

New basis sets in quantum mechanics of molecules. Hermite–Gaussian functions

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Abstract - Importance of the choice of suitable basis sets in *ab initio* calculations of the electronic structure and properties of molecules is briefly discussed. Particular attention is paid to a relatively new basis set of Hermite-Gaussian (HG) functions. Their properties and merits are considered in some detail and a review of recent results is given.

INTRODUCTION

The first step in any of the quantum mechanical calculations on atoms and molecules is the determination of total many-electron atomic and molecular wave functions, which in turn are built up from some one-electron functions as a rule, the latter are called atomic orbitals (AO's) if they refer to bound-state solutions of a single electron in a central field. The corresponding spherically symmetric potentials usually have at least a touch of physical reality, but sometimes completely hypothetical potentials are employed. Needless to say, AO's are centered at nuclei of the constituent atoms in a molecule. Hartree-Fock (HF) or, to be more specific, Roothaan-Hall equations for molecules define optimal molecular orbitals (MO's) in the sense of the average electronic Coulomb field. It is clear that a choice of atomic orbitals or basis set in general parametrizes the matrix representation of the HF hamiltonian affecting accuracy of calculations. Hence selection of suitable or optimal basis sets is central in computational quantum chemistry. Generally speaking, there are three main criteria which should be met by good basis sets (ref. 1). The first is related to their completeness. Problems arising in basis set truncation are analysed in depth by Klahn (ref. 2). The second criterion requires physical correctness of AO's. The underlying physical picture is of paramount importance and directly affects performance of the theoretical approach. For instance, enormous computational success of the molecular orbital formalism in the LCAO approximation can be traced down to AO's which are consistent with a sound concept of (modified) atoms in a molecule. On the other hand, poor performance of the single-center expansion method, where all basis set functions are placed at the heavy atom (like fluorine in HF or carbon in CH₄), is easily understood because existence of hydrogen atom(s) as separate structural unit(s) is denied in this particular theoretical procedure. Further, hybrid atomic orbitals (HAO's) provide a good description of a number of molecular local and global properties, since they reflect a local symmetry of an atom embedded in a molecular environment and deformation of AO's due to the field of neighbouring nuclei. (refs. 3-5). Suitable orthogonalized HAO's seem to offer optimal basis sets for various semiempirical schemes (refs. 6-8). Additional instructive examples are provided by electric field variant AO's, which are compatible with small off-center shifts of atomic charge densities in molecules subjected to external electric fields (refs. 9-11). Gauge invariant atomic (GIAO) basis sets greatly improve performance and yield physically meaningful molecular magnetic properties in a relatively simple manner (refs. 12-14). General requirements like e.g. cusp condition (ref. 15) insure better behaviour of the wave function near the nucleus etc. Finally, convenient basis sets should provide a satisfactory accuracy and ease of use. Hence, all molecular integrals should be calculable with a relatively small effort. In other words, the ratio P/E should be favourable for good basis sets, where P stands for performance (accuracy) whereas E denote the required effort (efficiency). It is not the aim of this paper to give a comprehensive review of basis sets used in quantum chemistry in the past or at present for several reasons, one of them being a space limitation. This is not even necessary because several excellent review articles and books are available (refs. 16-25). Instead, we shall make some general remarks and then concentrate on the central theme here: presentation of Hermite-Gaussian (HG) functions and discussion of their merits and prospects. Hermite-Gaussian basis sets are not widely known and we would like to fill this gap in the literature.

Two types of AO's which enjoyed a great success and popularity are Slater (STO) and Gaussian (GTO) functions. Slater orbitals are solutions of the central field problem:

$$V(r) = -(\zeta n/r) + [n(n-1) - l(l+1)]/2r^2 \quad (1)$$

and assume a form:

$$R_{nl}(r, \zeta) = C_n r^{n-1} \exp(-\zeta r) \quad (2)$$

where C_n is normalization constant $C_n = (2\zeta)^{n+1/2} / [(2n!)^{1/2}]$

Their form is simple and they have correct asymptotical behavior. Since STO satisfy the cusp condition, they provide also a good description of wave function in the vicinity of nuclei. Hence, Slater AO's are physically acceptable. Many outstanding researchers contributed to a design of algorithms for solving molecular integrals over STO's: Coulson, Roothaan, Ruedenberg, Kotani, Wahl, Cade and some others. It turned out that STO's suffer a serious drawback. Calculation of polycentric integrals is intricate and very time consuming. Shavitt and Karplus suggested the use of Gaussian-transform technique (ref. 26) which represented an improvement but the molecular integrals calculations were still too slow.

A decisive breakthrough was made by invoking Gaussian functions by Boys (ref. 27) and McWeeny (ref. 28). They are solutions of an artificial potential:

$$V(r) = 2\zeta^2 r^2 + [n(n-1) - 1(l+1)]/2r^2 \quad (3)$$

and are of a form:

$$R_n(r, \zeta) = C_n r^{n-1} \exp(-\zeta r^2) \quad (4)$$

where C_n is the corresponding normalization factor. It is not surprising that GTO's do not possess proper behavior at large distances because they decay too quickly. Since GTO's do not satisfy cusp condition they are not particularly suitable for representation of electronic density at very small distances either. Nevertheless, these shortcomings are overcompensated by the great efficiency in computing many-center integrals. Hence, larger GTO than STO basis sets can be employed. This is the reason why Gaussian AO's dominate contemporary computational quantum chemistry.

