

Hermite-Gaussian Expansion of Hydrogenic Orbitals

M. Primorac

Faculty of Forestry, University of Zagreb, Šimunska 25, 41000 Zagreb, Croatia, Yugoslavia

K. Kovačević

Ruder Bošković Institute, Bijenička 54, POB 1016, 41001 Zagreb, Croatia, Yugoslavia

Z. B. Maksić

*Ruder Bošković Institute, Bijenička 54, POB 1016, 41001 Zagreb, Croatia, Yugoslavia
Faculty of Science and Mathematics, Department of Physical Chemistry,
Marulićev trg 19, 41000 Zagreb, Yugoslavia*

Received March 6, 1989

Hydrogen 1s, 2s, 2p, 3s, 3p, 3d, 4s, 4p and 4d (HO) orbitals are expanded in series of Hermite-Gaussian (HG) functions. Adjustable parameters are determined by the integral least-square fit procedure. HG approximation of the fourth degree (HG4) proved particularly good and useful in representing hydrogen AOs. It yields hydrogen (and hydrogen-like) orbitals which are more accurately described than the corresponding GTO expansion. Hydrogen type orbitals (HTO) expressed in HG4 bases could be useful in molecular calculations involving heavier atoms because some STO orbitals do not perform well for higher principal quantum numbers. Use of STOs for inner-shells and HOs for outer valence shell electrons in heavy atoms might be advantageous. Both types of atomic orbitals could be well represented by HG functions. HG representation of polarization functions, which play an important role in describing charge redistribution upon formation of chemical bonds and are crucial in treating anions, might be useful too. The HG functions may also serve a purpose in solving the Schrödinger equation in momentum representation and in calculations of the X-ray scattering factors.

INTRODUCTION

Orbital approximation is one of the most fruitful concepts in molecular quantum mechanics from both computational and interpretative points of view. Slater type atomic orbitals (STO) played a distinguished role in the early quantum chemistry. They were subsequently replaced by more practical Gaussian type orbitals (GTO) which have dominated in rigorous molecular calculations for the last two decades. Neither STO nor GTO orbitals have a proper nodal radial behavior. On the other hand, the only atomic orbitals (AO) that are exact solutions of the Coulomb hamiltonian are hydrogen AOs. Consequently, they have proper nodes and form a complete and orthogonal

set. Their use in quantum chemical calculations is scarce because contribution of the continuum functions cannot be neglected.¹ In fact, performance of hydrogen orbitals (HO) was disappointing both in atomic² and molecular³ calculations. They were inferior to the simpler STO basis set. However, hydrogen and hydrogen-like orbitals might be useful in solving the momentum space Schrödinger equation.^{4,5} Hence, further examination of the HO basis set seems to be warranted. In particular, it is of great interest to find efficient procedures for computing molecular integrals over HO functions. Namely, polycentric integrals over HOs are extremely tedious. With this idea in mind, we expanded HOs in a series of Hermite-Gaussian (HG) functions. The latter enable expression of molecular integrals in closed forms.⁶⁻⁹ They were superior to earlier formulas for Cartesian Gaussians.¹⁰⁻¹⁴ HG functions seem to be particularly useful in calculations involving orbitals with higher angular momenta. They have been used in *ab initio* SCF calculations¹⁵ LCAO-X_α method,^{16,17} in calculations of correlation energy¹⁸ and photoelectron cross section¹⁹ and, finally, in the theoretical treatment of dynamic electron densities in molecular crystals.²⁰ The same idea was employed by McMurchi and Davidson²¹ who expanded the products of Cartesian coordinates belonging to Cartesian Gaussian functions placed on different centers, appearing in mixed charge distributions, in a series of Hermite polynomials. It is interesting to mention that HG functions were rediscovered by Golebiewski, Mrozek and Salvetti.²¹⁻²³ Generalization of the original HG basis set was discussed by several authors.^{8,9,23} As part of a larger project of implementing HG functions in *ab initio* programs for molecules^{24,25} we present here the least-square fit HG expansion of 1s, 2s, 2p, 3s, 3p, 3d, 4s, 4p and 4d hydrogen orbitals. The results are compared with the corresponding GTO series expansions. This will shed some light on the relative merits of the examined basis sets, which is in fact the most important outcome of the present study.

METHOD

HG functions are defined as follows:⁶

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

where coordinates $x_A = x - A_x$ etc. determine electron position relative to a nucleus A, $n = n_1 + n_2 + n_3$ and Hermite polynomials are denoted by H_{n_i} . An alternative

way of expressing $f_{n_1 n_2 n_3}(a_A, r_A)$ follows from the definition of Hermite polynomials and reads:

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

It immediately suggests that derivatives over nuclear coordinates can be interchanged with integration over electronic coordinates, thus leading to considerable simplification.

Our aim is to expand hydrogen orbitals in a series of HG functions. For this purpose HOs will be given in a general but real form:

$$\Phi_{KLM} = x^K y^L z^M R(r) \quad (3)$$

It is convenient to express the radial part $R(r)$ in terms of spherical Gaussian multiplied by even powers of radius r :

$$R(r) = \sum_{N=0}^{\infty} \left(\sum_{T_i} k_{ji} r^{2i} \right) \exp(-a_i r^2) \quad (4)$$

where the limiting indices N and T_i are functions of the tolerance of error. For a given pair of N and T_i , nonlinear and linear parameters a_i and k_{ji} , respectively, have to be optimized. Relation (4) can be written in an equivalent form in terms of HG functions:

$$R(r) = \sum_{i=1}^N \sum_{j=0}^{T_i} c_{ki} k! \sum_{k_1=0}^k \sum_{k_2=0}^{k-k_1} [k_1! k_2! (k-k_1-k_2)!]^{-1} f_{2k_1, 2k_2, 2(k-k_1-k_2)}(a_i, r) \quad (5)$$

where $k = k_1 + k_2 + k_3$. Coefficients k_{ji} and c_{ki} are linearly related:

$$k_{ij} = [(4a_i)^j / (2j)!] \sum_{k=j}^{T_i} (-1)^{k-j} k! c_{ki} \sum_{t=j}^k (2t)! / [t! (t-j)!] \sum_{s=0}^{k-t} \frac{(2s)! [2(k-t-s)]!}{(s!)^2 [(k-t-s)!]^2} \quad (6)$$

An inverse linear relation is easily found. According to formula (3), the radial part of the HO function should be multiplied by $x^{k_y} y^{k_x} z^m$ yielding:

$$\chi_{KLM} = \sum_{i=1}^N \sum_{k=0}^{T_i} c_{ki} [k! / k_1! k_2! k_3!] f_{2k_1+K, 2k_2+L, 2k_3+M}(a_i, r) \quad (7)$$

Here, summation over k implies a triple sum over k_1 , k_2 and k_3 confined to give a fixed value of $k = 0, 1, 2, \dots$ etc. Our numerical experiments encompass a range of values of $N = 1-5$ for two particular cases: a) $T_i = 1$ and b) $T_i = 2$. 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 pure GTO results obtained by putting $T_i = 0$.

