maximize the binding energy of the inner electrons should essentially maximize the total binding energy. The former, in turn, should be expected to be hydrogen-like in character.

That nothing fundamental in terms of a quantum mechanical description has been rendered by the present theory is underlined by the fact that no shell structure made its appearance in any of the densities which were obtained. Nevertheless, the improvement over Thomas–Fermi theory is considerable. Thus, the latter theory yields a divergent mean value of $1/r^2$ in marked contrast to the values obtained here.

We may draw attention to a similar statistical theory of Barnes and Cowan,[5] in which a "pseudo-potential" which varies inversely as the square of the radius is added to $V(r)$. Such an inclusion, while ad hoc, makes a truly significant improvement in the calculated atomic binding energies. The effect of this modification is to eliminate states of zero angular momentum, a feature of some arbitrariness. The theory reported here introduces no ad hoc exclusions of this sort, although the physical effect of reducing the charge density at the nucleus is similar.

## ACKNOWLEDGMENTS

[5] J. F. Barnes and R. D. Cowan, Phys. Rev. **132**, 236 (1963). See also P. H. Levine and O. Von Roos, ibid. **125**, 207 (1692); J. L. Schwartz and S. Borowitz, ibid. **133**, A122 (1964).

# Gaussian-Type Functions for Polyatomic Systems. I

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In view of rapid progress of computer capability, it is very desirable to have a reliable assessment of the usefulness of Gaussian-type orbitals as basis functions for large-scale molecular calculations. In the present paper several attempts are made to answer this question mainly at the level of atomic Hartree–Fock calculations. The necessary number of terms of Gaussian-type basis functions in the analytical Hartree–Fock expansion calculation is apparently more than twice as much as the number of terms needed in the expansion with Slater-type basis functions. However, this fact does not necessarily suggest a definite choice of Slater-type orbitals. Discussions pertinent to this point are presented in the latter part of the present paper.

## I. INTRODUCTION

THE advent of high-speed computers has encouraged us to launch a major programming effort on quantum-mechanical calculations of polyatomic systems. If we are to proceed with concepts and methods available at present, the most difficult problem is the calculation of necessary molecular integrals.

Slater-type orbitals have been widely used for atomic and molecular calculations. The effort to reach Hartree–Fock solutions by analytical expansion with Slater-type basis functions has been rewardingly successful in lighter atoms and diatomic molecules. However, attempts to evaluate general many-center molecular integrals with adequate accuracy in reasonable time have met with great difficulties. There has been no conspicuous change or breakthrough on the side of mathematical analysis. It is the spectacular advance of computer capability that brings prospects of future success. McLean[1] was the first to tackle the calculation of many-center integrals over Slater-type orbitals with considerable success in practical applications, but the programming effort was confined to linear molecular systems. McLean's scheme is essentially a direct numerical integration method supplemented with sophisticated program structure. The present limitation to linear systems can be relaxed if one is prepared to lengthen the calculation by an order of magnitude. Given the present status of computing equipment, this should turn out to be reasonable in the very near future. Recent work of Shavitt and Karplus[2] represents the most successful effort to date in handling general molecular integrals over Slater-type orbitals. The central idea is the application of the integral transform from exponentials to Gaussians:

$$\exp(-\zeta r) = \frac{\zeta}{2\sqrt{\pi}} \int_0^\infty \alpha^{-\frac{3}{2}} \exp\left(-\frac{\zeta^2}{4\alpha}\right) \exp(-\alpha r^2) d\alpha \quad (1.1)$$

It is obvious that by doing this additional integrals are introduced on top of the already multidimensional

[1] A. D. McLean, J. Chem. Phys. **32**, 1595 (1960).

[2] I. Shavitt and M. Karplus, J. Chem. Phys. **36**, 550 (1962).

integrals, but the reason for the success of this transformation lies in the fact that integrals over Gaussian functions $\exp(-\alpha r^2)$ are so simple in comparison to those over $\exp(-\zeta r)$, that one regains here the loss which is created by additional integrals over transformation variables. Because of this contrasting simplicity of evaluation of molecular integrals over Gaussian functions, several workers have hopefully proposed the use of Gaussian and associated functions, which we call Gaussian-type orbitals, instead of Slater-type orbitals in the quantum mechanical calculations of polyatomic systems.

The first systematic consideration of integrals over Gaussian-type integrals is that due to Boys.[3] Since then several papers with applications have been published. For instance, the treatment of the methane molecule by Nesbet[4] and later by Krauss[5] is worthy of mention, because they adopted Gaussian-type orbitals to carry out calculations without any dubious approximation of many-center integrals. At the time, this was something which could not be done with a reasonable amount of computer time with Slater-type orbitals. This is, the present author believes, a very important point to be taken into account when one contemplates using Gaussian-type orbitals in molecular calculations.

In the present paper several important findings on Gaussian-type orbitals are presented. In the following section we report results of the attempt to approximate a single Slater-type orbital in terms of a linear combination of Gaussian-type orbitals. Then, the effort to reach the Hartree–Fock solutions by Roothaan's expansion method with Gaussian-type orbitals is described.

It is the author's judgment that, in future calculations on polyatomic systems, both Slater-type and Gaussian-type functions will be used for several years to come, and that work using one type will complement that using the other type. A discussion pertinent to this point of view is presented in the last section.

## II. GAUSSIAN EXPANSION OF SLATER-TYPE ORBITALS

Various methods may be used to obtain approximate expansions of Slater-type orbitals in terms of Gaussian-type orbitals. The method being used in the present work is due to McWeeny.[6] We first describe the method and then present the numerical results. Methods based on least squares have also been under consideration and are discussed toward the end of this section.

### 1. McWeeny's Variational Method

It is to be noted first that the Slater-type orbitals are themselves exact eigenfunctions of a certain central-

[3] S. F. Boys, Proc. Roy. Soc. (London) A200, 542 (1950).
[4] R. K. Nesbet, dissertation, The University of Cambridge, 1954; J. Chem. Phys. 32, 1114 (1960).
[5] M. Krauss, J. Chem. Phys. 38, 564 (1963).
[6] R. McWeeny, Acta Cryst. 6, 631 (1953).

field problem. Once the Hamiltonians are established, they may be used to obtain approximate eigenfunctions as a linear combination of Gaussian-type orbitals by means of variational procedures. McWeeny[6] applied this method to $1s$, $2s$, and $2p$ Slater-type orbitals.

Let us first formulate the scheme in a general form and then apply it to several cases. The definition of the normalized Slater-type orbitals (STO's) is

$$\psi_s = R_{n_s}(r) Y_{lm}(\theta, \phi),$$

$$R_{n_s}(r) = [(2n_s)!]^{-\frac{1}{2}}(2Z/n_s)^{n_s+\frac{1}{2}}r^{n_s-1}\exp[-(Z/n_s)r].$$

$$(2.1)$$

Here, the parameter $Z$ is not restricted to integer values. It is easily verified that these STO's satisfy the following equations (in atomic units),

$$H_s\psi_s = E\psi_s, \qquad (2.2)$$

where

$$H_s = -\frac{1}{2}\Delta - (Z/r) - (1/2r^2)[l(l+1) - n_s(n_s-1)],$$

$$(2.3)$$

$$E = -\frac{1}{2}(Z/n_s)^2. \qquad (2.4)$$

The first term of the "additional potential"

$$-(1/2r^2)[l(l+1) - n_s(n_s-1)]$$

cancels out the angular dependent part of the kinetic-energy operator when the polar coordinate system is introduced. Thus,

$$H_s = -\frac{1}{2}\frac{\partial^2}{\partial r^2} - r^{-1}\frac{\partial}{\partial r} - \frac{Z}{r} + \frac{n_s(n_s-1)}{2r^2}. \qquad (2.5)$$