There are many ways of utilizing GTO's. For example, a Slater AO's can be expressed as linear combinations of Gaussian functions (refs. 29,30). On the other hand, contracted Gaussian with fixed linear coefficients found a widespread use (refs. 20-24). Further, angular dependence is sometimes simulated by spherical lobe-Gaussian functions (ref. 32). Additional flexibility is obtained by floating spherical Gaussian (FSGO) by allowing centers of GTO's to vary until optimal positions are achieved. Rearrangement of FSGO's centers enables a better description of changes in density distributions induced by the chemical bonding (refs. 33-35). We shall explicitly give, for the sake of the forthcoming discussion, Cartesian Gaussian functions:

$$\Phi(\vec{A}, \alpha) = N(\vec{A}, \alpha) x_A^l y_A^m z_A^n \exp(-\alpha r_A^2) \quad (5)$$

and ellipsoidal Gaussian functions suggested by Browne and Poshusta (ref. 36):

$$\Phi(\vec{A}, \vec{\alpha}) = N(\vec{A}, \vec{\alpha}) x_A^l y_A^m z_A^n \exp[-(\alpha_x x_A^2 + \alpha_y y_A^2 + \alpha_z z_A^2)] \quad (6)$$

Here $x_A = x - A_x$, where A_x denotes x-coordinate of the nucleus A, $\vec{\alpha}$ is a triad of nonlinear parameters α_x , α_y and α_z , and l , m and n are integers. Ellipsoidal Gaussian functions are natural extension of Cartesian GTO's and should be in principle useful in describing asymmetry of atomic charge density in molecular environments. The original algorithms for molecular integrals involved heavy numerical integrations (ref. 36). This fact prompted us to design similar functions-Hermite-Gaussian (HG) which yield substantially simpler integral expressions (ref. 37). It is interesting to mention that HG functions were later rediscovered by Golebiewsky and Salvetti (refs. 38,39) who baptized them modified Gaussian functions. In the next section we shall discuss some recent applications of Hermite-Gaussians in molecular calculations.

HERMITE-GAUSSIAN FUNCTIONS

HG functions are defined as follows:

$$f_{n_1, n_2, n_3}(a_A, \vec{r}_A) = a_A^{n/2} H_{n_1}(a_A^{1/2} x_A) H_{n_2}(a_A^{1/2} y_A) H_{n_3}(a_A^{1/2} z_A) \cdot \exp(-a_A r_A^2) \quad (7)$$

where coordinates $x_A = x - A_x$ etc. determine electron position relative to a nucleus A, $n = n_1 + n_2 + n_3$ and H_{n_i} denotes Hermite polynomials. An alternative and more useful way of expressing HG functions reads:

$$f_{n_1, n_2, n_3}(a_A, \vec{r}_A) = \partial_{A_x}^{n_1} \partial_{A_y}^{n_2} \partial_{A_z}^{n_3} \exp(-a_A r_A^2) \quad (8)$$

This form, involving derivatives over nuclear coordinates, immediately suggest great simplification in calculating molecular integrals via interchange of differentiations and integrations over electron coordinates. At the same time it indicates that geometry optimization and calculation of force constants can be naturally incorporated in the general algorithm. Another useful characteristics is separation in x, y and z coordinates for a number of integrals. Since Hermite polynomials are the simplest orthogonal polynomials with the $(-\infty, +\infty)$ range possessing a number of remarkable features (ref. 40) additional favourable properties of HG functions might be expected. Finally, every HG

function is symmetric or antisymmetric with respect to reflections in the planes $y_A z_A$, $x_A z_A$ and $x_A y_A$ according to a parity of numbers n_1 , n_2 and n_3 , respectively. There are also n_1 nodal planes parallel to yz coordinate plane etc.

Actual calculations of integrals can be performed in three stages:

- (i) putting the differentiation operators in front of the integral mark,
- (ii) calculation of the remaining integrals by using Boys' formula (ref. 27),
- (iii) differentiation with respect to the nuclear coordinates.

As a final result one obtains entities expressed by HG functions and two auxilliary functions:

$$g(\vec{k}, \vec{r}) = \partial_x^{k_1} \partial_y^{k_2} \partial_z^{k_3} \int_0^1 \exp(-r^2 t^2) dt \tag{9}$$

and

$$h(p, r, s; x) = \sum_{\substack{\min[p, s] \\ \max[0, s-r]}} \binom{p}{i} \binom{r}{s-i} x^i \tag{10}$$

Actual formulas for calculation of the matrix elements appearing in solution of Schrödinger equation involving Coulomb Hamiltonian and employing variation theorem are available (refs. 37,38) and will not be repeated here.

Total molecular energy is pivotal in quantum mechanical calculations. However, it is not very sensitive to finer details of the molecular wave function. Much more stringent criteria are provided by some one- and two-electron molecular properties which probe particular region or segment of the electron charge density. We examined integrals necessary for calculation of a wide variety of electric and magnetic properties as well as some relativistic corrections arising in the Breit Hamiltonian (ref. 41). More specifically, we considered the matrix elements of the following operators:

$$\begin{aligned} &x^2, y^2, z^2; \vec{r} \cdot \vec{\nabla}; \vec{r}_N / r_N^3; (r_N^2 - 3x_N^2) / r_N^5; (x_N^2 + y_N^2) / r_N^3; -x_N z_N / r_N^3; \vec{\nabla}_1^4; \delta(\vec{r}_{12}), (1/r_N^3) \vec{r}_N \cdot \vec{\nabla}; \\ &(r_{12}^2 - 3x_{12}^2) / r_{12}^5; \vec{r}_{12} \cdot \vec{\nabla}_2 / r_{12}^3; (1/r_{12}) \vec{\nabla}_1 \cdot \vec{\nabla}_2 \quad \text{and} \quad \vec{r}_{12} \cdot [(\vec{r}_{12} / r_{12}^3) \cdot \vec{\nabla}_1] \vec{\nabla}_2 \end{aligned} \tag{11}$$

It turned out that all these integrals could be reduced to the integrals already encountered in the minimum energy calculations. For instance, the one- and two- electron integrals involving $(1/r_{1k})^n$ operator, where k denotes either a nuclear or coordinate of the second electron, are expressed in terms of nuclear attraction and Coulomb repulsion integrals, respectively. Hence they can be computed with little additional effort if HG basis set is employed. It was found that the same conclusion holds for the matrix elements arising in the pseudo-potential calculations involving Bonasić-Huzinaga (ref. 42) potential, which in turn gives a good description of inner-shell electrons in heavy atoms.