Adjustable parameters are obtained by integral least-square fit criterion by minimizing Δ :

$$\Delta = \int (\chi - \Phi)^2 dr \quad (8)$$

where Φ is the exact hydrogen orbital and χ is the corresponding HG expansion (7). Writing Δ in some more detail

$$\Delta = \int \chi^2 dr + \int \Phi^2 dr - 2 \int \chi \Phi dr \quad (9)$$

one observes that the minimum in Δ requires maximum overlapping between approximate and exact hydrogen AO. One can define Δ as a measure of dissimilarity. The overlap integral $\int \chi \Phi dr$ involves calculation of integrals:

$$\int_0^{\infty} r^m \exp(-ar^2 - ar) dr \quad (10)$$

which lead to numerical difficulties if m is large and $(a/2a) \gg 1$. This type of integrals is carefully treated by locating a maximum of the integrand which is assumed for a value $r_{\max} = (1/4a) [(a^2 + 8aam)^{1/2} - a]$. It is useful to break down the integration in two parts by selecting r_{\max} as superior and inferior limit, respectively.

The optimal sets of nonlinear parameters a_i were found by applying the Fletcher modification²⁶ of the Davidon-Fletcher-Powell algorithm. Linear adjustable parameters $\{c_{ki}\}$ are then determined by solving linear equations which follow from the maximum overlap condition between χ and Φ .

Finally, a word on notation is in place. HG approximations of the second and fourth degree will be abbreviated as (m)HG2-N and (m)HG4-N, respectively. For example:

$$\begin{aligned} \text{sHG4-N} &= \sum_{i=1}^N \{c_{0i} f_{000} + c_{1i} (f_{200} + f_{020} + f_{002}) + c_{2i} [f_{400} + f_{040} + 2(f_{220} + f_{202} + f_{022})]\} = \\ &= \sum_{i=1}^N [k_{0i} + k_{1i} r^2 + k_{2i} r^4] \exp(-a_i r^2) \end{aligned} \quad (11)$$

$$P_x \text{HG4-N} = \sum_{i=1}^N \{c_{0i} f_{100} + c_{1i} (f_{300} + f_{120} + f_{102}) + c_{2i} [f_{500} + f_{140} + f_{104} + 2(f_{320} + f_{302} + f_{122})]\} = x \sum_{i=1}^N (k_{0i} + k_{1i} r^2 + k_{2i} r^4) \exp(-a_i r^2) \quad (12)$$

$$d_z^2 \text{HG4-N} = \sum_{i=1}^N \{c_{0i} f_{002} + c_{1i} (f_{202} + f_{022} + f_{004}) + c_{2i} [f_{402} + f_{042} + f_{006} + 2(f_{222} + f_{204} + f_{024})]\} = z^2 \sum_{i=1}^N (k_{0i} + k_{1i} r^2 + k_{2i} r^4) \exp(-a_i r^2) \quad (13)$$

Here, HG-functions (1) are given without arguments (a , r) for the sake of simplicity, Coefficients k_{0i} , k_{1i} and k_{2i} in formulas (11–13) have different values for different types of AOs although the same symbols are used.

RESULTS AND DISCUSSION

We shall consider GTO results ($T_i = 0$) first. The nonlinear parameters and deviations (error) Δ for hydrogen orbitals 1s, 2s, 3s and 4s are given in Table I. Numbers $N = 1-5$ denote participation of different pure spherical 1s Gaussians, thus weighting various segments of AOs. Clearly, the larger the N , the better is the accuracy. It should be pointed out that many parameter function Δ has many local minima. Their number sharply rises with an increase in N . Although a careful search of the lowest minima was undertaken, there is no guarantee that they were found in each case. A useful test is provided by 1s GTO expansion of Stewart.²⁷ Our results are in very good accordance with his findings. Nonlinear (screening) parameters for 1s, 2s, 3s and 4s HOs are given in Table I while Table II provides the GTO representation of hydrogen orbitals 2p, 3p, 4p and 3d.

TABLE I

GTO expansions for hydrogen orbitals 1s, 2s, 3s and 4s by the least-square fit method. (Numbers given in parentheses are powers of 10.)

N	1s		2s		3s		4s	
		a		a		a		a
1		2.70950(−1)		1.53504(−2)		2.66149(−3)		7.95050(−4)
	Δ	4.272(−2)		1.666(−1)		4.036(−1)		5.447(−1)
2		8.51823(−1)		3.23752(−1)		1.75193(−2)		2.63027(−3)
	Δ	1.51623(−1)		2.91086(−2)		5.55695(−3)		2.63020(−3)
3		3.158(−3)		4.090(−3)		5.348(−2)		1.890(−1)
	Δ	2.22766		1.43910		3.01380(−1)		1.47422(−2)
4		4.05771(−1)		2.48968(−1)		2.38172(−2)		8.32250(−3)
	Δ	1.09818(−1)		1.95822(−2)		5.00506(−3)		1.83986(−3)
5		3.305(−4)		1.283(−3)		1.326(−3)		2.218(−2)
	Δ	5.21801		1.13379		1.16102		3.10377(−1)
6		9.54415(−1)		2.10800(−1)		2.04893(−1)		2.25746(−2)
	Δ	2.65260(−1)		2.40845(−2)		2.49949(−2)		6.46054(−3)
7		8.80597(−2)		1.05479(−2)		4.94089(−3)		1.94062(−3)
	Δ	4.376(−5)		1.786(−4)		1.844(−4)		4.912(−4)
8		1.12794(+1)		3.56545		1.22056		1.27791
	Δ	2.07122		6.11228(−1)		2.2012(−1)		2.27732(−1)
9		5.78076(−1)		1.69235(−1)		2.37845(−2)		2.34139(−2)
	Δ	1.97342(−1)		2.76819(−2)		5.93756(−3)		6.38432(−3)
10		7.44089(−2)		1.27957(−2)		3.66704(−3)		1.94358(−3)
	Δ	6.885(−6)		1.976(−5)		6.328(−5)		7.188(−5)