For later convenience, we introduce a variable $\rho = Zr$ and write the eigenvalue operator as

$$Z^{-2}H_s = -\frac{1}{2}\frac{\partial^2}{\partial\rho^2} - \frac{1}{\rho}\frac{\partial}{\partial\rho} + \frac{n_s(n_s-1)}{2}\frac{1}{\rho^2} - \frac{1}{\rho}. \qquad (2.6)$$

Now let us introduce the normalized Gaussian-type orbitals (GTO's):

$$\chi_{g,i} = R_{n_g}(r) Y_{lm}(\theta, \phi), \qquad (2.7)$$

$$R_{n_g}(r) = N_i r^{n_g-1}\exp(-\zeta_i r^2)$$

$$= N_i Z^{-(n_g-1)}\rho^{n_g-1}\exp(-\alpha_i\rho^2), \qquad (2.8)$$

$$N_i = \left[\frac{2^{2n_g+\frac{3}{2}}}{(2n_g-1)!!\sqrt{\pi}}\right]^{\frac{1}{2}}(Z^2\alpha_i)^{(2n_g+1)/4}, \qquad (2.9)$$

$$\alpha_i = Z^{-2}\zeta_i. \qquad (2.10)$$

In the calculations of the present section we do not mix different values of $n_g$ just for simplicity when we set up linear combination of GTO's. This restriction is not inherent in the calculations of Sec. III. For convenience, we use the labels $(n_g l)_g$ for GTO's and $(n_s l)_s$ for STO's to avoid possible confusion. We must note that if the power of $r$ is written as $r^{n-1}$ then odd

TABLE I. $(\alpha)_{\text{opt}}$ from Eq. (2.13).

| $n_s$ | $n_g = 1$ | 3 | 5 | 2 | 4 | 6 |
|---|---|---|---|---|---|---|
| 1 | 0.2829 | | | | | |
| 2 | 0.02105 | 0.05016 | | 0.04527 | | |
| 3 | 0.003493 | 0.01478 | 0.01842 | 0.01060 | 0.01714 | |
| 4 | 0.0009790 | 0.005202 | 0.007587 | 0.003367 | 0.06570 | 0.008341 |
| 5 | 0.0003696 | 0.002187 | 0.003475 | 0.001346 | 0.02889 | 0.003963 |

$n_g$ goes with even $l$ and even $n_g$ with odd $l$. Thus we may name GTO's as $(1s)_g$, $(3s)_g$, $(5s)_g$, $\cdots$; $(2p)_g$, $(4p)_g$, $\cdots$; $(3d)_g$, $(5d)_g$, $\cdots$; etc. It is only under this restriction that various atomic and molecular integrals over GTO's can be performed with great ease.

A straightforward calculation gives the following results:

$$\langle X_{g,i} \mid Z^{-2}H_s \mid X_{g,j} \rangle$$

$$= \left[ (2n_g+1)\frac{\alpha_i\alpha_j}{(\alpha_i+\alpha_j)} + \frac{[n_s(n_s-1)-n_g(n_g-1)]}{(2n_g-1)}(\alpha_i+\alpha_j) \right.$$

$$\left. -\frac{(n_g-1)!2^{n_g}}{(2n_g-1)!!\sqrt{\pi}}(\alpha_i+\alpha_j)^{\frac{1}{2}} \right]\langle X_{g,i} \mid X_{g,j} \rangle, \quad (2.11)$$

$$\langle X_{g,i} \mid X_{g,j} \rangle = \left[ \frac{2(\alpha_i\alpha_j)^{\frac{1}{2}}}{(\alpha_i+\alpha_j)} \right]^{n_g+\frac{1}{2}}. \quad (2.12)$$

From these general formulas it is readily seen what can be done with a single Gaussian-type orbital to approximate a Slater-type orbital by applying the variational principle. The optimal single $\alpha$ value is

$$(\alpha)_{\text{opt}} = \left[ \frac{(n_g-1)!2^{n_g}\sqrt{2}}{(2n_g-3)!!\sqrt{\pi}} \frac{1}{4n_g+4n_s(n_s-1)-1} \right]^2, \quad (2.13)$$

and the corresponding approximate eigenvalue is

$$\langle Z^{-2}H_s \rangle_{\text{opt}} = -\frac{1}{2}\frac{(2n_g-1)}{4n_g+4n_s(n_s-1)-1}\left[ \frac{(n_g-1)!2^{n_g}\sqrt{2}}{(2n_g-1)!!\sqrt{\pi}} \right]^2$$

$$(2.14)$$

Numerical values from these two formulas are collected in Tables I and II. It is interesting to note that, for instance, a $(2p)_g$ GTO works better than a $(4p)_g$ GTO to approximate a $(3p)_s$ STO and a $(4p)_s$ STO as far as the energy is concerned. We return to this point later.

A computer program in FORTRAN II language has been used to obtain various approximate expansions of STO's in terms of GTO's:

$$\psi_s = \sum_i C_i\chi_{g,i}. \quad (2.15)$$

As mentioned earlier, $\chi_{g,i}$ is normalized, and the expansion coefficients $\{C_i\}$ are also normalized to give $\langle \psi_s \mid \psi_s \rangle = 1$. An advantage of using $\rho = Zr$ and $\alpha$ with normalized GTO's is that it makes it clear how to rescale a GTO expansion for arbitrary values of exponent of STO's without recalculating the expansion coefficients $\{C_i\}$. Suppose we want an approximate expansion of a Slater-type orbital, $r^{n_s-1}\exp(-\zeta_s r) Y_{lm}(\theta, \phi)$, in terms of GTO's, $r^{n_g-1}\exp(-\zeta_g r^2) Y_{lm}(\theta, \phi)$. First we decide on a value of $n_g$ and the number of terms to be used in the expansion. Then the optimization of the quantity $\langle Z^{-2}H_s \rangle(Z = n_s\zeta_s)$ by using (2.11) and (2.12) gives us a set of $\{C_i\}$ and $\{\alpha_i\}$.

To determine the optimum set of $\{\zeta_{g,i}\}$ we use the formula,

$$\zeta_{g,i} = (n_s\zeta_s)^2\alpha_i, \quad (2.16)$$

which follows from (2.10). The fact is that we need to work out a best expansion with given length of expansion only once for each Slater-type orbital.

Numerical results so far obtained are shown in Tables III to VII. Some of them overlap the results published by McWeeny,[6] Singer,[7] Whitten,[8] and Reeves,[9] but usually with different values of parameters. This is due to the existence of multiple minima of approximate eigenvalues in the space spanned by variational parameters. Difficulty in achieving true minimization, because of these multiple minima, grows rapidly with increase in the number of variational parameters. Because of this difficulty it is not claimed that we have obtained and listed true optimum values of $\{\alpha_i\}$ in the tables. The existence of multiple minima is very annoying in

TABLE II. $\langle Z^{-2}H_s \rangle$ from Eq. (2.14).

| $n_s$ | $n_g = 1$ | 3 | 5 | 2 | 4 | 6 |
|---|---|---|---|---|---|---|
| 1 | −0.4244 | | | | | |
| 2 | −0.1157 | −0.09531 | | −0.11318 | | |
| 3 | −0.04716 | −0.05174 | −0.04400 | −0.05476 | −0.04776 | |
| 4 | −0.02497 | −0.03069 | −0.02824 | −0.03087 | −0.02956 | −0.02692 |
| 5 | −0.01534 | −0.01990 | −0.01911 | −0.01951 | −0.01961 | −0.01856 |

[7] J. V. L. Longstaff and K. Singer, Proc. Roy. Soc. (London) A258, 421 (1960).
[8] J. L. Whitten, J. Chem. Phys. 39, 349 (1963).
[9] C. M. Reeves, J. Chem. Phys. 39, 1 (1963).