We shall dwell now on possible generalizations of HG functions. An obvious extension is introduction of ellipsoidal HG functions in full analogy with functions (6):

$$f_{n_1 n_2 n_3}(\vec{a}_A, \vec{b}_A, \vec{r}_A) = \prod_{i=1}^3 f_{n_i}(a_{iA}, b_{iA}, r_{iA}) \tag{12}$$

where $r_{1A} = x_A$ etc. and

$$f_{n_1}(a_{1A}, b_{1A}, r_{1A}) = H_{n_1}(a_{1A}^{1/2} x_A) \exp(-b_{1A} x_A^2) \tag{13}$$

with analogous expressions for y and z coordinates. Here \vec{a}_A and \vec{b}_A denote triads of numbers (a_{1A}, a_{2A}, a_{3A}) and (b_{1A}, b_{2A}, b_{3A}) , respectively. In other words, exponential and polynomial "screening" parameters are uncoupled. It should be pointed out that functions (12) were christened by Katriel and Adam (ref. 43) as generalized HG functions. We find this term somewhat ambiguous because it might suggest the use of generalized Hermite polynomials (ref. 44) which is not the case. Consequently, a better specification would be given by ellipsoidal HG functions (EHG) which will be invariably used in this paper. Other terminological possibilities were considered by Primorac (ref. 45). Let's consider briefly some basic integrals over EHG functions (ref. 45,46). For this purpose it is convenient to develop EHG functions (12) in terms of components of HG functions which have the same exponential and polynomial "screenings":

$$f_{n_1 n_2 n_3}(\vec{a}_A, \vec{b}_A, \vec{r}_A) = \prod_{i=1}^3 \sum_{m_{iA}}^{n_{iA}} c(n_{iA}, a_{iA}, b_{iA}, m_{iA}) H_{m_{iA}}(b_{iA}^{1/2} r_{iA}) \exp(-b_{iA} r_{iA}^2) \quad (14)$$

where

$$c(n_{1A}, a_{1A}, b_{1A}, m_{1A}) = \delta_{n_{1A}-m_{1A}} \{n_{1A}! / m_{1A}! [(n_{1A} - m_{1A}) / 2]!\} \omega_{1A}^{m_{1A}} (\omega_{1A} - 1)^{(n_{1A} - m_{1A}) / 2} \quad (15)$$

and δ is a parity switch factor

$$\delta_{n_{1A}-m_{1A}} = \begin{cases} 1 & \text{if } n_{1A} - m_{1A} \text{ is even} \\ 0 & \text{if } n_{1A} - m_{1A} \text{ is odd} \end{cases}$$

This expression enables reduction of most of the one-electron integrals to the known formulas for HG functions themselves. However, if the operator does not allow separation into three Cartesian components like e.g. the Coulomb potential $1/r_N$ of the nucleus N, another approach is necessary. The same applies to the two-electron operators. Then the exponential function should be written as a product of the spherical part and the ellipticity correction:

$$\prod_{i=x, y, z} \exp(-b_{iA} r_{iA}^2) = \exp(-d_A r_A^2) \prod_{i=x, y, z} \exp(-b'_{iA} r_{iA}^2) \quad (16)$$

The spherical portion multiplied with the H polynomials $\prod_{i=x, y, z} H_{n_{iA}}(d_A^{1/2} r_{iA})$ leads to the integrals which can be tackled in analytical fashion. The problem is to eliminate ellipsoidal Gaussian part. This is attempted by a truncated series:

$$H_{n_1}(a_{1A}^{1/2} r_{1A}) \exp[-(b_{1A} - d_A) r_{1A}^2] = \sum_{m_{1A}}^{m_{1A}(\max)} e(a_{1A}, b_{1A}, d_A, m_{1A}) \cdot H_{m_{1A}}(d_A^{1/2} r_{1A}) \quad (17)$$

where the upper limit $m_{1A}(\max)$ depends on the predetermined accuracy. The summation is restricted to either even or odd m_{1A} depending on the parity of the $H_{n_{iA}}$ polynomial. The expression (17) can be viewed as a development of the differently scaled HG functions $H(a^{1/2}x)\exp(-bx^2)$ (where $a \neq b$) in a series of the customary HG functions of the $H(d^{1/2}x)\exp(-dx^2)$ type. It is noteworthy in this connection that statistical distribution functions are frequently expanded in terms of the HG basis and that the first few terms usually suffice (ref. 47). Expansion coefficients in (17) are straightforwardly obtained:

$$e(a_{1A}, b_{1A}, d_A, m_{1A}) = \left\{ [d_A / b_{1A}]^{1/2} / [2^{m_{1A}} m_{1A}!] \right\} \sum_{k_{1A}}^{\min(n_{1A}, m_{1A})} 2^{k_{1A}} (k_{1A})! \cdot c(n_{1A}, a_{1A}, b_{1A}, k_{1A}) c(m_{1A}, d_A, b_{1A}, k_{1A}) \quad (18)$$

Hence, the EHG expansion takes a form:

$$f_{n_1 n_2 n_3}(\vec{a}_A, \vec{b}_A, \vec{r}_A) = \sum_{m_{1A}} \sum_{m_{2A}} \sum_{m_{3A}} k(m_{1A}, m_{2A}, m_{3A}) f_{m_{1A} m_{2A} m_{3A}}(d_A, \vec{r}_A) \quad (19)$$

where

$$k(m_{1A}, m_{2A}, m_{3A}) = \prod_{i=x, y, z} e(a_{iA}, b_{iA}, d_A, m_{iA}) d_A^{-m_{iA}/2} \quad (20)$$

It follows that integrals over EHG functions can be reduced to integrals over customary HG functions too with some additional efforts (ref. 46).

