140	−1.7918	−1.7899
$\langle 1/r_N \rangle$	21.6187	21.6233	21.6367	21.6385
E_z (N)	−0.3040	−0.2514	−0.2138	−0.2138
q_{zz} (N)	1.0619	0.8826	1.2480	1.2474
$\langle \delta(r-N) \rangle$	195.1300	195.4635	195.4258	195.1851

[a] See the footnotes to Table II. [b] See Table III.A.

associated with the presence of two first-row nuclei, we should expect to see the differences between the various contracted basis sets greatly magnified.

The internuclear distance employed in this calculation is that used in a number of previous calculations[19,20] and corresponds to the observed equilibrium distance, 2.068 a.u.[21] The z axis is the internuclear axis.

In Table III we list the total energies, orbital energies and selected one-electron properties obtained for the nitrogen molecule with these contracted basis sets. As expected, and in contrast to the results on water, we note a marked difference between the results obtained with the various contrasted basis sets for the nitrogen molecule: the [3s2p] set yields an energy nearly 0.06 a.u. higher than the [4s2p] set, which in turn gives an energy nearly 0.01 a.u. above that of the [4s3p] set. The difference between the [5s3p] and [4s3p] sets, on the other hand, is seen to be negligible.

The most significant changes in the one-electron properties are for the quadrupole moment, electric fields, and field gradients, in line with the known sensitivity of these properties to the accuracy of the wavefunction. One point of special interest is the large fluctuations which occur in the field gradient. Not only does this reflect the sensitivity of this property to the flexibility of the p-orbital set, but it also illustrates the

strong coupling between the s and p orbitals in the nitrogen molecule. It should also be noted that the order of $\epsilon_{3\sigma_g}$ and $\epsilon_{1\pi u}$ is quite sensitive to the basis set.

The results presented in Table III emphasize the accuracy of the [4s3p] contracted Gaussian basis set. Although the choice was not quite so obvious from the calculations on water, the substantial differences between the [4s2p] and [4s3p] sets in the calculations on the nitrogen molecule strongly support our choice of this particular set as the optimum contracted basis set for accurate calculations on larger polyatomic molecules. Of course, should circumstances rule out the use of the larger basis set, the double-zeta set should in many instances be satisfactory.

C. Accuracy of the Contracted Gaussian Basis Sets

In order to establish the accuracy of the contracted Gaussian basis sets proposed here, the results presented in Sec. II.B for the nitrogen molecule are compared with those obtained using Slater basis sets. While the $(9s5p)$ Gaussian basis sets yield atomic energies which are *worse* than double-zeta Slater sets, the point of interest here is the relative accuracy afforded by the two types of functions for *molecules*.

In Table IV we list the total energies and orbital energies for the nitrogen molecule obtained with a

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TABLE IV. Calculations on the nitrogen molecule with various atomic Slater basis sets: total energies and orbital energies. (All quantities are in atomic units.)

Properties	Basis set		
	$(4s2p)$[a]	$(4s3p)$	$(5s3p)$[b]
$E_{\rm HF}$	-108.8617	-108.8865	-108.8967
$\epsilon_{1\sigma_g}$		-15.7099	-15.7169
$\epsilon_{2\sigma_g}$		-1.5336	-1.5381
$\epsilon_{3\sigma_g}$		-0.6324	-0.6374
$\epsilon_{1\sigma_u}$		-15.7062	-15.7133
$\epsilon_{2\sigma_u}$		-0.7792	-0.7823
$\epsilon_{1\pi_u}$		-0.6286	-0.6311

[a] Reference 19.
[b] Reference 20.

number of atom-optimized Slater basis sets.[19,20a] Comparing these results with those given in Table III for the Gaussian sets, we see that the $[4s3p]$ Gaussian set gives a slightly *lower* energy (0.0012 a.u.) than the corresponding $(4s3p)$ Slater set, and a considerably better energy than the double-zeta Slater set[19] (0.0260 a.u.). In fact, the double-zeta Gaussian set gives an energy some 0.017 a.u. below that for the corresponding Slater set. However, both the $[4s3p]$ and $[5s3p]$ Gaussian sets are ~ 0.009 a.u. above the more extensive $(5s3p)$ Slater set.[20]