TABLE II

GTO expansions for hydrogen orbitals 2p, 3p, 4p and 3d by the least-square fit method

	2p	3p	4p	3d
	a	a	a	a
1	4.39917(—2)	5.65800(—3)	1.51445(—3)	1.44698(—2)
Δ	4.765(—2)	2.178(—1)	3.946(—1)	5.009(—2)
2	1.08098(—1)	6.97950(—2)	6.53016(—3)	9.26318(—3)
Δ	2.67360(—2)	6.76499(—3)	2.76832(—3)	3.08625(—2)
	3.092(—3)	4.542(—3)	8.983(—2)	2.981(—3)
3	2.29809(—1)	2.37340(—1)	7.02064(—2)	7.09720(—3)
Δ	5.89799(—2)	5.76919(—2)	9.19022(—3)	1.82200(—2)
	2.00245(—2)	6.91406(—3)	2.44324(—3)	5.81008(—2)
	2.684(—4)	1.418(—3)	1.949(—3)	2.269(—4)
4	4.49443(—1)	1.90274(—1)	1.85298(—1)	5.87459(—3)
Δ	1.16542(—1)	4.99390(—2)	4.98160(—2)	1.31960(—2)
	4.10873(—2)	8.28273(—3)	9.81950(—3)	3.24513(—2)
	1.63584(—2)	4.05069(—3)	2.40065(—3)	1.02070(—1)
	2.904(—5)	1.424(—4)	2.614(—4)	2.112(—5)
5	8.29701(—1)	4.70590(—1)	2.07752(—1)	5.07644(—3)
Δ	2.16101(—1)	1.22022(—1)	5.44185(—2)	2.25507(—2)
	7.70010(—2)	4.36179(—2)	9.06057(—3)	1.04704(—2)
	3.18266(—2)	8.78478(—3)	3.34658(—3)	5.46841(—2)
	1.40083(—2)	4.37770(—3)	2.04577(—3)	1.70986(—1)
	3.717(—6)	8.960(—6)	6.421(—5)	2.312(—6)

It is obvious that a single Gaussian provides a poor fit of HOs. The corresponding overlapping is generally unsatisfactory, as well as the orbital energies. For this purpose it is useful to define a similarity measure $SM = (1 - \Delta/2) \cdot 100\%$. Single Gaussian SM values of various hydrogen orbitals are given in parentheses as follows: 1s (97.9%), 2s (91.7%), 2p (97.6%), 3s (78.6%), 3p (89.1%), 4s (72.8%), 4p (80.3%) and 3d (97.5%). One concludes that there is a relatively high similarity between the 1s Gaussian orbital and the 1s HO and 2p HO, but the differences are highly pronounced in other orbitals, being dramatic in s-type AOs. The corresponding orbital energies exhibit large deviations from the exact values²⁸ (in kcal/mol): 1s (47.5) 2s (—31.2), 2p (7.4), 3s (—231.3), 3p (19.5), 4s (—7.9), 4p (—4.0) and 3d (2.4). The negative sign means that approximate AOs have lower energies than true solutions, implying that a small overlap between the true wavefunction and a trial one might easily lead to unphysical situations. Another measure of the quality of approximate HOs is given by the virial theorem²⁹ which states that for exact wave function $E = -T = (1/2) V$ where T and V stand for kinetic and potential energy, respectively. Ratio ($V/-T$) is listed here for a single 1sG representation of HOs: 1s (1.95), 2s (1.13), 3s (1.051), 4s (1.03), 2p (1.97), 3p (1.21), 4p (1.10) and 3d (1.98). It follows that orbitals with large overlapping (1s, 2p and 3d) satisfy the virial theorem relatively well. Introduction of the second Gaussian considerably improves SM values which in % read: 1s (99.8%), 2s (99.8%), 2p (99.8%), 3s (97.3%), 3p (99.8%), 4s (90.6%) and 4p (95.5%). This trend is followed by improved orbital energies and virial theorem ratios.²⁸ However, one observes that representations of 4s, 4p and perhaps 3s HOs require more than two 1s Gaussians, a conjecture which is supported by the calculation of some additional properties.²⁸

TABLE III

HG expansions of the order two (HG2) for hydrogen orbitals 1s, 2s, 3s and 4s by the least-square fit method

N	1s		2s		3s		4s	
		a		a		a		a
1		2.70950(-1)		4.48068(-2)		9.55541(-3)		2.63016(-3)
	Δ	4.272(-2)		8.796(-2)		6.472(-2)		1.890(-1)
2		8.51831(-1)		3.23754(-1)		8.66512(-2)		6.10696(-2)
	Δ	1.51623(-1)		1.91084(-2)		8.15135(-3)		3.20285(-3)
3		3.158(-3)		4.090(-3)		1.139(-2)		1.108(-2)
	Δ	2.22816		7.17435(-1)		3.18036(-1)		3.45393(-1)
4		4.05787(-1)		9.33531(-2)		1.71769(-2)		1.39157(-2)
	Δ	1.09828(-1)		1.75125(-2)		4.64559(-3)		2.71057(-3)
5		3.305(-4)		7.828(-4)		1.077(-3)		1.196(-3)
	Δ	5.23210		1.55292		1.24897		4.65574(-1)
6		9.55728(-1)		2.84025(-1)		2.23036(-1)		5.19893(-2)
	Δ	2.65427(-1)		5.02320(-2)		1.92639(-2)		9.16646(-3)
7		8.81349(-2)		1.45925(-2)		4.79274(-3)		1.97193(-3)
	Δ	4.376(-5)		1.093(-4)		1.321(-4)		2.334(-4)
8		1.12946(+1)		3.44358		1.67838		1.29992
	Δ	2.06937		6.39824(-1)		3.06319(-1)		2.39483(-1)
9		5.78465(-1)		1.81372(-1)		5.60058(-2)		3.66409(-2)
	Δ	1.97221(-1)		3.05520(-2)		1.25716(-2)		8.49292(-3)
10		7.44642(-2)		1.20525(-2)		4.30595(-3)		1.90769(-3)
	Δ	6.884(-6)		1.486(-5)		3.186(-5)		3.663(-5)