As a final comment we would like to point out that HG functions have the same flexibility as FSGO if the addition theorem for the Hermite polynomials (ref. 40) is utilized. Some integrals over shifted HG functions were discussed by Primorac (ref. 45).

HERMITE–GAUSSIAN EXPANSION OF HYDROGENIC ORBITALS

Hydrogen orbitals are quantum mechanical solutions of the Schrödinger equation. Their exact expectation values are also known. For that purpose they were chosen as test functions which, if expanded in a series of HG functions, will shed some light on the quality of HG basis sets. Additionally, hydrogen-like orbitals might be useful in solving momentum space Schrödinger equation (refs. 48,49). Therefore our numerical experiments should contribute to tractability of polycentric integrals over hydrogen orbitals, which are extremely tedious otherwise. Furthermore, hydrogen AO's satisfy cusp condition whereas atomic centered HG functions do not. It would be of some interest to examine possibilities of improving behavior of AO's at the nuclei by a deliberate choice of HG functions.

Aiming at expansion of hydrogen orbitals in a series of HG functions we shall express the former in a general but real form:

$$\Psi_{KLM} = X^K Y^L Z^M R(r) \quad (21)$$

It is convenient to express the radial part in (21) in terms of spherical Gaussians multiplied by even powers of r :

$$R(r) = \sum_{i=1}^N \left(\sum_{j=0}^{T_i} k_{ji} r^{2j} \right) \exp(-a_i r^2) \quad (22)$$

where the limiting indices N and T_i are functions of the error tolerance. An equivalent formula based on HG functions reads:

$$R(r) = \sum_{i=1}^N \sum_{k=0}^{T_i} c_{ki} k! \sum_{k_1=0}^k \sum_{k_2=0}^{k-k_1} [k! k_2! (k-k_1-k_2)!]^{-1} f_{2k_1, 2k_2, 2(k-k_1-k_2)}(a_i, \vec{r}) \quad (23)$$

Coefficients k_{ji} and c_{ki} are linearly related which is easily found. Multiplying $R(r)$ in (23) by $x^K y^L z^M$ one obtains:

$$\Phi_{KLM} = \sum_{i=1}^N \sum_{k=0}^{T_i} c_{ki} [k! / k_1! k_2! k_3!] f_{2k_1+K, 2k_2+L, 2k_3+M}(a_i, \vec{r}) \quad (24)$$

where summation over k implies a triple sum over k_1 , k_2 and k_3 confined to give a fixed value of $k = k_1 + k_2 + k_3$ ($k=0, 1, 2, \dots$ etc.). Our numerical experiments encompass a range of values of $N=1-5$ for two particular cases: (a) $T_i=1$ and (b) $T_i=2$ (ref. 50). They will be named HG approximations of the second and fourth degree, respectively, for an obvious reason. Quality of these two approximations will be compared with the GTO results obtained by putting $T_i=0$.

Adjustable linear and non-linear parameters in the series (24) are obtained by integral least-square fit criterion by minimizing Δ :

$$\Delta = \int (\Phi_{KLM} - \Psi_{KLM})^2 dv \quad (25)$$

where Ψ_{KLM} stands for the exact hydrogen orbital and Φ_{KLM} represents its HG expansion (24). It is easy to see that minimum of Δ condition is equivalent to maximum overlap requirement between approximate representation and exact hydrogen AO. Since Δ is obviously related to differences in Φ_{KLM} and Ψ_{KLM} one can alternatively define a similarity measure (SM) as $SM = 100(1 - \Delta)$ (in %).

Before discussing results a word on notation is necessary. HG approximations of the second and fourth degrees will be abbreviated by (m)HG2- N and (m)HG4- N , respectively. Here (m) denotes the angular type of the orbital (e.g. s, p_x etc.) and N determines the number of non-linear parameters (23). They weigh various (inner and outer) portions of AO's.

In addition to the orbital energy, four one-electron operators r^n ($n=-2, -1, 1, 2$) are examined. Their expectation values were calculated by using 1s GTO's, HG2 and HG4 basis set expansions (ref. 51). The virial ratios $\langle -1/r \rangle / E$ and spatial similarity measures SM were considered too. The corresponding values for hydrogen 1s-3d AO's are given in Table 1. Perusal of the presented data shows that the use of a single non-linear parameter a_1 is not satisfactory, the