TABLE III. $\langle Z^{-2}H_s \rangle$ in a.u.: $1s$, $2p$ STO's.

| | $N$, number of terms in GTO expansion | | | |
|---|---|---|---|---|
| | $(1s)_s - (1s)_g$ | | $(2p)_s - (2p)_g$ | |
| $N$ | Present calc. | Singer[a] | Present calc. | Reeves[b] |
| 1 | −0.424413 | | −0.113177 | −0.113177 |
| 2 | −0.485813 | −0.486 | −0.123289 | −0.123289 |
| 3 | −0.496979 | −0.49689 | −0.124728 | −0.124728 |
| 4 | −0.499277 | −0.49928 | −0.124952 | −0.124952 |
| 5 | −0.499809 | −0.49976 | −0.124991 | |
| 6 | −0.499940 | −0.49988 | −0.124998 | |
| 7 | −0.499976 | | | |
| 8 | −0.499991 | −0.49992 | | |
| 9 | −0.499997 | | | |
| 10 | −0.499999 | | | |
| Exact value = −0.5 | | | Exact value = −0.125 | |

[a] See Ref. 7.
[b] See Ref. 9.

applying the variational procedure. Different sets of $\{\alpha_i\}$ can give essentially the same energy. The set actually chosen can be the one which is most suitable for a specific application. Such an example will be presented in the second paper of this series when we evaluate many-center integrals between STO's by using Gaussian expansion approximations.

We now turn to the point raised in the brief comment on Tables I and II. McWeeny[6] approximated Slater-type $(2s)_s$ orbitals in terms of $r^2 \exp(-\alpha_i r^2)$, not $\exp(-\alpha_i r^2)$. However, as far as the energy is concerned, the results in Table IV clearly show that $\exp(-\alpha_i r^2)$ works better than $r^2 \exp(-\alpha_i r^2)$. Even for a $(3s)_s$ STO, $\exp(-\alpha_i r^2)$ is still quite adequate as shown in Table IV. A similar situation can be seen in the case of a $(3p)_s$ STO.

This fact seems to be a mixed blessing as regards the use of Gaussian-type orbitals. On the one hand, it is an indication of slow convergence in approximating STO's by GTO's. On the other hand, the adequacy of using GTO's with lower $n_g$ values should be very helpful to reduce complications in molecular integral calculations.

## 2. Method of Least Squares

This is the method most frequently adopted for various kinds of curve fitting. Applications to the Gaussian expansion are discussed by Boys and Shavitt.[10] A computer program for least-squares fitting has been written for the present purpose but we have found that the program based on McWeeny's method is more convenient to use. However, there is no denying that the method of least squares is inherently more versatile, especially with a choice of a weighted function, than the straightforward variational method. But if one tries to find optimum values of parameters by using a least-

squares method, one has to deal with similar problems of multiple minima, and these could well be worse than in the minimum energy method.

Optimally we would like to have a method of curve fitting which is not marred by the trouble of multiple minima. We present here a possible mathematical device which could sidestep such trouble. This is an adaptation to Gaussian's of a method originally devised for (and successfully applied to) exponential functions.[11] It consists of a set of well-defined mathematical procedures, although it has not been put into a numerical test.

The objective is to find a suitable Gaussian expansion of a well-behaved arbitrary function $f(x)$:

$$f(x) \sim C_1 \exp(\alpha_1 x^2) + C_2 \exp(\alpha_2 x^2) + \cdots + C_m \exp(\alpha_m x^2).$$

$$(2.17)$$

Assume that with proper choice of $\{\alpha_i\}$ and $\{C_i\}$ the following $n (n \geq 2m)$ equations are satisfied:

$$f_k = f(x_k) = \sum_{j=1}^{m} C_j \exp(\alpha_j x_k^2), \qquad k = 1, \cdots, n, \quad (2.18)$$

where $x_k = (kw)^{\frac{1}{2}}$, $w$ being a constant increment. This requirement cannot generally be satisfied, but let us proceed on the basis that it can for the moment. Later we introduce least-squares procedures to correct this point.

It is convenient to use a new set of parameters

$$v_j = \exp(\alpha_j w^2) \qquad (2.19)$$

in place of $\alpha_j$. Now suppose that $m$ real values of $v_j$ are known. Then it is always possible to construct an $m$th-order algebraic equation.

$$v^m + S_1 v^{m-1} + S_2 v^{m-2} + \cdots + S_m = 0, \qquad (2.20)$$

which yields $v_1, v_2, \cdots, v_m$ as its $m$ real roots. Of course, these $\{v_j\}$ are the very quantities we wish to determine. However, if there is any method to determine the coefficients, $S_1, S_2, \cdots, S_m$, the above equation will give us $v_1, v_2, \cdots, v_m$ as its roots. This may be achieved in the following way.

From (2.18), (2.19), and (2.20) it is easily verified that

$$f_l S_m + f_{l+1} S_{m-1} + \cdots + f_{l+m-1} S_1 + f_{l+m} = 0,$$

$$l = 1, 2, \cdots, n - m. \qquad (2.21)$$

Here we have $n - m \geq m$ equations from which $S_1$, $S_2, \cdots, S_m$ can be determined. In principle, $m$ equations should be enough to determine $m$ unknown $\{S_i\}$. However, this is totally inadequate as a curve-fitting

[10] S. F. Boys and I. Shavitt, Proc. Roy. Soc. (London) A254, 487 (1960).

[11] R. A. Buckingham, *Numerical Methods* (Pitman Publishing Corporation, New York, 1957).

TABLE IV. $\langle Z^{-2}H_s\rangle$ in a.u.: $2s$, $3s$, $3p$ STO's.

| | $N$, number of terms in GTO expansion | | | | | |
|---|---|---|---|---|---|---|
| | $(2s)_s-(1s)_g$ | $(2s)_s-(3s)_g$ | $(3s)_s-(1s)_g$ | $(3s)_s-(3s)_g$ | $(3p)_s-(2p)_g$ | $(3p)_s-(4p)_g$ |
| 1 | −0.11575 | −0.09531 | −0.047157 | −0.051738 | −0.054763 | −0.047758 |
| 2 | −0.12380 | −0.11610 | −0.055461 | −0.055080 | −0.055420 | −0.053877 |
| 3 | −0.12441 | −0.12230 | −0.055515 | −0.055493 | −0.055519 | −0.055189 |
| 4 | −0.12493 | −0.12415 | −0.055549 | −0.055544 | −0.055549 | −0.055472 |

Exact value for $2s = -0.125$.     Exact value for $3s$, $3p = -(1/18) = -0.055555$.

TABLE V. Parameters of GTO expansion. $(1s)_s-(1s)_g$.

| $N$ | $\alpha_i$ | $C_i$ |
|---|---|---|
| 2 | 0.201527 | 0.82123 |
| | 1.33248 | 0.27441 |
| 3 | 0.151374 | 0.64767 |
| | 0.681277 | 0.40789 |
| | 4.50038 | 0.07048 |
| 4 | 0.123317 | 0.50907 |
| | 0.453757 | 0.47449 |
| | 2.01330 | 0.13424 |
| | 13.3615 | 0.01906 |
| 5 | 0.101309 | 0.37602 |
| | 0.321144 | 0.50822 |
| | 1.14680 | 0.20572 |
| | 5.05796 | 0.04575 |
| | 33.6444 | 0.00612 |
| 6 | 0.082217 | 0.24260 |
| | 0.224660 | 0.49221 |
| | 0.673320 | 0.29430 |
| | 2.34648 | 0.09280 |
| | 10.2465 | 0.01938 |
| | 68.1600 | 0.00255 |
| 7 | 0.060738 | 0.11220 |
| | 0.155858 | 0.44842 |
| | 0.436661 | 0.38487 |
| | 1.370498 | 0.15161 |
| | 4.970178 | 0.03939 |
| | 22.17427 | 0.00753 |
| | 148.2732 | 0.00097 |
| 8 | 0.0525423 | 0.06412 |
| | 0.123655 | 0.35846 |
| | 0.315278 | 0.42121 |
| | 0.886632 | 0.21210 |
| | 2.765179 | 0.06848 |
| | 9.891184 | 0.01694 |
| | 43.93024 | 0.00322 |
| | 293.5708 | 0.00041 |
| 9 | 0.0441606 | 0.03645 |
| | 0.106151 | 0.29898 |
| | 0.250988 | 0.40433 |
| | 0.618330 | 0.25781 |
| | 1.714744 | 0.10769 |
| | 5.478296 | 0.03108 |
| | 19.72537 | 0.00720 |
| | 87.39897 | 0.00138 |
| | 594.3123 | 0.00017 |
| 10 | 0.0285649 | 0.00775 |
| | 0.0812406 | 0.20267 |
| | 0.190537 | 0.41300 |
| | 0.463925 | 0.31252 |
| | 1.202518 | 0.14249 |
| | 3.379649 | 0.04899 |
| | 10.60720 | 0.01380 |
| | 38.65163 | 0.00318 |
| | 173.5822 | 0.00058 |
| | 1170.498 | 0.00007 |