TABLE IV

HG expansions of the order two (HG2) for hydrogen orbitals 2p, 3p, 4p and 3d by the least-square fit method

N	2p		3p		4p		3d	
		a		a		a		a
1		4.39917(-2)		1.46715(-2)		4.15020(-3)		1.44697(-2)
	Δ	4.765(-2)		1.077(-1)		9.470(-2)		5.009(-2)
2		1.08098(-1)		6.97934(-2)		3.01130(-2)		9.26318(-3)
	Δ	2.67360(-2)		6.76507(-3)		3.76604(-3)		3.08608(-2)
3		3.092(-3)		4.542(-3)		1.280(-2)		2.981(-3)
	Δ	2.29809(-1)		1.31456(-1)		7.36399(-2)		7.09723(-3)
4		5.89799(-2)		2.52156(-2)		6.54286(-3)		1.82199(-2)
	Δ	2.00245(-2)		6.17803(-3)		2.19181(-3)		5.81011(-2)
5		2.686(-4)		7.251(-4)		1.416(-3)		2.269(-4)
	Δ	4.49565(-1)		2.43740(-1)		2.17689(-1)		5.87414(-3)
6		1.16565(-1)		6.30710(-2)		5.64806(-2)		1.31954(-2)
	Δ	4.10928(-2)		1.49579(-2)		7.24011(-3)		3.24502(-2)
7		1.63597(-2)		5.22192(-3)		2.28061(-3)		1.02068(-1)
	Δ	2.904(-5)		8.367(-5)		1.169(-4)		2.112(-5)
8		8.30083(-1)		4.59300(-1)		2.67423(-1)		5.07680(-3)
	Δ	2.16080(-1)		1.19870(-1)		6.97766(-2)		2.25513(-2)
9		7.69949(-2)		4.32000(-2)		1.72087(-2)		1.04710(-2)
	Δ	3.18326(-2)		8.85000(-3)		4.80203(-3)		5.46851(-2)
10		1.40155(-2)		4.40000(-3)		1.99903(-3)		1.70989(-1)
	Δ	3.717(-6)		8.889(-6)		2.458(-5)		2.312(-6)

Description of HOs of the type of 1s, 2s, 3s and 4s orbitals at the HG second degree level of approximation is presented in Table III. The corresponding data for 2p, 3p and 4p orbitals are given in Table IV. Perusal of the results collected in Tables I, II and Tables III, IV shows that HG approximation of the second degree is somewhat better than the GTO representation in energy when comparing HG2—5 and GTO-5 basis sets for 3s and 4p HOs. Results for 1s, 2s, 2p, 3p are virtually the same whilst 4s GTO-5 has slightly better energy. This is in accordance with the earlier finding of Huzinaga³⁰ that $r^2 \exp(-\alpha r^2)$ has slightly worse energetic performance than the pure 1s $\exp(-\alpha r^2)$ Gaussian. Hence, our data corroborate Huzinaga's conclusion as far as energetic properties are concerned. However, description of higher HOs at medium and large distance is better by the HG2 set²⁸ as evidenced by the calculation of $\langle r \rangle$ and $\langle r^2 \rangle$ properties. In particular, fewer HG2 functions than 1s GTOs are necessary for a satisfactory representation of 3s, 4s and 4p HOs as revealed by the $\langle r \rangle$ and $\langle r^2 \rangle$ criteria.²⁸ Single HG2-1 functions exhibit the same general features as the 1s single GTOs but some characteristics are definitely better. For example, the SM values of the former are: 1s (97.9%), 2s (95.6%), 2p (97.6%), 3s (96.8%), 4s (90.6%) and 4p (95.3%), indicating that similarity with HOs is considerably increased. Surprisingly, virial ratios are not dramatically improved: 1s (1.96), 2s (1.50), 2p (1.97), 3s (1.33), 3p (1.67), 4s (1.1) and 4p (1.36) although they do show a shift in the right direction. The most flexible and most accurate basis set is provided by HG4—5 functions. Orbital energies are exactly reproduced, the 4s orbital being an exception since the error is 0.02 kcal/mol. This is of course negligible for chemical purposes. It is well known that the cusp condition cannot be satisfied with Gaussian functions, but the HG4—5 function describes very well electron distribution in the near vicinity of the nucleus and is superior to the GTO-5 representation. Since HG4—5 functions represent a basis set of choice if highly accurate calculations are desired, we list both linear and nonlinear least-square parameters in Tables V—IX. Finally, coefficients k_{0i} , k_{1i} and k_{2i} for the HG4—5 set are summarized in Table IX. They correspond to five a_i values listed at the bottom of Tables V—IX. Survey of the results shows that 1s, 2p, 3p, and 4d orbitals are particularly well reproduced. The single most important result of the present analysis is perhaps the finding that hydrogen AOs of higher n are appropriately described by HG4 functions. This is remarkable because higher STO orbitals are very inaccurate. One can, therefore, imagine a basis set for heavy atoms composed of STOs for inner-shells and hydrogen AOs for peripheral valence electrons. The former can be expressed either in GTOs or HG-functions, whereas the latter should be represented by HG4 functions. This idea requires additional numerical experiments.