HG4-1 representation of 2p and 3d AO's being exceptions. Introduction of the second non-linear parameter leads to a great improvement for all three basis sets. Apparently, inner and outer portions of AO's should be described by separate Gaussians. It is noteworthy that a good description of 3s AO requires at least 3 non-linear parameters. The average values of $\langle r^n \rangle$ operators and orbital energies for GTO expansion are given in table 2. It should be stressed that the second moments $\langle r^2 \rangle$ and diamagnetic shieldings (which are proportional to $\langle r^{-1} \rangle$) are extremely insensitive to finer details of atomic and molecular wave functions (refs. 3,5). Consequently, both entities were defined as necessary but not sufficient conditions which acceptable wave functions should satisfy (ref.52). In other words, wave functions which do not satisfy these minimal requirements should be either improved or discarded. As an illustration we mention that an error of 0.5 ppm in diamagnetic shielding corresponds to an error of ~ 9 kcal mol $^{-1}$ in orbital energy of hydrogen AO. Survey of the data in Table 2 clearly shows that single GTO representation is unsatisfactory. Introduction of the second Gaussian is necessary and approximate description of 2s, 2p and 3p AO's is then quite good as far as $\langle r^{-1} \rangle$ and $\langle r^2 \rangle$ criteria are concerned. As the main quantum number n increases use of only two Gaussians becomes less and less appropriate, 3p, and 3d AO's being exceptions. This is not unexpected because Gaussians fall off quite rapidly and larger sets of values of nonlinear parameters and the corresponding $\exp(-ar^2)$ functions are necessary to describe more and more extensive domains of higher AO's.

Results obtained by HG2 basis set are somewhat better than GTO description, but a substantial overall improvement in accuracy is obtained by the HG4 basis sets (Table 3). For instance, 2s AO is very well described by the HG4-2 basis, which is not the case for the GTO-2 and HG-2 results. This is evidenced by the exact virial ratio and very good accordance of the calculated HG4-2 properties with exact values. The same holds for 3d AO where a single nonlinear parameter HG4-1 suffices for a satisfactory description. Insensitivity of $\langle r^{-1} \rangle$ and $\langle r^2 \rangle$ properties can be illustrated by HG4-2 results for 4s AO. Although the above mentioned criteria are roughly satisfied, the virial of 1.8 is obviously unsatisfactory.

As a general conclusion one can say that AO's obeying $n-l=1$ condition are very accurately reproduced which is achieved by smaller number of non-linear parameters. The HG4-N basis sets are superior to the GTO-N functions possessing the same number of non-linear parameters.

Behavior of AO's near nucleus deserves a closer scrutiny. Although the nuclear cusp condition can not be fully satisfied with HG4-5 basis functions, they are superior to the GTO-5 basis set. This is illustrated by Figure 1 where performance of both sets is compared and tested against the exact 1s H orbital. Improvement obtained by HG4-5 functions is impressive indeed. Preliminary calculations have shown that nuclear cusp requirement is easily satisfied by adding off-center HG functions to the set without considerable increase in computational effort.

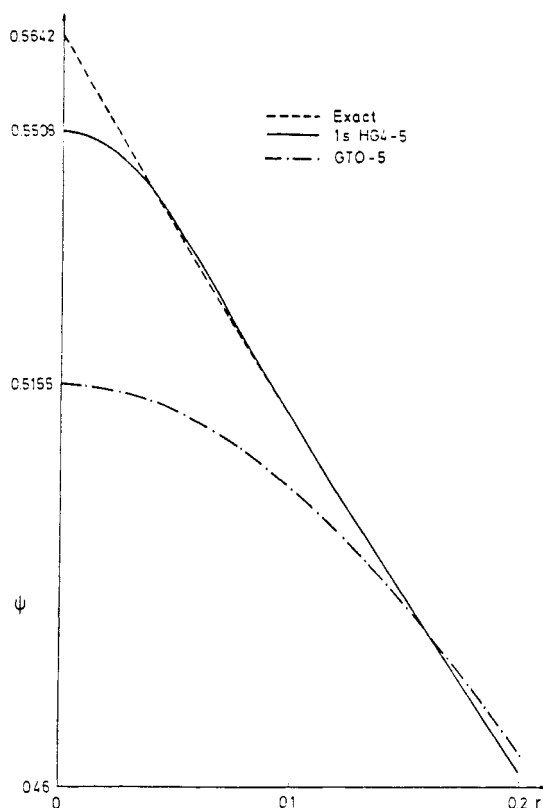


Figure 1. Behavior of 1s hydrogen AO and its HG4-5 and GTO-5 representations near proton (r in a.u.).

TABLE 1. Average Values of Some One-electron Properties for Hydrogen AOs Approximated by Linear Combinations of Pure Gaussians (GTOs)*