In Table V we compare the properties for the nitrogen molecule obtained with the $[4s3p]$ Gaussian basis set and the $(4s3p)$ Slater set. The exponents of the $(4s3p)$ Slater set are those obtained by Bagus, Gilbert, Roothaan, and Cohen[22] and are the optimum exponents for the ground state (^4S) of the nitrogen atom. The wavefunction for the nitrogen molecule in this basis was not available in the literature and was computed. We see that, although the energies of the two wavefunctions are nearly identical, the charge distributions differ in some significant ways. For example, the molecule in the Slater basis is somewhat "larger" than in the Gaussian basis as measured by $\langle x^2 \rangle$ and $\langle z^2 \rangle$; also, the force on the nuclei is just half as large for the Slater as for the Gaussian basis. On the other hand, the quadrupole moment, the electronic potential at the nuclei, and the field gradients are quite comparable for the two wavefunctions. All in all, we can conclude that the two basis sets, the $[4s3p]$ contracted Gaussian set and the nominal $(4s3p)$ Slater set, provide molecular wavefunctions of similar accuracy.

The result for the $[4s3p]$ Gaussian set at first seems somewhat puzzling since the atomic energy of the Gaussian set is some 0.0055 a.u. *above* that of the nominal $(4s3p)$ Slater set. Why then should the Gaussian set give an energy for the nitrogen molecule

0.0012 a.u. *below* that of the nominal set? This phenomenum can probably be attributed to two factors:

(1) The decreased importance (energetically) of the atomic regions relative to the valence regions in a molecule. It is, of course, the exponentiallike atomic regions which are most poorly described by Gaussian functions.

(2) The presence of two s functions in the Gaussian basis which are heavily concentrated in the valence region (the $3s$ function in the Slater set is not as effective in this respect as can be seen from the atomic expansion coefficients[22]).

III. RATIONALIZATION

In any study such as this it is very important to search for a meaningful rationalization of the results if possible. In this way the rather limited observations can be extended to a larger class of systems. During the course of this investigation it became clear that all of the results could be explained by a simple and physically appealing rationalization. In this section we will discuss this interpretation and show how the concepts so derived can be applied to other cases.

The optimum splittings of the contracted functions which were obtained in the last section can be explained by the application of the following two rules:

Rule A: Those members of each group which are most strongly concentrated in the internuclear regions should be allowed to vary freely.

TABLE V. Comparison of calculations on the nitrogen molecule using a $(4s3p)$ Slater basis and a $[4s3p]$ Gaussian basis: total energies, orbital energies, and selected one-electron properties. (All quantities are in atomic units.)

Properties[a]	Slater $(4s3p)$	Gaussian $[4s3p]$
$E_{\rm HF}$	-108.8865	-108.8877
$\epsilon_{1\sigma_g}$	-15.7099	-15.7072
$\epsilon_{2\sigma_g}$	-1.5336	-1.5252
$\epsilon_{3\sigma_g}$	-0.6324	-0.6267
$\epsilon_{1\sigma_u}$	-15.7062	-15.7036
$\epsilon_{2\sigma_u}$	-0.7792	-0.7723
$\epsilon_{1\pi_u}$	-0.6286	-0.6237
$\langle x^2 \rangle$(c.m.)	7.7443	7.5704
$\langle z^2 \rangle$(c.m.)	24.4246	24.3304
Θ_{zz}(c.m.)	-1.7121	-1.7918
$\langle 1/r_{\rm N} \rangle$	21.6363	21.6367
$E_z({\rm N})$	-0.1294	-0.2138
$q_{zz}({\rm N})$	1.2433	1.2480

[a] See the footnotes to Table II.

Rule B: If, within a particular group, one of the primitives spans two (or more) spaces, then this function should be allowed to vary freely.

In Rule *B* by spaces we mean orbital spaces, e.g., the 1*s* space and the 2*s* space of atoms, etc. These rules can be easily understood just on physical grounds.