The radial residues $r^2(\Phi - \chi)$ for $\Phi = 1s, 2s$ and $3s$ hydrogen orbitals and χ corresponding to their HG4—5 expansions are depicted in Figures 1—3 as functions of r . The radial residue function exhibits typical oscillatory behaviour, which is a consequence of the least-square fit procedure. An important feature of the HG4—5 representation is that oscillations have higher frequencies and smaller amplitudes than the corresponding GTO basis with the same number of pure Gaussian ($N = 5$), particularly at small distances from the nucleus. Amplitudes of the latter are scaled down by 0.25 in

TABLE V
HG expansions of the order four (*HG4*) for hydrogen orbitals *1s* and *2s* by the least-square fit method

N	1s				2s				
	a	C ₀₁	C ₁₁	C ₂₁	a	C ₀₁	C ₁₁	C ₂₁	
1	Δ	3.126312(-1) 7.489(-3)	3.90955(-1)	5.92489(-2)	5.24676(-3)	4.480969(-2) 8.796219(-2)	-1.09178(-1)	-2.00057(-2)	-2.14564(-8)
2	Δ	1.542141(-1) 1.690296 1.391(-4)	1.38385(-1) 4.63840(-1)	6.45407(-3) 6.85259(-2)	1.096687(-3) 4.20104(-3)	1.643082(-2) 4.053792(-1) 4.537(-4)	-3.22848(-2) 2.39029(-1)	1.23407(-4) 3.53445(-2)	-1.46815(-4) 2.43999(-3)
3	Δ	1.067755(-1) 6.511407(-1) 6.904295	6.71295(-2) 3.13226(-1) 2.69711(-1)	2.71310(-4) 2.60134(-2) 3.90341(-2)	3.52763(-4) 1.68994(-3) 2.27806(-3)	1.821835(-2) 2.639756(-1) 2.804605 1.022(-5)	-3.79063(-2) 1.42772(-1) 1.47707(-1)	-5.66236(-4) 1.14636(-2) 2.14062(-2)	-1.65528(-4) 8.24361(-4) 1.25400(-3)
4	Δ	7.549651(-2) 3.361623(-1) 1.709788 1.503072(+1) 4.151(-7)	2.82399(-2) 2.10751(-1) 2.23326(-1) 1.70541(-1)	-6.72728(-4) 1.04738(-2) 1.55404(-2) 2.33731(-2)	1.00082(-4) 7.73733(-4) 9.20808(-4) 1.39263(-3)	1.507764(-2) 5.922236(-2) 3.541585(-1) 3.667834 2.384(-6)	-2.55452(-2) -1.88307(-2) 1.47580(-1) 1.29325(-1)	2.61472(-4) -3.13338(-3) 1.19379(-2) 1.85588(-2)	-8.53845(-5) 4.59902(-5) 7.85311(-4) 1.08607(-3)
5	Δ	8.164212(-2) 3.556802(-1) 8.894961(-1) 5.413515 6.430702(+1) 8.242(-8)	3.41141(-2) 1.95295(-1) 1.22514(-1) 1.81929(-1) 1.01046(-1)	-5.54350(-4) 1.11062(-2) 2.55037(-3) 1.69413(-2) 1.52580(-2)	1.25452(-4) 6.49324(-4) 5.24961(-4) 9.39565(-4) 8.62931(-4)	8.222501(-3) 2.368672(-2) 1.812522(-1) 6.412882(-1) 5.7566681 5.501(-7)	-2.68777(-3) -4.38720(-2) 7.97492(-2) 9.96265(-2) 9.95697(-2)	1.01010(-4) -1.03936(-3) 3.40995(-3) 5.64965(-3) 1.38714(-2)	-3.03464(-6) -1.01212(-4) 2.04565(-4) 4.23192(-4) 8.20590(-4)

TABLE VI
 HG expansions of the order four (HG4) for hydrogen orbitals 3s and 4s by the least square fit method

N	3s			4s		
	a	C _{0i}	C _{2i}	a	C _{0i}	C _{2i}
1	9.555397(-3)	3.30991(-2)	8.17402(-3)	5.309646(-3)	-2.56684(-2)	-1.36308(-2)
	6.172(-2)			8.434(-2)		
2	8.151272(-3)	2.90385(-2)	5.206435(-3)	3.202845(-3)	-1.28123(-2)	-4.32546(-3)
	8.664904(-2)	-6.95103(-2)	1.61671(-2)	6.106906(-2)	-7.93717(-2)	-1.25158(-2)
	1.138(-2)			1.018(-2)		
3	5.253503(-3)	2.56730(-2)	-1.83429(-4)	2.726347(-3)	-1.36627(-2)	-2.37590(-3)
	1.620834(-2)	-5.84750(-2)	-2.92632(-3)	1.406515(-2)	2.77644(-2)	7.63885(-3)
	4.100793(-1)	1.423447(-1)	2.10277(-2)	5.253925(-1)	1.06379(-1)	1.66546(-2)
	1.332(-4)			9.337(-4)		
4	4.740662(-3)	1.76167(-2)	-1.10870(-4)	1.511055(-3)	-7.89226(-3)	3.74839(-4)
	2.286912(-2)	-5.19431(-2)	-8.99948(-4)	8.441422(-3)	4.60203(-2)	3.67563(-3)
	2.449951(-1)	8.12937(-2)	6.13754(-3)	3.850756(-2)	-5.17632(-2)	-3.61802(-3)
	2.481999	8.36496(-2)	1.19358(-2)	4.76894(-1)	9.60200(-2)	1.42019(-2)
	1.875(-6)			4.686(-5)		
5	4.58974(-3)	1.64885(-2)	-1.85733(-4)	1.678880(-3)	-9.67634(-3)	3.00529(-3)
	2.775973(-2)	-6.72172(-2)	-3.23314(-3)	7.388279(-3)	4.50677(-2)	1.88168(-3)
	1.053520(-1)	3.37688(-2)	9.83551(-4)	2.614582(-2)	-5.209744(-2)	-1.84816(-3)
	5.977237(-1)	7.99875(-2)	6.63905(-3)	2.280260(-1)	5.24064(-2)	3.75892(-3)
	6.414206	5.69242(-2)	8.34429(-3)	2.380242	5.78929(-2)	8.47237(-3)
	2.858(-7)			9.125(-7)		

TABLE VII
 HG expansions of the order four for hydrogen orbitals 2p and 3p by the least-square fit method