	N	-E	$\langle r^{-1} \rangle$	$\langle r^{-2} \rangle$	$\langle r \rangle$	$\langle r^2 \rangle$
1s	1	4.24218(-1)	8.30643(-1)	1.08380	1.53284	2.76804
	2	4.81155(-1)	9.59098(-1)	1.62050	1.50324	2.97212
	3	4.94907(-1)	9.89205(-1)	1.83854	1.50039	2.99612
	4	4.98481(-1)	9.96838(-1)	1.92735	1.50005	2.99935
	5	4.99504(-1)	9.98974(-1)	1.96523	1.50001	2.99988
Exact		5.00000(-1)	1.00000	2.00000	1.50000	3.00000
2s	1	1.74685(-1)	1.97711(-1)	6.14017(-2)	6.43991	4.88585(+1)
	2	1.17612(-1)	2.30693(-1)	1.44072(-1)	6.01233	4.19722(+1)
	3	1.23598(-1)	2.47141(-1)	2.20163(-1)	6.00518	4.18288(+1)
	4	1.23417(-1)	2.46426(-1)	2.12469(-1)	6.00018	4.20052(+1)
	5	1.24653(-1)	2.49373(-1)	2.37675(-1)	5.99957	4.19910(+1)
Exact		1.25000(-1)	2.50000(-1)	2.50000(-1)	6.00000	4.20000(+1)
3s	1	7.83329(-2)	8.23251(-2)	1.06459(-2)	1.54660(+1)	2.81797(+2)
	2	7.05743(-2)	9.24912(-2)	1.89474(-2)	1.40105(+1)	2.17357(+2)
	3	5.32835(-2)	1.04796(-1)	4.06796(-2)	1.35131(+1)	2.07110(+2)
	4	5.50597(-2)	1.10017(-1)	6.27934(-2)	1.35022(+1)	2.06919(+2)
	5	5.51186(-2)	1.10177(-1)	6.38396(-2)	1.34999(+1)	2.06988(+2)
Exact		5.55556(-2)	1.11111(-1)	7.40740(-2)	1.35000(+1)	2.07000(+2)
4s	1	4.38031(-2)	4.49957(-2)	3.18026(-3)	2.82964(+1)	9.43321(+2)
	2	4.08771(-2)	4.71616(-2)	4.63550(-3)	2.66316(+1)	7.73225(+2)
	3	3.73961(-2)	5.39137(-2)	7.93873(-3)	2.44361(+1)	6.62257(+2)
	4	3.03184(-2)	5.99133(-2)	1.74685(-2)	2.40067(+1)	6.48055(+2)
	5	3.10724(-2)	6.21164(-2)	2.71108(-2)	2.40017(+1)	6.47998(+2)
Exact		3.12500(-2)	6.25000(-2)	3.12500(-2)	2.40000(+1)	6.48000(+2)
2p	1	1.13154(-1)	2.23133(-1)	5.86556(-2)	5.07217	2.84145(+1)
	2	1.22827(-1)	2.45178(-1)	7.65394(-2)	5.00668	2.98282(+1)
	3	1.24584(-1)	2.49096(-1)	8.14614(-2)	5.00069	2.99799(+1)
	4	1.24912(-1)	2.49813(-1)	8.27836(-2)	5.00008	2.99973(+1)
	5	1.24980(-1)	2.49957(-1)	8.31602(-2)	5.00001	2.99996(+1)
Exact		1.25000(-1)	2.50000(-1)	8.33333(-2)	5.00000	3.00000(+1)
3p	1	6.58771(-2)	8.00221(-2)	7.54400(-3)	1.41432(+1)	2.20926(+2)
	2	5.37962(-2)	1.06475(-1)	1.97563(-2)	1.25300(+1)	1.80015(+2)
	3	5.53264(-2)	1.10711(-1)	2.40858(-2)	1.25052(+1)	1.79372(+2)
	4	5.53374(-2)	1.10609(-1)	2.37630(-2)	1.25010(+1)	1.80015(+2)
	5	5.55278(-2)	1.11053(-1)	2.45148(-2)	1.25000(+1)	1.80000(+2)
Exact		5.55556(-2)	1.11111(-1)	2.46914(-2)	1.25000(+1)	1.80000(+2)
4p	1	3.76144(-2)	4.14005(-2)	2.01926(-3)	2.73371(+1)	8.25384(+2)
	2	3.54888(-2)	4.77674(-2)	3.18706(-3)	2.45395(+1)	6.52003(+2)
	3	3.05107(-2)	6.04153(-2)	8.20083(-3)	2.30300(+1)	6.00450(+2)
	4	3.11433(-2)	6.22617(-2)	9.98507(-3)	2.30030(+1)	5.99751(+2)
	5	3.11690(-2)	6.23150(-2)	1.00663(-2)	2.30001(+1)	5.99938(+2)
Exact		3.12500(-2)	6.25000(-2)	1.04167(-2)	2.30000(+1)	6.00000(+2)
3d	1	5.17320(-2)	1.02380(-1)	1.15760(-2)	1.06128(+1)	1.20941(+2)
	2	5.49460(-2)	1.09790(-1)	1.41160(-2)	1.05100(+1)	1.25486(+2)
	3	5.54660(-2)	1.10910(-1)	1.46680(-2)	1.05009(+1)	1.25947(+2)
	4	5.55410(-2)	1.11080(-1)	1.47820(-2)	1.05001(+1)	1.25994(+2)
	5	5.55520(-2)	1.11110(-1)	1.48070(-2)	1.05000(+1)	1.25999(+2)
Exact		5.55556(-2)	1.11111(-1)	1.48148(-2)	1.05000(+1)	1.26000(+2)

* In atomic units. Numbers given in parentheses are powers of 10.

TABLE 2. Comparison of Similarity Measures (SM) (in %) and Virial Ratios ($\langle -1/r \rangle / E$) for Various Basis Sets.

N	GTO		HG2		HG4	
	SM	Virial	SM	Virial	SM	Virial
1s-orbital						
1	95.7	1.958	95.7	1.958	99.3	1.985
2	99.7	1.993	99.7	1.993	100.0	1.999
3	100.0	1.999	100.0	1.999	100.0	2.000
4	100.0	2.000	100.0	2.000	100.0	2.000
5	100.0	2.000	100.0	2.000	100.0	2.000
2s-orbital						
1	83.8	1.132	91.2	1.496	91.2	1.496
2	99.6	1.961	99.6	1.961	100.0	2.000
3	99.9	1.999	99.9	1.992	100.0	1.992
4	100.0	1.997	100.0	1.998	100.0	2.000
5	100.0	2.000	100.0	2.000	100.0	2.000
2p-orbital						
1	95.2	1.972	95.2	1.972	99.3	1.992
2	99.7	1.996	99.7	1.996	100.0	2.000
3	100.0	1.999	100.0	1.999	100.0	2.000
4	100.0	2.000	100.0	2.000	100.0	2.000
5	100.0	2.000	100.0	2.000	100.0	2.000
3s-orbital						
1	59.6	1.051	93.5	1.334	93.8	1.334
2	94.6	1.331	98.9	1.847	98.9	1.847
3	99.9	1.967	99.9	1.970	100.0	1.995
4	100.0	1.998	100.0	1.998	100.0	2.000
5	100.0	1.999	100.0	1.999	100.0	2.000
3p-orbital						
1	78.2	1.215	89.2	1.666	89.2	1.666
2	99.5	1.979	99.5	1.979	100.0	1.997
3	99.9	2.001	99.9	1.997	100.0	2.000
4	100.0	1.999	100.0	1.999	100.0	2.000
5	100.0	2.000	100.0	2.000	100.0	2.000
3d-orbital						
1	95.0	1.979	95.0	1.979	99.3	1.994
2	99.7	1.997	99.7	1.997	100.0	2.000
3	100.0	2.000	100.0	2.000	100.0	2.000
4	100.0	2.000	100.0	2.000	100.0	2.000
5	100.0	2.000	100.0	2.000	100.0	2.000