procedure. Thus the reasonable procedure to be taken here would be the following: (1) Pick $w$ and $n$. (2) Compute $f_k = f(x_k)$ with $x_k = (kw)^{\frac{1}{2}}$. (3) Solve a set of $n-m$ equations (2.21) by means of a standard least-squares method to obtain $S_1$, $S_2$, $\cdots$, $S_m$. (4) Find the $m$ roots $v_1$, $v_2$, $\cdots$, $v_m$ of the equation (2.20). (5) Calculate $\alpha_j$ from (2.19). (6) Apply once again a least-squares procedure to determine the coefficients $C_1$, $C_2$, $\cdots$, $C_m$ in (2.17) by using $\{f_k\}$.

It is easy to extend the present scheme to the Gaussian-type functions, $r^{n_g-1}\exp(-\alpha r^2)$, with $n_g$ larger than one.

## III. ATOMIC SELF-CONSISTENT-FIELD CALCULATIONS WITH GAUSSIAN-TYPE BASIS FUNCTIONS

In Roothaan's expansion method relatively few STO's are needed to closely approximate Hartree–Fock solutions of atoms. For example, six $s$ functions and four $p$ functions are enough to give seven-figure accuracy in total energy for the ground states of the first-row atoms.[12] It should be instructive, especially with pro-

TABLE VI. Parameters of GTO expansion. $(2p)_s-(2p)_g$.

| $N$ | $\alpha_i$ | $C_i$ |
|---|---|---|
| 2 | 0.032392 | 0.78541 |
| | 0.139276 | 0.32565 |
| 3 | 0.024684 | 0.57860 |
| | 0.079830 | 0.47406 |
| | 0.337072 | 0.09205 |
| 4 | 0.020185 | 0.41444 |
| | 0.055713 | 0.53151 |
| | 0.174211 | 0.18295 |
| | 0.733825 | 0.02639 |
| 5 | 0.017023 | 0.28504 |
| | 0.042163 | 0.52969 |
| | 0.111912 | 0.27049 |
| | 0.346270 | 0.06550 |
| | 1.458369 | 0.00833 |
| 6 | 0.015442 | 0.21705 |
| | 0.035652 | 0.49334 |
| | 0.085676 | 0.32224 |
| | 0.227763 | 0.10439 |
| | 0.710128 | 0.02055 |
| | 3.009711 | 0.00241 |

[12] E. Clementi, C. C. J. Roothaan, and M. Yoshimine, Phys. Rev. **127**, 1618 (1962).

TABLE VII. Parameters of GTO expansion.

| | (2s)<sub>s</sub>—(1s)<sub>g</sub> | | | (2s)<sub>s</sub>—(3s)<sub>g</sub> | | | (3s)<sub>s</sub>—(1s)<sub>g</sub> | |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| $N$ | $\alpha_i$ | $C_i$ | $N$ | $\alpha_i$ | $C_i$ | $N$ | $\alpha_i$ | $C_i$ |
| 2 | 0.026725 | 1.0078 | 2 | 0.045936 | 0.81372 | 2 | 0.0065103 | 1.05120 |
| | 0.10456 | −0.04872 | | 0.20563 | 0.33894 | | 0.076432 | −0.15798 |
| 3 | 0.014660 | 0.44492 | 3 | 0.037585 | 0.66009 | 3 | 0.0066851 | 1.06712 |
| | 0.037634 | 0.60335 | | 0.13675 | 0.44967 | | 0.056599 | −0.15411 |
| | 0.98413 | −0.05385 | | 0.61246 | 0.11033 | | 0.22040 | −0.02115 |
| 4 | 0.016500 | 0.54627 | 4 | 0.031669 | 0.53789 | 4 | 0.0047430 | 0.47178 |
| | 0.042726 | 0.50899 | | 0.10053 | 0.49646 | | 0.0086456 | 0.61886 |
| | 0.58274 | −0.05708 | | 0.35008 | 0.17988 | | 0.057156 | −0.16770 |
| | 4.6935 | −0.00843 | | 1.54205 | 0.03814 | | 0.22271 | −0.01895 |

| | (3s)<sub>s</sub>—(3s)<sub>g</sub> | | | (3p)<sub>s</sub>—(2p)<sub>g</sub> | | | (3p)<sub>s</sub>—(4p)<sub>g</sub> | |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| 2 | 0.010769 | 0.76147 | 2 | 0.0064787 | 0.55899 | 2 | 0.014413 | 0.78986 |
| | 0.036358 | 0.35875 | | 0.016457 | 0.50670 | | 0.050378 | 0.36321 |
| 3 | 0.0082807 | 0.53553 | 3 | 0.0071691 | 0.65491 | 3 | 0.011149 | 0.59414 |
| | 0.022528 | 0.51193 | | 0.018954 | 0.41337 | | 0.032400 | 0.49513 |
| | 0.075079 | 0.10596 | | 0.14851 | −0.01769 | | 0.11271 | 0.12343 |
| 4 | 0.00721080 | 0.40977 | 4 | 0.0051045 | 0.31376 | 4 | 0.0091999 | 0.495203 |
| | 0.017891 | 0.55618 | | 0.011265 | 0.57213 | | 0.026107 | 0.52730 |
| | 0.049976 | 0.17847 | | 0.023277 | 0.18931 | | 0.067819 | 0.19064 |
| | 0.18578 | 0.01918 | | 0.23747 | −0.01371 | | 0.23712 | 0.04176 |

spective molecular calculations in mind, to see how many GTO's would be necessary to achieve more or less the same accuracy. For this purpose the computer program written by Roothaan and his collaborators[13] has been modified to use Gaussian-type basis functions in the expansion method instead of Slater-type basis functions. Necessary modifications and changes in the program were cut down to less than 300 words in FAP language for the IBM 7090 computer. This has been accomplished by preparing the whole mathematical setup for the Gaussian-type basis functions to resemble as closely as possible that of the original Slater-type basis functions.