N	2p			3p				
	a	C _{0i}	C _{1i}	C _{2i}	C _{0i}	C _{1i}	C _{2i}	
1	Δ 4.903499(-2) 7.103(-3)	2.45809(-3)	3.12011(-4)	2.02483(-5)	1.467145(-2) 1.077(-1)	-6.77687(-3)	-9.09137(-4)	-6.94238(-15)
2	Δ 2.626847 1.878078(-1) 8.953(-5)	5.87426(-3) 4.77992(-2)	2.56560(-4) 5.56038(-3)	3.22602(-6) 2.47338(-5)	5.888203(-3) 8.557089(-2) 3.545(-4)	-1.06726(-3) 2.747401(-2)	-4.41929(-6) 3.24372(-3)	-3.83166(-6) 1.62797(-4)
3	Δ 1.996519(-2) 9.571317(-2) 6.820145(-1) 2.460(-6)	2.68669(-3) 2.62318(-2) 3.52344(-2)	2.81574(-5) 1.96583(-3) 3.95388(-3)	1.09841(-5) 9.32616(-5) 1.61976(-4)	6.426224(-3) 6.098017(-2) 4.150788(-1) 7.289117(-6)	-1.32485(-3) 1.406144(-2) 2.55784(-2)	-2.52862(-5) 9.61336(-4) 2.87549(-3)	-4.42966(-6) 5.07340(-5) 1.19349(-4)
4	Δ 1.654623(-2) 6.895375(-2) 9.976846(-2) 7.292978(-1) 6.154(-7)	1.44148(-3) -1.31827(-1) 3.83574(-1) 3.21434(-2)	-1.05289(-5) 7.35117(-3) 2.09113(-2) 3.51202(-3)	4.58281(-6) -1.82573(-6) 3.81884(-4) 1.45553(-4)	5.458783(-3) 2.351908(-2) 6.602873(-2) 4.579954(-1) 1.429(-6)	-8.19771(-4) -2.93185(-3) 2.12729(-2) 2.43106(-2)	3.65040(-6) -3.85413(-4) 1.67585(-3) 2.70438(-3)	-2.25840(-6) -2.39398(-5) 6.99327(-5) 1.12039(-4)
5	Δ 1.443186(-2) 6.840110(-2) 9.797072(-2) 1.947547(-1) 1.612715 5.173(-8)	8.836844(-4) 2.793221 -6.90858 6.54693(-1) 2.422484(-2)	-1.66419(-5) -1.11849(-1) -3.18424(-1) 3.98473(-2) 2.67668(-3)	2.40695(-6) 2.13819(-3) -5.78913(-3) 7.00711(-4) 1.08165(-4)	4.318687(-3) 8.902592(-3) 4.857109(-2) 2.131495(-1) 1.348452 3.783(-8)	-3.02568(-4) -1.19698(-3) 9.02161(-3) 1.69452(-2) 1.413746(-2)	5.57792(-6) 1.19602(-5) 3.97814(-4) 1.22691(-3) 1.49020(-3)	-5.25012(-7) -7.00552(-7) 2.44144(-5) 4.99612(-5) 6.13857(-5)

TABLE VIII
 HG expansions of the order four (HG4) for hydrogen orbitals 4p and 3d by the least-square method

N	4p					3d						
	a	C _{0i}	C _{1i}	C _{2i}	a	C _{0i}	C _{1i}	C _{2i}	a	C _{0i}	C _{1i}	C _{2i}
1	Δ 4.156200(-3) 9.470(-2)	-1.39261(-3)	-2.17121(-4)	9.79394(-14)	1.578995(-2) 6.734072(-3)	8.36980(-4)	9.23646(-5)	4.74145(-6)				
2	Δ 3.765500(-3) 3.010500(-2) 1.280(-2)	-1.13549(-3) 5.42259(-3)	-1.46938(-4) 1.03731(-3)	-1.51573(-13) 5.65534(-9)	8.979344(-3) 4.978469(-2) 6.405(-5)	1.45823(-4) 2.35944(-3)	6.33857(-6) 2.29291(-4)	6.11221(-7) 8.07057(-6)				
3	Δ 1.973548(-3) 1.195256(-2) 9.902484(-2) 1.095(-4)	-2.99680(-4) 3.42105(-3) -2.10711(-2)	7.77555(-6) 1.65028(-4) -2.47100(-3)	-6.87743(-7) -8.59812(-10) -1.16980(-4)	7.294509(-3) 3.053507(-2) 1.710349(-1) 2.596(-6)	6.77706(-5) 1.21073(-3) 2.07528(-3)	1.209957(-6) 8.63201(-5) 1.85742(-4)	2.33306(-7) 3.16349(-6) 5.83703(-6)				
4	Δ 2.317284(-3) 8.046819(-3) 6.094474(-2) 3.845344(-1) 1.419(-6)	-4.54689(-4) 1.83500(-3) -9.35040(-3) -1.69730(-2)	1.31438(-7) 7.65235(-6) -5.72055(-4) -1.87077(-3)	-9.55845(-7) 3.66109(-6) -3.01499(-5) -7.83523(-5)	5.027945(-3) 1.494467(-2) 5.177054(-2) 2.648179(-1) 2.979(-8)	1.27299(-5) 3.58573(-4) 1.20399(-3) 1.79920(-3)	-1.921695(-7) 1.35483(-5) 7.30917(-5) 1.63339(-4)	2.57058(-8) 6.87357(-7) 2.48044(-6) 5.14722(-6)				
5	Δ 2.262109(-3) 8.618842(-3) 2.341032(-2) 1.026624(-1) 7.880121(-1) 4.280(-7)	-4.19194(-4) 1.90635(-3) -3.47406(-4) -1.27495(-2) -1.57714(-2)	1.39202(-6) -1.72949(-6) 5.80434(-5) -9.46124(-4) -1.86397(-3)	-8.20606(-7) 1.55690(-6) -5.23412(-6) 4.27667(-5) -7.55817(-5)	4.998349(-3) 1.501785(-2) 5.136864(-2) 2.474294(-1) 5.010412(-1) 7.111(-9)	1.24742(-5) 3.65019(-4) 1.15851(-3) 1.91259(-3) -1.48118(-3)	-2.00921(-7) 1.41109(-5) 6.71711(-5) 1.56816(-4) -4.08527(-5)	2.55651(-8) 7.05932(-7) 2.24896(-6) 7.05742(-6) 1.48999(-6)				