Those functions which are most likely to be influenced by molecular formation are those which extend into the valence regions. In the (9*s*5*p*/4*s*) set it is those basis functions with the smaller exponents of each of the groups which are most concentrated in the interatomic regions of the molecule.[23] Hence, the coefficients of these functions should be allowed to vary freely. Rule *A* can, thus, be explained quite simply.

Rule *B* is a little more subtle. If a group of basis functions span two different orbital spaces as do, for example, the *s* functions of oxygen, then some primitives may contribute substantially to both spaces. If this is the case, then we find that the weight of these functions relative to the others in the set changes considerably from orbital to orbital. Functions such as these must be allowed to vary freely in either an atomic or a molecular environment. This freedom is particularly important because these basis functions are concentrated in regions of space which are energetically important. Thus, in general, splittings dictated by Rule *B* take precedent over those of Rule *A*, e.g., the optimum splitting of the oxygen *s* functions in the [3*s*] set is (6/1/2) not (7/1/1).

An example of this latter type of basis function in the present case is afforded by the oxygen *s* function with an orbital exponent of $\zeta = 9.5322$. Examining Huzinaga's atomic results,[13] we note at once that this function not only contributes heavily to the 1*s* atomic orbital, but it also makes a substantial contribution to the 2*s* orbital. The coefficient of this function should, thus, be allowed to vary freely. Note that the primitive with an exponent of $\zeta = 3.4136$, even though it is more extended in space, contributes little to the atomic 2*s* orbital. Therefore, this function is best grouped with the other 1*s*-type primitives.

Because of the physical, rather than mathematical, nature of the results presented here, it is expected that the optimum splittings will directly apply to the other first-row atoms from boron through neon in a wide variety of molecular environments. For the convenience of the reader, the various contracted Gaussian basis sets for the first-row atoms, boron through fluorine, are given in Appendix A.

In Appendix B we give the energies for various states of the atoms boron through fluorine obtained with the contracted basis sets from Appendix A. In addition, for the [4*s*2*p*] and [4*s*3*p*] sets we give the orbital energies and expansion coefficients for the ground states of these atoms.

IV. DISCUSSION

An important concept which has arisen from these calculations is that a given primitive basis has an optimum contracted size beyond which a further increase in flexibility of the basis set results in negligible improvements in the molecular wavefunctions and below which further contraction results in excessive loss of accuracy. For the (9*s*5*p*) Gaussian basis set considered here for the first-row atoms, the optimum contracted set is seen to be the [4*s*3*p*] set. That little is gained upon going from the [4*s*] to the [5*s*] set can be understood by noting that the (9*s*) primitive set contains only two valence *s* functions, both of which are uncontracted in the [4*s*] set. In addition, the core functions can be conveniently partitioned into two groups, the functions of which enter the 1*s* and 2*s* orbitals in approximately the same way. Thus, increasing the flexibility of this contracted set merely corresponds to allowing additional freedom in the core which is of little importance in molecules.

Comparison of Huzinaga's (9*s*) set[13] to Whitten's (10*s*) set[8] (see Sec. II.A) shows that it is somewhat better to determine the exponents and coefficients from an atomic calculation with uncontrated basis functions and *then* determine the best way to contract these functions for use in molecular calculations. In using this procedure, however, the rules outlined in Sec. III should be kept in mind. Thus, while the (9*s*) set contracts satisfactorily to a [4*s*] set, the same cannot be said for Huzinaga's (10*s*) set[13] which requires at least 5–6 functions. In doing the atomic calculation we must keep in mind the use to which the results are to be put and choose sets which will optimally contract to the desired size.

While the [4*s*3*p*] basis sets discussed here will yield molecular wavefunctions of relatively high accuracy, larger, more flexible basis sets will be required to reach the Hartree–Fock limit (including, of course, the addition of polarization functions). However, such basis sets cannot be obtained from the (9*s*5*p*) primitive sets. Work is in progress on the contraction of (10*s*6*p*) [13] and (11*s*7*p*) [24,25] primitive sets.[26]

VI. COMPUTER PROGRAMS

All of the Gaussian calculations were performed with a version of the Gaussian SCF system MOSES, written by Geller and Sachs,[27] modified to make use of some spatial symmetry. The one-electron properties for the Gaussian wavefunctions were calculated with a revised IBM 7094 version of a program originally written by Neumann[3] for the CDC 6600.