The atomic orbitals are expanded in terms of basis functions according to

$$\phi_{i\lambda\alpha} = \sum_p \chi_{p\lambda\alpha} C_{i\lambda p}. \qquad (3.1)$$

The symmetry species is represented by $\lambda$, the subspecies by $\alpha$, $i$ labels the orbitals which cannot be distinguished any more by symmetry, and $p$ has the same role for the basis functions. Let the basis functions be given by

$$\chi_{p\lambda\alpha}(r, \theta, \phi) = R_{\lambda p}(r) Y_{\lambda\alpha}(\theta, \phi). \qquad (3.2)$$

The matrices and supermatrices which enter the calcu-

[13] C. C. J. Roothaan and P. S. Bagus, *Methods in Computational Physics* (Academic Press Inc., New York, 1963), Vol. 2, p. 47.

lation in Roothaan's expansion method are

$$S_{\lambda pq} = \int_0^\infty (du) u^2 R_{\lambda p}(u) R_{\lambda q}(u), \qquad (3.3)$$

$$U_{\lambda pq} = \int_0^\infty (du) u R_{\lambda p}(u) R_{\lambda q}(u), \qquad (3.4)$$

$$T_{\lambda pq} = \frac{1}{2} \int_0^\infty du [u^2 R'_{\lambda p}(u) R'_{\lambda q}(u) + \lambda(\lambda+1) R_{\lambda p}(u) R_{\lambda q}(u)], \qquad (3.5)$$

$$J^\nu_{\lambda pq,\mu rs} = \int_0^\infty (du) u^{-\nu+1} \int^u dv \cdot v^{\nu+2}$$

$$\times [R_{\lambda p}(u) R_{\lambda q}(u) R_{\mu r}(v) R_{\mu s}(v)$$

$$+ R_{\mu r}(u) R_{\mu s}(u) R_{\lambda q}(v) R_{\lambda q}(v)], \qquad (3.6)$$

$$K^\nu_{\lambda pq,\mu rs} = \frac{1}{2} \int_0^\infty du \cdot u^{-\nu+1} \int^u dv \cdot v^{\nu+2}$$

$$\times [R_{\lambda p}(u) R_{\mu r}(u) R_{\lambda q}(v) R_{\mu s}(v)$$

$$+ R_{\lambda q}(u) R_{\mu s}(u) R_{\lambda p}(v) R_{\mu r}(v)$$

$$+ R_{\lambda p}(u) R_{\mu s}(u) R_{\lambda q}(v) R_{\mu r}(v)$$

$$+ R_{\lambda q}(u) R_{\mu r}(u) R_{\lambda p}(v) R_{\mu s}(v)]. \qquad (3.7)$$

TABLE VIII. Calculated total and orbital energy for helium $(1s)^2\ ^1S$.

| $N$ | $E$ | $\epsilon$ |
|---|---|---|
| 1 | $-2.3009869$ | $-0.65638$ |
| 2 | $-2.7470661$ | $-0.858911$ |
| 3 | $-2.8356798$ | $-0.903577$ |
| 4 | $-2.8551603$ | $-0.914124$ |
| 5 | $-2.8598949$ | $-0.916869$ |
| 6 | $-2.8611163$ | $-0.917688$ |
| 7 | $-2.8614912$ | $-0.917895$ |
| 8 | $-2.8616094$ | $-0.917931$ |
| 9 | $-2.8616523$ | $-0.917946$ |
| 10 | $-2.8616692$ | $-0.917952$ |

Hartree–Fock value

$$E = -2.861680 \qquad \epsilon = -0.91795$$

The basis functions are now taken to be normalized Gaussian-type functions, namely,

$$R_{\lambda p}(r) = N(n_{\lambda p},\ \zeta_{\lambda p}) r^{n_{\lambda p}-1} \exp(-\zeta_{\lambda p} r^2), \qquad (3.8)$$

$$N(n_{\lambda p},\ \zeta_{\lambda p}) = [(2/\pi)^{\frac{1}{2}} 2^{2n_{\lambda p}+1} \zeta_{\lambda p}^{n_{\lambda p}+\frac{1}{2}}/(2n_{\lambda p}-1)!!]^{\frac{1}{2}}. \qquad (3.9)$$

It is to be noted that the parameter $\zeta_{\lambda p}$ has the dimension of $(\text{length})^{-2}$ instead of $(\text{length})^{-1}$. As noted before, odd $n_{\lambda p}$ goes with even $\lambda$ and even $n_{\lambda p}$ with odd $\lambda$. For these basis functions the integrals defined by Eqs. (3.3) through (3.7) assume the following forms:

$$S_{\lambda pq} = [V_{2n_{\lambda p}}(\zeta_{\lambda p}) V_{2n_{\lambda q}}(\zeta_{\lambda q})]^{-\frac{1}{2}} V_{n_{\lambda p}+n_{\lambda q}}[\tfrac{1}{2}(\zeta_{\lambda p}+\zeta_{\lambda q})], \qquad (3.10)$$

$$U_{\lambda pq} = (2/\pi)^{\frac{1}{2}} 2 [V_{2n_{\lambda p}}(\zeta_{\lambda p}) V_{2n_{\lambda q}}(\zeta_{\lambda q})]^{-\frac{1}{2}}$$
$$\times V_{n_{\lambda p}+n_{\lambda q}-1}[\tfrac{1}{2}(\zeta_{\lambda p}+\zeta_{\lambda q})], \qquad (3.11)$$

$$T_{\lambda pq} = \tfrac{1}{2}\zeta_{\lambda p}\zeta_{\lambda q}[V_{2n_{\lambda p}}(\zeta_{\lambda p}) V_{2n_{\lambda q}}(\zeta_{\lambda q})]^{-\frac{1}{2}}$$
$$\times V_{n_{\lambda p}+n_{\lambda q}+2}[\tfrac{1}{2}(\zeta_{\lambda p}+\zeta_{\lambda q})]$$
$$- \{W_{\lambda, n_{\lambda p}}(\zeta_{\lambda p}) + W_{\lambda, n_{\lambda q}}(\zeta_{\lambda q})\} V_{n_{\lambda p}+n_{\lambda q}}[\tfrac{1}{2}(\zeta_{\lambda p}+\zeta_{\lambda q})]$$
$$+ W_{\lambda, n_{\lambda p}}(\zeta_{\lambda p}) W_{\lambda, n_{\lambda q}}(\zeta_{\lambda q}) V_{n_{\lambda p}+n_{\lambda q}-2}[\tfrac{1}{2}(\zeta_{\lambda p}+\zeta_{\lambda q})], \qquad (3.12)$$

TABLE IX. Orbital parameters for $\mathrm{He}(1s)^2\ ^1S$.

| $N$ | $\zeta_i$ | $C_i$ |
|---|---|---|
| 2 | 0.532149 | 0.82559 |
|   | 4.097728 | 0.28317 |
| 3 | 0.382938 | 0.65722 |
|   | 1.998942 | 0.40919 |
|   | 13.62324 | 0.08026 |
| 4 | 0.298073 | 0.51380 |
|   | 1.242567 | 0.46954 |
|   | 5.782948 | 0.15457 |
|   | 38.47497 | 0.02373 |
| 5 | 0.244528 | 0.39728 |
|   | 0.873098 | 0.48700 |
|   | 3.304241 | 0.22080 |
|   | 14.60940 | 0.05532 |
|   | 96.72976 | 0.00771 |
| 6 | 0.193849 | 0.26768 |
|   | 0.589851 | 0.46844 |
|   | 1.879204 | 0.29801 |
|   | 6.633653 | 0.10964 |
|   | 28.95149 | 0.02465 |
|   | 192.4388 | 0.00330 |
| 7 | 0.160274 | 0.18067 |
|   | 0.447530 | 0.43330 |
|   | 1.297177 | 0.34285 |
|   | 4.038781 | 0.15815 |
|   | 14.22123 | 0.04727 |
|   | 62.24915 | 0.00971 |
|   | 414.4665 | 0.00127 |
| 8 | 0.137777 | 0.11782 |
|   | 0.347207 | 0.36948 |
|   | 0.918171 | 0.36990 |
|   | 2.580737 | 0.21021 |
|   | 7.921657 | 0.07999 |
|   | 28.09935 | 0.02134 |
|   | 124.5050 | 0.00415 |
|   | 833.0522 | 0.00053 |
| 9 | 0.129793 | 0.09809 |
|   | 0.308364 | 0.31570 |
|   | 0.725631 | 0.34783 |
|   | 1.802569 | 0.24466 |
|   | 4.951881 | 0.11748 |
|   | 15.41660 | 0.03844 |
|   | 55.41029 | 0.00939 |
|   | 246.8036 | 0.00178 |
|   | 1663.571 | 0.00023 |
| 10 | 0.107951 | 0.05242 |
|   | 0.240920 | 0.24887 |
|   | 0.552610 | 0.36001 |
|   | 1.352436 | 0.28403 |
|   | 3.522261 | 0.14909 |
|   | 9.789053 | 0.05709 |
|   | 30.17990 | 0.01721 |
|   | 108.7723 | 0.00412 |
|   | 488.8941 | 0.00076 |
|   | 3293.694 | 0.00010 |