TABLE IX

GTO, HG2 and HG4 expansions for hydrogen orbital 4d by the least-square fit method

N		GTO	HG2	HG4
		a	a	a
1		2.73852(-3)	6.53101(-3)	6.53101(-3)
	Δ	2.523(-1)	1.192(-1)	1.192(-1)
2		3.19737(-3)	3.19729(-3)	2.81030(-3)
	Δ	2.44030(-2)	2.44030(-2)	2.94191(-2)
3		4.671(-3)	4.671(-3)	2.784(-4)
	Δ	3.26074(-3)	2.91598(-3)	2.24982(-2)
4		7.05362(-2)	4.15397(-2)	3.01957(-3)
	Δ	2.09601(-2)	1.00441(-2)	1.16481(-1)
5		1.494(-3)	6.587(-4)	6.071(-6)
	Δ	3.88784(-3)	6.25547(-3)	5.01145(-3)
6		2.06630(-3)	2.47664(-3)	2.40007(-3)
	Δ	1.83356(-2)	2.21027(-2)	2.18196(-2)
7		5.69470(-2)	6.95509(-2)	1.13065(-1)
	Δ	1.149(-4)	6.570(-5)	8.016(-7)
8		3.99388(-3)	4.05284(-3)	4.72666(-3)
	Δ	2.11416(-3)	2.15192(-3)	2.50585(-3)
9		1.66996(-2)	1.63871(-2)	2.11322(-2)
	Δ	4.11201(-2)	3.94162(-2)	9.27915(-2)
10		1.31593(-1)	1.22513(-1)	2.83865(-1)
	Δ	6.421(-6)	5.849(-6)	1.150(-7)

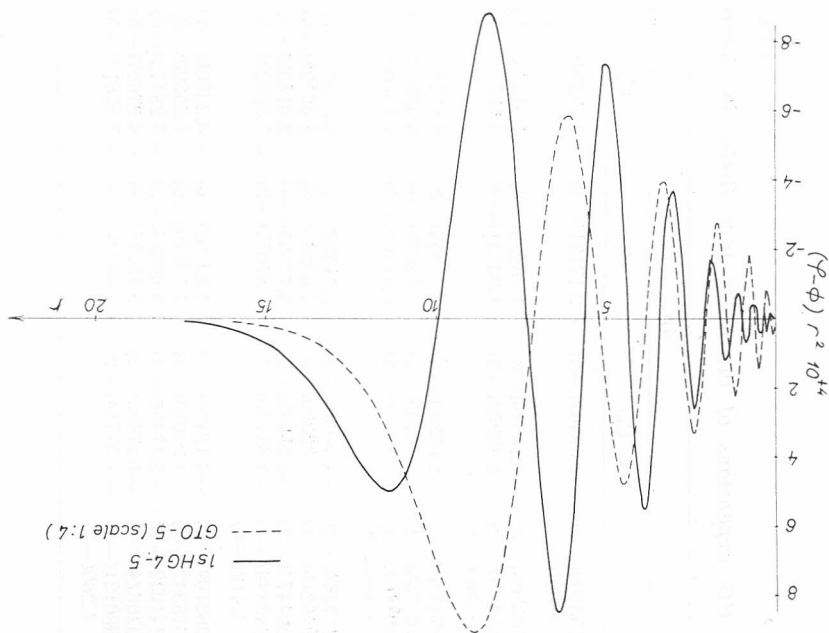


Figure 1. Comparison of radial residues for the 1s hydrogen orbital represented by 1s HG4-5 and 1s GTO-5 basis sets. GTO-5 residues are scaled down in a ratio 1:4, because they would be too large otherwise. Atomic units are used.

TABLE X

Linear coefficients of polynomial expansions of 1s, 2s, 3s, 4s, 2p, 3p, 4p, 3d and 4d hydrogen orbitals for HG4-5 basis sets

k_0	k_{11}	k_{21}	k_{01}	k_{11}	k_{21}	k_{01}	k_{11}	k_{21}
1s								
4.497(-2)	-8.365(-4)	1.33790(-5)	-3.476(-3)	4.919(-6)	-3.283(-9)	1.982(-2)	-1.425(-5)	1.243(-8)
1.676(-1)	1.020(-3)	1.314(-3)	-4.371(-2)	5.496(-5)	-9.086(-7)	-5.831(-2)	-4.824(-5)	-2.157(-6)
1.387(-1)	-2.081(-2)	6.646(-3)	7.156(-2)	9.926(-5)	1.075(-4)	3.802(-2)	-7.264(-4)	3.005(-5)
1.367(-1)	4.132(-2)	4.406(-1)	9.120(-2)	-2.877(-3)	2.785(-3)	6.410(-2)	6.050(-4)	2.282(-3)
6.127(-2)	3.733(-1)	5.710(+1)	6.558(-2)	1.708(-2)	4.351(-1)	3.568(-2)	1.690(-2)	3.162(-1)
4s								
-1.239(-2)	3.649(-6)	-6.846(-10)	3.333(-4)	-1.166(-6)	3.854(-9)	-5.676(-5)	4.604(-8)	-4.118(-11)
3.522(-2)	4.427(-5)	2.096(-8)	2.203	-2.458(-2)	1.674(-4)	-2.670(-4)	2.122(-7)	-3.353(-10)
-4.585(-1)	-5.831(-5)	-8.822(-7)	-2.839	-3.835(-2)	-1.113(-3)	3.730(-3)	-2.447(-5)	8.124(-7)
4.692(-2)	-7.222(-4)	2.366(-4)	3.127(-1)	1.391(-2)	7.507(-5)	1.070(-2)	-1.222(-4)	6.627(-5)
3.672(-2)	5.361(-3)	4.481(-2)	3.200(-2)	-5.766(-3)	2.286(-2)	1.818(-2)	-2.864(-3)	8.295(-3)
4p								
-5.213(-5)	2.097(-8)	-1.278(-11)	4.344(-7)	-4.482(-10)	2.043(-13)	2.392(-8)	-9.836(-11)	-9.435(-13)
3.976(-4)	-2.901(-7)	6.871(-10)	2.075(-5)	-4.079(-8)	1.530(-10)	3.472(-7)	-1.879(-10)	4.061(-14)
-5.081(-4)	5.863(-6)	-2.809(-8)	1.602(-4)	-5.823(-7)	1.951(-8)	-3.977(-5)	1.158(-7)	-7.696(-10)
-5.944(-3)	6.614(-5)	-9.243(-6)	1.480(-3)	-9.526(-5)	6.842(-6)	-2.989(-4)	2.979(-6)	-1.955(-7)
-1.834(-2)	1.301(-3)	-2.666(-3)	-1.070(-3)	-3.795(-4)	1.199(-5)	-3.156(-4)	4.913(-5)	-5.433(-7)
3s								
2p								
-1.239(-2)	3.649(-6)	-6.846(-10)	3.333(-4)	-1.166(-6)	3.854(-9)	-5.676(-5)	4.604(-8)	-4.118(-11)
3.522(-2)	4.427(-5)	2.096(-8)	2.203	-2.458(-2)	1.674(-4)	-2.670(-4)	2.122(-7)	-3.353(-10)
-4.585(-1)	-5.831(-5)	-8.822(-7)	-2.839	-3.835(-2)	-1.113(-3)	3.730(-3)	-2.447(-5)	8.124(-7)
4.692(-2)	-7.222(-4)	2.366(-4)	3.127(-1)	1.391(-2)	7.507(-5)	1.070(-2)	-1.222(-4)	6.627(-5)
3.672(-2)	5.361(-3)	4.481(-2)	3.200(-2)	-5.766(-3)	2.286(-2)	1.818(-2)	-2.864(-3)	8.295(-3)
3p								
4d								