The calculations on the nitrogen molecule in a (4*s*3*p*) Slater basis were done using the McL–Yosh Linear Molecule program (QCPE 104), written by McLean and Yoshimine,[28] which is available from the Quantum Chemistry Program Exchange (Department of Chemistry, Indiana University).

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The Gaussian atomic Hartree–Fock program was kindly supplied to the author by E. Clementi. It was modified for use with contracted basis sets by W. J. Hunt.

APPENDIX A: RECOMMENDED CONTRACTED SETS FOR THE FIRST-ROW ATOMS, BORON THROUGH FLUORINE, AND HYDROGEN

In Tables I.A–V.A the [3s], [4s], [5s], [2p], and [3p] contracted basis functions are given for the first-

TABLE I.A. Contracted Gaussian basis sets for a $(9s5p)$ *boron* primitive basis set.

Exponents	Boron s sets		
	[3s]	[4s]	[5s]
2788.4100	0.002122	0.002122	0.006340
419.0390	0.016171	0.016171	0.048310
96.4683	0.078356	0.078356	0.234078
28.0694	0.263250	0.263250	0.786421
9.3760	0.596729	0.596729	0.801018
1.3057	0.230397	0.230397	0.309273
3.4062	1.000000	1.000000	1.000000
0.3245	0.526887	1.000000	1.000000
0.1022	0.530557	1.000000	1.000000

Exponents	Boron p sets	
	[2p]	[3p]
11.3413	0.017987	0.038707
2.4360	0.110339	0.237448
0.6836	0.383111	0.824446
0.2134	0.647860	1.000000
0.0701	1.000000	1.000000

TABLE II.A. Contracted Gaussian basis sets for a $(9s5p)$ *carbon* primitive basis set.

Exponents	Carbon s sets		
	[3s]	[4s]	[5s]
4232.6100	0.002029	0.002029	0.006228
634.8820	0.015535	0.015535	0.047676
146.0970	0.075411	0.075411	0.231439
42.4974	0.257121	0.257121	0.789108
14.1892	0.596555	0.596555	0.791751
1.9666	0.242517	0.242517	0.321870
5.1477	1.000000	1.000000	1.000000
0.4962	0.542048	1.000000	1.000000
0.1533	0.517121	1.000000	1.000000

Exponents	Carbon p sets	
	[2p]	[3p]
18.1557	0.018534	0.039196
3.9864	0.115442	0.244144
1.1429	0.386206	0.816775
0.3594	0.640089	1.000000
0.1146	1.000000	1.000000

TABLE III.A. Contracted Gaussian basis sets for a $(9s5p)$ *nitrogen* primitive basis set.

Exponents	Nitrogen s sets		
	[3s]	[4s]	[5s]
5909.4400	0.002004	0.002004	0.006240
887.4510	0.015310	0.015310	0.047669
204.7490	0.074293	0.074293	0.231317
59.8376	0.253364	0.253364	0.788869
19.9981	0.600576	0.600576	0.792912
2.6860	0.245111	0.245111	0.323609
7.1927	1.000000	1.000000	1.000000
0.7000	0.552334	1.000000	1.000000
0.2133	0.508031	1.000000	1.000000

Exponents	Nitrogen p sets	
	[2p]	[3p]
26.7860	0.018257	0.038244
5.9564	0.116407	0.243846
1.7074	0.390111	0.817193
0.5314	0.637221	1.000000
0.1654	1.000000	1.000000

TABLE IV.A. Contracted Gaussian basis sets for a (9s5p) *oxygen* primitive bais set.