TABLE X. Total energy (in a.u.) for the Li to Ne atoms. Comparison between GTO and STO calculations.

| Atom | State | GTO $9-(1s)_\sigma,\ 5-(2p)_\sigma$ | GTO $10-(1s)_\sigma,\ 6-(2p)_\sigma$ | STO best double[a] | STO accurate[b] |
|---|---|---|---|---|---|
| Li | $^2S$ | $-7.4322794$ | $-7.4325033$ | $-7.4327184$ | $-7.4327257$ |
| Be | $^1S$ | $-14.572068$ | $-14.572579$ | $-14.572368$ | $-14.573020$ |
| B | $^2P$ | $-24.527130$ | $-24.528282$ | $-24.527890$ | $-24.529052$ |
| C | $^3P$ | $-37.685247$ | $-37.687324$ | $-37.686677$ | $-37.688611$ |
| N | $^4S$ | $-54.395336$ | $-54.398909$ | $-54.397873$ | $-54.400911$ |
| O | $^3P$ | $-74.800289$ | $-74.806295$ | $-74.804180$ | $-74.809360$ |
| F | $^2P$ | $-99.395586$ | $-99.404870$ | $-99.401164$ | $-99.409284$ |
| Ne | $^1S$ | $-128.52674$ | $-128.54094$ | $-128.53480$ | $-128.54701$ |

[a] E. Clementi, J. Chem. Phys. **40**, 1944 (1964).
[b] See Ref. 11.

TABLE XI. Orbital exponents of the Gaussian basis set: $9-(1s)_g$, $5-(2p)_g$.

| | Li($^2S$) | Be($^1S$) | B($^2P$) | C($^3P$) | N($^4S$) | O($^3P$) | F($^2P$) | Ne($^1S$) |
|---|---|---|---|---|---|---|---|---|
| 1s | 1.15685 | 2.18473 | 3.40623 | 5.14773 | 7.19274 | 9.53223 | 12.2164 | 14.9060 |
| 1s | 9.35329 | 17.6239 | 28.0694 | 42.4974 | 59.8376 | 81.1696 | 104.053 | 132.463 |
| 1s | 31.9415 | 60.3255 | 96.4683 | 146.097 | 204.749 | 273.188 | 350.269 | 432.759 |
| 1s | 138.730 | 262.139 | 419.039 | 634.882 | 887.451 | 1175.82 | 1506.03 | 1821.39 |
| 1s | 0.44462 | 0.85895 | 1.30566 | 1.96655 | 2.68598 | 3.41364 | 4.36885 | 5.12741 |
| 1s | 0.076663 | 0.18062 | 0.32448 | 0.49624 | 0.70004 | 0.93978 | 1.20775 | 1.49117 |
| 1s | 3.15789 | 5.93258 | 9.37597 | 14.1892 | 19.9981 | 27.1836 | 34.8432 | 43.7659 |
| 1s | 921.271 | 1741.38 | 2788.41 | 4232.61 | 5909.44 | 7816.54 | 9994.79 | 12102.2 |
| 1s | 0.028643 | 0.058350 | 0.10219 | 0.15331 | 0.21329 | 0.28461 | 0.36340 | 0.44676 |
| 2p | | | 0.21336 | 0.35945 | 0.53136 | 0.71706 | 0.93826 | 1.20292 |
| 2p | | | 0.68358 | 1.14293 | 1.70740 | 2.30512 | 2.99586 | 3.86542 |
| 2p | | | 2.43599 | 3.98640 | 5.95635 | 7.90403 | 10.0820 | 12.9187 |
| 2p | | | 11.3413 | 18.1557 | 26.7860 | 35.1832 | 44.3555 | 56.4511 |
| 2p | | | 0.070114 | 0.11460 | 0.16537 | 0.21373 | 0.27329 | 0.34440 |

where

$$V_i(x) = (i-1)!!/[(x)^{\frac{1}{2}}]^{i+1}, \qquad (3.13)$$

$$W_{ij}(x) = 2x^{-1}(j-i-1), \qquad (3.14)$$

and

$J^\nu_{\lambda pq,\mu rs}$

$= (2/\pi)^{\frac{1}{2}} 2 [V_{2n_{\lambda p}}(\zeta_{\lambda p}) V_{2n_{\lambda q}}(\zeta_{\lambda q}) V_{2n_{\mu r}}(\zeta_{\mu r}) V_{2n_{\mu s}}(\zeta_{\mu s})]^{-\frac{1}{2}}$

$\times \{V_{n_{\lambda p}+n_{\lambda q}-\nu-1}[\frac{1}{2}(\zeta_{\lambda p}+\zeta_{\lambda q})]V_{n_{\mu r}+n_{\mu s}+\nu}[\frac{1}{2}(\zeta_{\mu r}+\zeta_{\mu s})]$

$\times C_{n_{\mu p}+n_{\lambda q}-\nu-1,n_{\mu r}+n_{\mu s}+\nu}[(\zeta_{\lambda p}+\zeta_{\lambda q})/(\zeta_{\mu r}+\zeta_{\mu s})]$

$+ V_{n_{\mu r}+n_{\mu s}-\nu-1}[\frac{1}{2}(\zeta_{\mu r}+\zeta_{\mu s})]V_{n_{\lambda p}+n_{\lambda q}+\nu}[\frac{1}{2}(\zeta_{\lambda p}+\zeta_{\lambda q})]$

$\times C_{n_{\mu r}+n_{\mu s}-\nu-1,n_{\lambda p}+n_{\lambda q}+\nu}[(\zeta_{\mu r}+\zeta_{\mu s})/(\zeta_{\lambda p}+\zeta_{\lambda q})]\}, \qquad (3.15)$

$K^\nu_{\lambda pq,\mu rs}$

$= (2/\pi)^{\frac{1}{2}} [V_{2n_{\lambda p}}(\zeta_{\lambda p}) V_{2n_{\lambda q}}(\zeta_{\lambda q}) V_{2n_{\mu r}}(\zeta_{\mu r}) V_{2n_{\mu s}}(\zeta_{\mu s})]^{-\frac{1}{2}}$

$\times \{V_{n_{\lambda p}+n_{\mu r}-\nu-1}[\frac{1}{2}(\zeta_{\lambda p}+\zeta_{\mu r})]V_{n_{\lambda q}+n_{\mu s}+\nu}[\frac{1}{2}(\zeta_{\lambda q}+\zeta_{\mu s})]$

$\times C_{n_{\lambda p}+n_{\mu r}-\nu-1,n_{\lambda q}+n_{\mu s}+\nu}[(\zeta_{\lambda p}+\zeta_{\mu r})/(\zeta_{\lambda q}+\zeta_{\mu s})]$

$+ V_{n_{\lambda q}+n_{\mu s}-\nu-1}[\frac{1}{2}(\zeta_{\lambda q}+\zeta_{\mu s})]V_{n_{\lambda p}+n_{\mu r}+\nu}[\frac{1}{2}(\zeta_{\lambda p}+\zeta_{\mu r})]$

$\times C_{n_{\lambda q}+n_{\mu s}-\nu-1,n_{\lambda p}+n_{\mu r}+\nu}[(\zeta_{\lambda q}+\zeta_{\mu s})/(\zeta_{\lambda p}+\zeta_{\mu r})]$

$+ V_{n_{\lambda p}+n_{\mu s}-\nu-1}[\frac{1}{2}(\zeta_{\lambda p}+\zeta_{\mu s})]V_{n_{\lambda q}+n_{\mu r}+\nu}[\frac{1}{2}(\zeta_{\lambda q}+\zeta_{\mu r})]$

$\times C_{n_{\lambda p}+n_{\mu s}-\nu-1,n_{\lambda q}+n_{\mu r}+\nu}(\zeta_{\lambda p}+\zeta_{\mu s})/(\zeta_{\lambda q}+\zeta_{\mu r})]$