TABLE 3. Average Values of Some One-electron Properties for Hydrogen AOs Approximated by Linear Combinations of Functions Belonging to HG4 Basis Set.*

	N	-E	$\langle r^{-1} \rangle$	$\langle r^{-2} \rangle$	$\langle r \rangle$	$\langle r^2 \rangle$
1s	1	4.67343(-1)	9.27907(-1)	1.46009	1.50722	2.93778
	2	4.96672(-1)	9.92985(-1)	1.87791	1.50017	2.99810
	3	4.99566(-1)	9.99094(-1)	1.96792	1.50000	2.99985
	4	4.99863(-1)	9.99696(-1)	1.98433	1.50000	3.00001
	5	4.99983(-1)	9.99970(-1)	1.99660	1.50000	2.99999
	Exact	5.00000(-1)	1.00000	2.00000	1.50000	3.00000
2s	1	1.14834(-1)	1.71833(-1)	3.28915(-2)	6.24731	4.15260(+1)
	2	1.22109(-1)	2.43239(-1)	1.94205(-1)	6.00125	4.20135(+1)
	3	1.24798(-1)	2.49568(-1)	2.40457(-1)	6.00007	4.19984(+1)
	4	1.24861(-1)	2.49704(-1)	2.42507(-1)	6.00002	4.20001(+1)
	5	1.24930(-1)	2.49844(-1)	2.45067(-1)	6.00000	4.20000(+1)
	Exact	1.25000(-1)	2.50000(-1)	2.50000(-1)	6.00000	4.20000(+1)
3s	1	6.59129(-2)	8.79217(-2)	1.56299(-2)	1.40230(+1)	2.13309(+2)
	2	5.10170(-2)	9.42268(-2)	1.92992(-2)	1.35835(+1)	2.06915(+2)
	3	5.47110(-2)	1.09131(-1)	5.77144(-2)	1.35012(+1)	2.07024(+2)
	4	5.54853(-2)	1.10956(-1)	7.08550(-2)	1.35000(+1)	2.06999(+2)
	5	5.55376(-2)	1.11074(-1)	7.28276(-2)	1.35000(+1)	2.07000(+2)
	Exact	5.55556(-2)	1.11111(-1)	7.40740(-2)	1.35000(+1)	2.07000(+2)
4s	1	3.03507(-2)	4.41294(-2)	2.86766(-3)	2.49158(+1)	6.51222(+2)
	2	2.95210(-2)	5.31577(-2)	5.45702(-3)	2.41397(+1)	6.48762(+2)
	3	3.08929(-2)	6.17168(-2)	2.58402(-2)	2.40082(+1)	6.47505(+2)
	4	3.09558(-2)	6.18161(-2)	2.51993(-2)	2.40008(+1)	6.48022(+2)
	5	3.12182(-2)	6.24327(-2)	2.98706(-2)	2.40001(+1)	6.48003(+2)
	Exact	3.12500(-2)	6.25000(-2)	3.12500(-2)	2.40000(+1)	6.48000(+2)
2p	1	1.20968(-1)	2.40930(-1)	7.24129(-2)	5.01454	2.96233(+1)
	2	1.24786(-1)	2.49537(-1)	8.22164(-2)	5.00025	2.89921(+1)
	3	1.24990(-1)	2.49980(-1)	8.32331(-2)	4.99999	2.99993(+1)
	4	1.24992(-1)	2.49981(-1)	8.32405(-2)	5.00000	2.99999(+1)
	5	1.24999(-1)	2.49997(-1)	8.33141(-2)	5.00000	3.00000(+1)
	Exact	1.25000(-1)	2.50000(-1)	8.33333(-2)	5.00000	3.00000(+1)
3p	1	4.88234(-2)	8.13433(-2)	7.57703(-3)	1.31179(+1)	1.79937(+2)
	2	5.51182(-2)	1.10066(-1)	2.30668(-2)	1.25026(+1)	1.80043(+2)
	3	5.55437(-2)	1.11085(-1)	2.46004(-2)	1.25001(+1)	1.79994(+2)
	4	4.55467(-2)	1.11091(-1)	2.46144(-2)	1.25000(+1)	1.80000(+2)
	5	5.55549(-2)	1.11110(-1)	2.46809(-2)	1.25000(+1)	1.80000(+2)
	Exact	5.55556(-2)	1.11111(-1)	2.46914(-2)	1.25000(+1)	1.80000(+2)
4p	1	3.42849(-2)	4.67052(-2)	2.92955(-3)	2.45165(+1)	6.43032(+2)
	2	2.93139(-2)	5.64639(-2)	6.00328(-3)	2.31471(+1)	5.99819(+2)
	3	3.11074(-2)	6.21617(-2)	9.85730(-3)	2.30017(+1)	6.00048(+2)
	4	3.12440(-2)	6.24854(-2)	1.03680(-2)	2.30001(+1)	5.99999(+2)
	5	3.12487(-2)	6.24982(-2)	1.04073(-2)	2.30000(+1)	5.99996(+2)
	Exact	3.12500(-2)	6.25000(-2)	1.04167(-2)	2.30000(+1)	6.00000(+2)
3d	1	5.44309(-2)	1.08556(-1)	1.36197(-2)	1.05216(+1)	1.24886(+2)
	2	5.55179(-2)	1.11030(-1)	1.47448(-2)	1.05002(+1)	1.25981(+2)
	3	5.55545(-2)	1.11110(-1)	1.48122(-2)	1.05000(+1)	1.26000(+2)
	4	5.55554(-2)	1.11111(-1)	1.48141(-2)	1.05000(+1)	1.26000(+2)
	5	5.55555(-2)	1.11111(-1)	1.48147(-2)	1.05000(+1)	1.26000(+2)
	Exact	5.55556(-2)	1.11111(-1)	1.48148(-2)	1.05000(+1)	1.26000(+2)