	Oxygen s sets		
Exponents	[3s]	[4s]	[5s]
7816.5400	0.002031	0.002031	0.006436
1175.8200	0.015436	0.015436	0.048924
273.1880	0.073771	0.073771	0.233819
81.1696	0.247606	0.247606	0.784798
27.1836	0.611832	0.611832	0.803381
3.4136	0.241205	0.241205	0.316720
9.5322	1.000000	1.000000	1.000000
0.9398	0.563459	1.000000	1.000000
0.2846	0.497338	1.000000	1.000000

	Oxygen p sets	
Exponents	[2p]	[3p]
35.1832	0.019580	0.040023
7.9040	0.124189	0.253849
2.3051	0.394727	0.806842
0.7171	0.627375	1.000000
0.2137	1.000000	1.000000

TABLE V.A. Contracted Gaussian basis sets for a (9s5p) *fluorine* primitive basis set.

	Fluorine s sets		
Exponents	[3s]	[4s]	[5s]
9994.7900	0.002017	0.002017	0.006431
1506.0300	0.015295	0.015295	0.048757
350.2690	0.073110	0.073110	0.233065
104.0530	0.246420	0.246420	0.785549
34.8432	0.612593	0.612593	0.802728
4.3688	0.242489	0.242489	0.317752
12.2164	1.000000	1.000000	1.000000
1.2078	0.572817	1.000000	1.000000
0.3634	0.488416	1.000000	1.000000

	Fluorine p sets	
Exponents	[2p]	[2p]
44.3555	0.020868	0.042011
10.0820	0.130092	0.261899
2.9959	0.396219	0.797662
0.9383	0.620368	1.000000
0.2733	1.000000	1.000000

TABLE VI.A. Contracted Gaussian basis sets for the (4s) *hydrogen* primitive set. Scale factor is unity.

	Hydrogen s sets	
Exponents[a]	[2s]	[3s]
13.3615	0.032828	0.130844
2.0133	0.231208	0.921539
0.4538	0.817238	1.000000
0.1233	1.000000	1.000000

[a] Exponents for the scale factor of 1.2 used in this work are (19.2406, 2.8992, 0.6534, 0.1776); the basis functions are actually normalized for $\zeta_s = 1.2$.

row atoms, boron through fluorine. The primitive basis sets are the (9s5p) basis sets of Huzinaga.[13] Table VI.A contains the [2s] and [3s] contracted functions for hydrogen with the exponents appropriate for a Slater orbital of exponent 1.0. To adjust the Gaussian exponents to fit a Slater orbital of exponent ζ_i, just multiply each of the Gaussian exponents by ζ_i^2, the contraction coefficients need not be changed. All of the basis functions have been normalized. The contracted functions are separated by lines.

APPENDIX B: ATOMIC HARTREE–FOCK CALCULATIONS ON THE ATOMS BORON THROUGH FLUORINE USING THE CONTRACTED GAUSSIAN BASIS SETS

In order to facilitate the calculation of dissociation energies, potential energy curves, etc., Table I.B gives the atomic Hartree–Fock energies for those states of the atoms boron through fluorine which arise from the $1s^2 2s^2 2p^N$, $N=1, \cdots, 5$, configuration. Even though they were optimized for the ground state, we see that the [4s2p] and [4s3p] Gaussian sets also provide adequate represenations of all of the states arising from the $1s^2 2s^2 2p^N$ configuration. Considering the similarity of these states, this is, of course, not unexpected. Comparing the energies for the uncontracted set[13] with those for the [4s3p] set, we see that little is lost upon contracting the atomic sets: B(0.0007), C(0.0007), N(0.0009), O(0.0014), and F(0.0022), all in atomic units.

Tables II.B and III.B contain the orbital energies and expansion coefficients from the atomic Hartree–Fock calculations on the ground states of the atoms boron through fluorine. Only the results for the [4s2p] and [4s3p] basis sets have been given. Such information for

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TABLE I.B. Hartree–Fock energies and virial ratios $(-V/T)$ for the first-row atoms boron through fluorine obtained using the contracted Gaussian basis sets given in Appendix A.