$+ V_{n_{\lambda q}+n_{\mu r}-\nu-1}[\frac{1}{2}(\zeta_{\lambda q}+\zeta_{\mu r})]V_{n_{\lambda p}+n_{\mu s}+\nu}[\frac{1}{2}(\zeta_{\lambda p}+\zeta_{\mu s})]$

$\times C_{n_{\lambda q}+n_{\mu r}-\nu-1,n_{\lambda p}+n_{\mu s}+\nu}[(\zeta_{\lambda q}+\zeta_{\mu r})/(\zeta_{\lambda p}+\zeta_{\mu s})]\}, \qquad (3.16)$

where

$$C_{\alpha,\beta}(t) = (1+t)^{-(\alpha+\beta)/2} \sum_{\lambda=1}^{\alpha} \frac{(\lambda+\beta-2)!!}{(\lambda-1)!!(\beta-1)!!}\left(\frac{t}{1+t}\right)^{(\lambda-1)/2}. \qquad (3.17)$$

A very close resemblance is apparent between the formulas listed above and those used in the original STO version of the program described in detail by

Roothaan and Bagus.[13] Tables VIII and IX show numerical results of a series of calculations designed to reach the Hartree–Fock solution in terms of Gaussian expansion for the ground state of helium. With 10 GTO's we have obtained almost six figure accuracy in total energy, but this appears to be a rather disappointing finding if we recall that a linear combination of only two STO's gives a better result.

Results of calculations for the first-row atoms are shown in Tables X through XIV. We have used various sizes of basis sets but only two sets, one with nine $(1s)_g$ and five $(2p)_g$ and the other with 10 $(1s)_g$ and six $(2p)_g$ are shown here. Because of the existence of multiple minima, it is not claimed that the values of orbital exponents are truly optimized, although a considerable amount of machine time has already been consumed in optimization. A set of mixed basis functions consisting of seven $(1s)_g$ and two $(3s)_g$ orbitals was also used for the ground state of helium but the result turned out to be poorer than that of nine $(1s)_g$ basis functions. Similar attempts have been made also for lithium, carbon, and nitrogen; but so far nothing has come out to encourage the inclusion of $(3s)_g$ orbitals to describe the $1s$ and $2s$ atomic orbitals of the first-row atoms.

## IV. DISCUSSIONS

The purpose of the present paper has been primarily to present several numerical facts about Gaussian-type orbitals. To some people, the results presented here may be a confirmation of their belief that Slater-type orbitals should be the choice for molecular and solid-state calculations. There is no denying that the Gaussian-type orbitals are far inferior basis functions to the Slater-type orbitals in representing atomic orbitals. If the true Hartree–Fock solution with seven or eight figure accuracy is one's objective, Slater-type orbitals should definitely be one's choice. To other people, how-

TABLE XII. Orbital exponents of the Gaussian basis set: $10-(1s)_g$, $6-(2p)_g$.

| | Li($^2S$) | Be($^1S$) | B($^2P$) | C($^3P$) | N($^4S$) | O($^3P$) | F($^2P$) | Ne($^1S$) |
|---|---|---|---|---|---|---|---|---|
| 1s | 1.90603 | 3.66826 | 6.25286 | 9.40900 | 13.4578 | 17.8966 | 23.3705 | 29.1672 |
| 1s | 16.7798 | 32.6562 | 55.8340 | 84.5419 | 120.899 | 160.920 | 209.192 | 261.476 |
| 1s | 60.0718 | 117.799 | 202.205 | 307.539 | 439.998 | 585.663 | 757.667 | 946.799 |
| 1s | 267.096 | 532.280 | 916.065 | 1397.56 | 1998.96 | 2660.12 | 3431.25 | 4262.61 |
| 1s | 0.71791 | 1.35431 | 2.31177 | 3.50002 | 4.99299 | 6.63901 | 8.62372 | 10.7593 |
| 1s | 0.26344 | 0.38905 | 0.68236 | 1.06803 | 1.56866 | 2.07658 | 2.69163 | 3.34255 |
| 1s | 0.077157 | 0.15023 | 0.26035 | 0.40017 | 0.580017 | 0.77360 | 1.00875 | 1.24068 |
| 1s | 0.540327 | 10.4801 | 17.8587 | 26.9117 | 38.4711 | 51.1637 | 66.7261 | 83.3433 |
| 1s | 1782.90 | 3630.38 | 6249.59 | 9470.52 | 13515.3 | 18045.3 | 23342.2 | 28660.2 |
| 1s | 0.028536 | 0.052406 | 0.089400 | 0.13512 | 0.19230 | 0.25576 | 0.33115 | 0.40626 |
| 2p | | | 0.15033 | 0.24805 | 0.37267 | 0.48209 | 0.62064 | 0.78526 |
| 2p | | | 0.39278 | 0.65771 | 0.99207 | 1.32052 | 1.73193 | 2.21058 |
| 2p | | | 1.06577 | 1.78730 | 2.70563 | 3.60924 | 4.78819 | 6.21877 |
| 2p | | | 3.48347 | 5.77636 | 8.48042 | 11.4887 | 15.2187 | 19.7075 |
| 2p | | | 15.4594 | 25.3655 | 35.9115 | 49.8279 | 65.6593 | 84.8396 |
| 2p | | | 0.057221 | 0.091064 | 0.13460 | 0.16509 | 0.20699 | 0.25665 |

TABLE XIII. Orbital energies and expansion coefficients[a]: $9-(1s)_g$, $5-(2p)_g$.

| Li($^2S$) | Be($^1S$) | B($^2P$) | C($^3P$) | N($^4S$) | O($^3P$) | F($^2P$) | Ne($^1S$) |
|---|---|---|---|---|---|---|---|
| 1s | 1s | 1s | 1s | 1s | 1s | 1s | 1s |
| −2.47761 | −4.73230 | −7.69485 | −11.3249 | −15.6283 | −20.6663 | −26.3784 | −32.7650 |
| 0.42505 | 0.42643 | 0.43331 | 0.43809 | 0.44611 | 0.46137 | 0.46223 | 0.47268 |
| 0.16064 | 0.15845 | 0.16002 | 0.15459 | 0.15043 | 0.14389 | 0.14291 | 0.13791 |
| 0.04984 | 0.04799 | 0.04763 | 0.04534 | 0.04411 | 0.04287 | 0.04240 | 0.04133 |
| 0.01042 | 0.00995 | 0.00983 | 0.00934 | 0.00909 | 0.00897 | 0.00887 | 0.00909 |
| 0.16878 | 0.16037 | 0.14005 | 0.14581 | 0.14553 | 0.14017 | 0.14063 | 0.12994 |
| 0.00253 | 0.00265 | 0.00113 | 0.00199 | 0.00127 | −0.00058 | −0.00035 | −0.00212 |
| 0.34455 | 0.35122 | 0.36273 | 0.35867 | 0.35658 | 0.35555 | 0.35527 | 0.36255 |
| 0.00137 | 0.00130 | 0.00129 | 0.00122 | 0.00119 | 0.00118 | 0.00117 | 0.00120 |
| −0.00013 | −0.00045 | 0.00036 | 0.00041 | 0.00080 | 0.00139 | 0.00143 | 0.00183 |
| 2s | 2s | 2s | 2s | 2s | 2s | 2s | 2s |
| −0.1930 | −0.30906 | −0.49441 | −0.70506 | −0.9440 | −1.24216 | −1.56878 | −1.92455 |
| −0.10956 | −0.14223 | −0.16661 | −0.17699 | −0.18556 | −0.19590 | −0.20032 | −0.20769 |
| −0.02679 | −0.03141 | −0.03530 | −0.03606 | −0.03633 | −0.03574 | −0.03624 | −0.03537 |
| −0.00786 | −0.00878 | −0.00968 | −0.00974 | −0.00978 | −0.00979 | −0.00987 | −0.00978 |
| −0.00164 | −0.00184 | −0.00201 | −0.00202 | −0.00203 | −0.00207 | −0.00208 | −0.00217 |
| −0.10761 | −0.07969 | −0.05960 | −0.05267 | −0.04544 | −0.03740 | −0.03201 | −0.01923 |
| 0.55797 | 0.54191 | 0.55856 | 0.57408 | 0.58434 | 0.59566 | 0.60464 | 0.61429 |
| −0.06067 | −0.07274 | −0.08535 | −0.08938 | −0.09227 | −0.09508 | −0.09721 | −0.10138 |
| −0.00021 | −0.00024 | −0.00026 | −0.00026 | −0.00026 | −0.00027 | −0.00027 | −0.00028 |
| 0.54423 | 0.57355 | 0.56245 | 0.54768 | 0.53747 | 0.52576 | 0.51555 | 0.50212 |
| | | 2p | 2p | 2p | 2p | 2p | 2p |
| | | −0.30920 | −0.43248 | −0.56633 | −0.62941 | −0.72586 | −0.84405 |
| | | 0.51687 | 0.50734 | 0.50679 | 0.49376 | 0.48636 | 0.48583 |
| | | 0.30565 | 0.30611 | 0.31026 | 0.31066 | 0.31063 | 0.30927 |
| | | 0.08803 | 0.09150 | 0.09258 | 0.09774 | 0.10199 | 0.10164 |
| | | 0.01435 | 0.01469 | 0.01452 | 0.01541 | 0.01636 | 0.01632 |
| | | 0.30567 | 0.31735 | 0.31773 | 0.33604 | 0.34424 | 0.34961 |