* In atomic units. Numbers given in parentheses are powers of 10.

DISCUSSION

Molecular integrals over HG functions are simpler than the corresponding expressions over GTO's (refs. 31,36,53). Their advantage increases as the quantum numbers n and l become larger. Matrix elements of the SCF Hamiltonian over EHG functions are given in a form which is significantly simpler than the algorithm provided by Katriel and Adam (refs. 54,55). Their procedure involves development of a product of the two HG functions centered at two different nuclei in a series of the complete set of the harmonic oscillator functions placed at the third centres. It is well known that this kind of approach implies a slow convergence in instances, e.g. when two centers are far apart or when non-linear parameters of the two considered HG functions are widely different. This drawback is circumvented in our procedure. In this connection it should be mentioned that HG functions are related to harmonic oscillator functions suggested for calculations in nuclear physics by Talmi (ref. 56) and in quantum chemistry by Roberts (ref. 57) and by Moshinsky and Novaro (ref. 58). However, integrals over HG and EHG functions are expressed in considerably simpler way and their computation is more efficient.

It is remarkable that all molecular properties integrals can be reduced to those encountered in the SCF calculations. Derivatives over nuclear coordinates and non-linear parameters are easily incorporated in the general algorithm (ref. 59).

Another advantageous feature is that calculations with HG functions in momentum space is simpler than by using GTO's. Successful description of hydrogen AO's by HG4-N basis sets indicate that it would be worthwhile to expand Laguerre functions (ref. 17) in terms of Hermite-Gaussians.

One should stress that HG functions were successfully subject to practical tests mostly through the work of Salvetti et al. (ref. 59-62) and some others (refs. 63-71). We note in passing that the same idea underlying introduction of HG functions was used by McMurchie and Davidson (ref. 72) who expanded product of Cartesian coordinates of two centers in terms of Hermite polynomials around the third point lying on the intermolecular distance and specified by the corresponding product of pure Gaussians.

Recently HG functions were applied to calculations of the electronic structure in diatomics H_2 , HeH^+ and HF (ref. 73). It was found that non-linear parameters can be transferred from GTO's to HG functions. Ab initio calculations of force constants in H_2O , HF, H_2S and NaH based on HG functions gave results in better agreement with experiment than the GTO estimates of the comparable basis set (ref. 74). It appears that potential surface is too flat if GTO functions are used (ref. 24) whilst better curvature is obtained with HG basis.

As far as future prospects are concerned, we feel confident that HG functions will prove useful in improving nuclear cusps of the total wave functions and will provide a relatively simple description of electron correlation by explicit inclusion of r_{ij} coordinates.

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ERRATA

1. ***Pure & Appl. Chem.*, Vol. 66, No. 4, pp. 873–889, 1994**

The April issue of *Pure and Applied Chemistry* (Volume 66, No. 4) included the IUPAC Recommendation 'Structure-based nomenclature for irregular single-strand organic polymers' prepared by a Working Group consisting of R. B. Fox, N. M. Bikales, K. Hatada and J. Kahovec. Unfortunately, pages 887 and 888 were printed incorrectly. The full article was therefore reproduced correctly in a loose insert which came with the September issue (Volume 66 No. 9). These pages should be substituted for those originally produced when the Volume is bound.

2. ***Pure & Appl. Chem.*, Vol. 66, No. 6, pp. 1267–1286, 1994**

The June issue of *Pure and Applied Chemistry* (Volume 66, No. 6) included the articles 'Theoretical basis of non-equilibrium near atmospheric pressure plasma chemistry' by A. A. Fridman and V. D. Rosanov, and 'Modelling of dielectric barrier discharge chemistry' by B. Eliasson, W. Egli and U. Kogelschatz. Unfortunately, the front pages of these two papers were transposed during production so that the body of both papers was printed out of position within the issue, and given the wrong page numbers and running headlines.

Both articles were reproduced in their entirety in a loose insert that came with the August issue (Volume 66, No. 8), along with a revised contents list. These should be substituted for the original items when the volume is bound.

3. ***Pure & Appl. Chem.*, Vol. 61, pp. 2075–2085, 1989**

Article entitled 'New basis sets in quantum mechanics of molecules. Hermite-Gaussian function' by Z. B. Maksić, K. Kovačević, M. Primorac.

(i) Page 2075, insert the following additional author to the three above:

T. Živković

(ii) Page 2079, line 9 from bottom:

for SM = 100 (1 - Δ) (in %)

read SM = 100 (1 - ½Δ) (in %)