Atom	State	Uncontracted (9s5p)	Contracted			
			[3s2p]	[4s2p]	[4s3p]	[5s3p]
Boron	^2P	−24.527130	−24.526230	−24.526415	−24.526415	−24.526549
			1.997390	1.999023	1.999029	1.998954
Carbon	^3P	−37.685247	−37.684406	−37.684508	−37.684508	−37.684856
			1.998448	1.999490	1.999493	1.999365
	^1D			−37.627015	−37.627102	
				1.999767	1.999486	
	^1S			−37.544018	−37.544661	
				2.000035	1.999338	
Nitrogen	^4S	−54.395336	−54.394359	−54.394392	−54.394392	−54.395111
			1.999415	1.999865	1.999862	1.999726
	^2D			−54.289264	−54.289405	
				2.000260	1.999867	
	^2P			−54.220590	−54.221001	
				2.000484	1.999835	
Oxygen	^3P	−74.800289	−74.798819	−74.798837	−74.798837	−74.800140
			2.000355	2.000172	2.000166	2.000011
	^1D			−74.718442	−74.718496	
				2.000413	2.000164	
	^1S			−74.599381	−74.599720	
				2.000742	2.000132	
Fluorine	^2P	−99.395586	−99.393249	−99.393300	−99.393300	−99.395311
			2.000897	2.000435	2.000422	2.000249

TABLE II.B. Orbital energies and expansion coefficients for the Hartree–Fock wavefunctions for the ground states of the atoms boron through fluorine. Basis set: [4s2p].

Atom (state)	B(^2P)	C(^3P)	N(^4S)	O(^3P)	F(^2P)
Orbital	1s	1s	1s	1s	1s
ϵ_i	−7.69285	−11.32398	−15.62888	−20.66878	−26.38296
1s	0.60784	0.60141	0.59375	0.58112	0.57995
1s′	0.43331	0.43795	0.44610	0.46138	0.46224
2s	0.00117	0.00201	0.00127	−0.00061	−0.00038
2s′	0.00034	0.00040	0.00081	0.00140	0.00144
Orbital	2s	2s	2s	2s	2s
ϵ_i	−0.49451	−0.70505	−0.94411	−1.24137	−1.56729
1s	−0.13480	−0.14114	−0.14444	−0.14584	−0.14865
1s′	−0.18638	−0.19174	−0.19608	−0.20262	−0.20428
2s	0.53464	0.55973	0.57730	0.59550	0.61014
2s′	0.57509	0.55505	0.54103	0.52589	0.51298
Orbital	2p	2p	2p	2p	2p
ϵ_i	−0.30969	−0.43286	−0.56663	−0.62959	−0.72591
2p	0.79742	0.79252	0.79529	0.78716	0.78418
2p′	0.30620	0.31747	0.31774	0.33588	0.34398

TABLE III.B. Orbital energies and expansion coefficients for the Hartree–Fock wavefunctions for the ground states of the atoms boron through fluorine. Basis set: $[4s3p]$.

Atom (state)	B(^2P)	C(^3P)	N(^4S)	O(^3P)	F(^2P)
Orbital	$1s$	$1s$	$1s$	$1s$	$1s$
ϵ_i	-7.69290	-11.32400	-15.62886	-20.66872	-26.38282
$1s$	0.60785	0.60141	0.59375	0.58112	0.57995
$1s'$	0.43331	0.43795	0.44610	0.46138	0.46224
$2s$	0.00116	0.00201	0.00127	-0.00061	-0.00038
$2s'$	0.00034	0.00040	0.00081	0.00140	0.00144
Orbital	$2s$	$2s$	$2s$	$2s$	$2s$
ϵ_i	-0.49452	-0.70705	-0.94411	-1.24137	-1.56730
$1s$	-0.13480	-0.14114	-0.14444	-0.14584	-0.14865
$1s'$	-0.18638	-0.19174	-0.19608	-0.20262	-0.20428
$2s$	0.53465	0.55973	0.57729	0.59549	0.61013
$2s'$	0.57507	0.55504	0.54103	0.52590	0.51299
Orbital	$2p$	$2p$	$2p$	$2p$	$2p$
ϵ_i	-0.30969	-0.43286	-0.56663	-0.62959	-0.72592
$2p$	0.37034	0.37468	0.37968	0.38514	0.38960
$2p'$	0.51697	0.50737	0.50673	0.49377	0.48635
$2p''$	0.30596	0.31741	0.31777	0.33593	0.34407

the other states and/or basis sets is available upon request.

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