[a] The first entry in each column is the orbital energy (in atomic units) and the following are the expansion coefficients corresponding to the basis set given in Table XI.

TABLE XIV. Orbital energies and expansion coefficients[a]: $10-(1s)_g$, $6-(2p)_g$.

| Li(²S) | Be(¹S) | B(²P) | C(³P) | N(⁴S) | O(³P) | F(²P) | Ne(¹S) |
|---|---|---|---|---|---|---|---|
| 1s | 1s | 1s | 1s | 1s | 1s | 1s | 1s |
| −2.47765 | −4.73223 | −7.69503 | −11.3252 | −15.6284 | −20.6680 | −26.3817 | −32.7711 |
| 0.41995 | 0.43211 | 0.42870 | 0.42695 | 0.42369 | 0.42385 | 0.42181 | 0.42200 |
| 0.09236 | 0.08689 | 0.08051 | 0.07736 | 0.07389 | 0.07284 | 0.07080 | 0.07011 |
| 0.02425 | 0.02239 | 0.02038 | 0.01934 | 0.01833 | 0.01801 | 0.01754 | 0.01732 |
| 0.00467 | 0.00422 | 0.00381 | 0.00358 | 0.00399 | 0.00333 | 0.00327 | 0.00324 |
| 0.33028 | 0.33942 | 0.35377 | 0.35790 | 0.36706 | 0.36853 | 0.37564 | 0.37656 |
| 0.04546 | 0.03710 | 0.04397 | 0.04877 | 0.05356 | 0.05441 | 0.05670 | 0.05721 |
| −0.00170 | −0.00791 | −0.00806 | −0.00756 | −0.00664 | −0.00674 | −0.00673 | −0.00675 |
| 0.24636 | 0.24152 | 0.23088 | 0.22679 | 0.21952 | 0.21809 | 0.21300 | 0.21212 |
| 0.00060 | 0.00053 | 0.00047 | 0.00045 | 0.00042 | 0.00042 | 0.00041 | 0.00041 |
| 0.00090 | 0.00183 | 0.00207 | 0.00213 | 0.00202 | 0.00213 | 0.00218 | 0.00226 |
| 2s | 2s | 2s | 2s | 2s | 2s | 2s | 2s |
| −0.19630 | −0.30919 | −0.49463 | −0.70551 | −0.94500 | −1.24386 | −1.57175 | −1.92939 |
| −0.08090 | −0.10274 | −0.11441 | −0.12134 | −0.12455 | −0.12923 | −0.13126 | −0.13358 |
| −0.01473 | −0.01628 | −0.01676 | −0.01701 | −0.01681 | −0.01709 | −0.01696 | −0.01704 |
| −0.00385 | −0.00414 | −0.00417 | −0.00418 | −0.00409 | −0.00414 | −0.00411 | −0.00411 |
| −0.00073 | −0.00077 | −0.00077 | −0.00076 | −0.00075 | −0.0076 | −0.00076 | −0.00076 |
| −0.13167 | −0.15719 | −0.17008 | −0.17554 | −0.18034 | −0.18361 | −0.18708 | −0.18903 |
| −0.04738 | 0.04809 | 0.07448 | 0.08502 | 0.08213 | 0.09512 | 0.09710 | 0.10831 |
| 0.56761 | 0.59099 | 0.60399 | 0.60689 | 0.60379 | 0.60828 | 0.60756 | 0.61435 |
| −0.04270 | −0.04911 | −0.05202 | −0.05399 | −0.05400 | −0.05525 | −0.05497 | −0.05560 |
| −0.00009 | −0.00010 | −0.00010 | −0.00010 | −0.00009 | −0.00009 | −0.00009 | −0.00010 |
| 0.54248 | 0.47194 | 0.44484 | 0.43809 | 0.44676 | 0.43379 | 0.43415 | 0.41924 |
| | | 2p | 2p | 2p | 2p | 2p | 2p |
| | | −0.30964 | −0.43305 | −0.56708 | −0.63119 | −0.72892 | −0.84904 |
| | | 0.43629 | 0.43276 | 0.42652 | 0.42475 | 0.42268 | 0.42027 |
| | | 0.35746 | 0.35871 | 0.35881 | 0.35801 | 0.36114 | 0.36527 |
| | | 0.17925 | 0.18263 | 0.18131 | 0.19028 | 0.19216 | 0.19244 |
| | | 0.05366 | 0.05479 | 0.05480 | 0.05797 | 0.05799 | 0.05676 |
| | | 0.00895 | 0.00875 | 0.00907 | 0.00891 | 0.00880 | 0.00857 |
| | | 0.19799 | 0.20347 | 0.21524 | 0.21977 | 0.22402 | 0.22777 |

[a] The first entry in each column is the orbital energy (in atomic units) and the following are the expansion coefficients corresponding to the basis set given in Table XII.

ever, the results summarized in Table X should offer much encouragement to proceed further with Gaussian-type orbitals. To pursue very accurate Hartree–Fock solutions in the calculation of large polyatomic systems could be unrealistic, because of economy and also possibly because of the approximate nature of the Hartree–Fock solutions. If the required accuracy is of a few tenths of an electron volt per atom measured by the Hartree–Fock standard, the number of necessary Gaussian-type basis functions is not prohibitively large, as is shown in Table X. Let $N_s$ and $N_g$ be the number of Slater- and Gaussian-type basis functions which give roughly comparable accuracy and $\alpha$ be their ratio: $N_g = \alpha N_s$. If the required time to perform molecular calculations using the expansion method increases in proportion to $N^4$, $N$ being the number of basis functions used, then the time factor between comparable calculations based on Slater-type and Gaussian-type basis functions would roughly be $\alpha^4$. Recently, Harrison[14] expressed a rather optimistic opinion about this point by taking $\alpha \cong 2$. The present author inclines to think that $\alpha$ has to be larger than 2 and only if a single molecular integral over GTO's can be computed

$10^3$ times faster than over STO's (as an average), would the GTO basis have a definite edge over the STO basis.

After these and other considerations in the course of the present work, the author has come to the conclusion that is stated in the first section, namely that both classes of functions, STO's and GTO's, can be complementary to each other for various kinds of molecular and solid-state calculations at least for several years to come.

## ACKNOWLEDGMENTS

[14] M. C. Harrison, J. Chem. Phys. 41, 499 (1964).