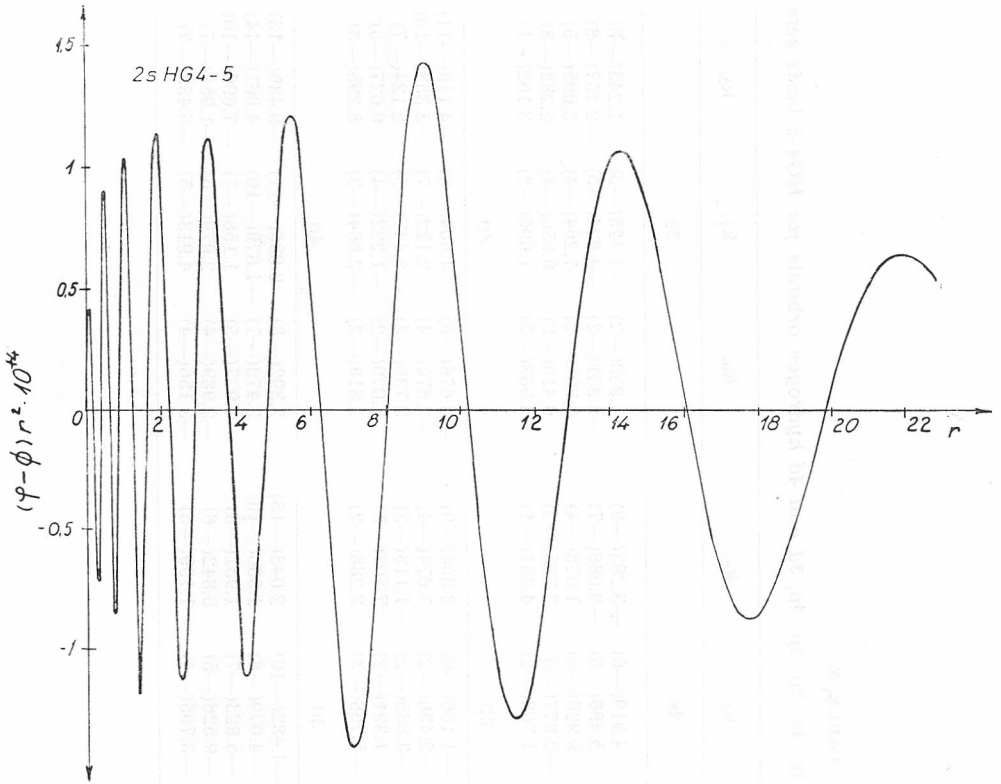


Figure 2. Radial differences (residues) between 2sH and its approximate 2s HG4-5 representation (in a. u.).

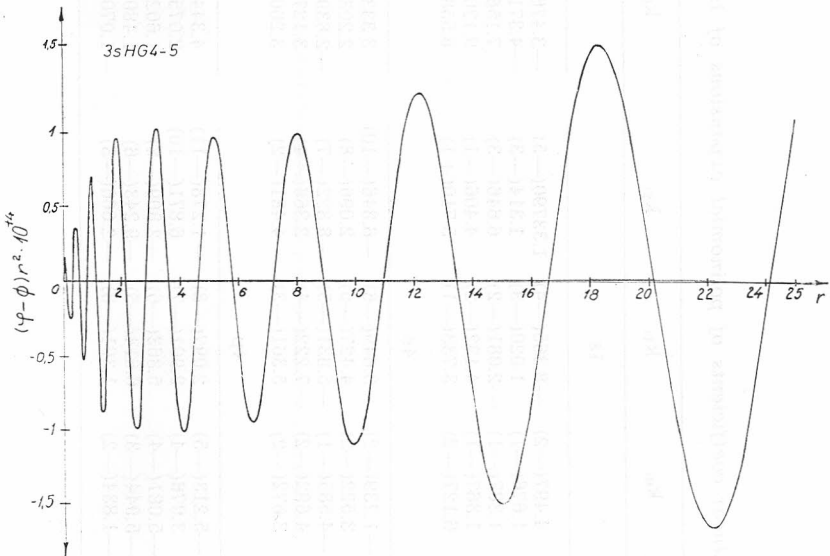


Figure 3. Radial differences (residues) between 3sH and its approximate 3s HG4-5 representation in (a. u.).

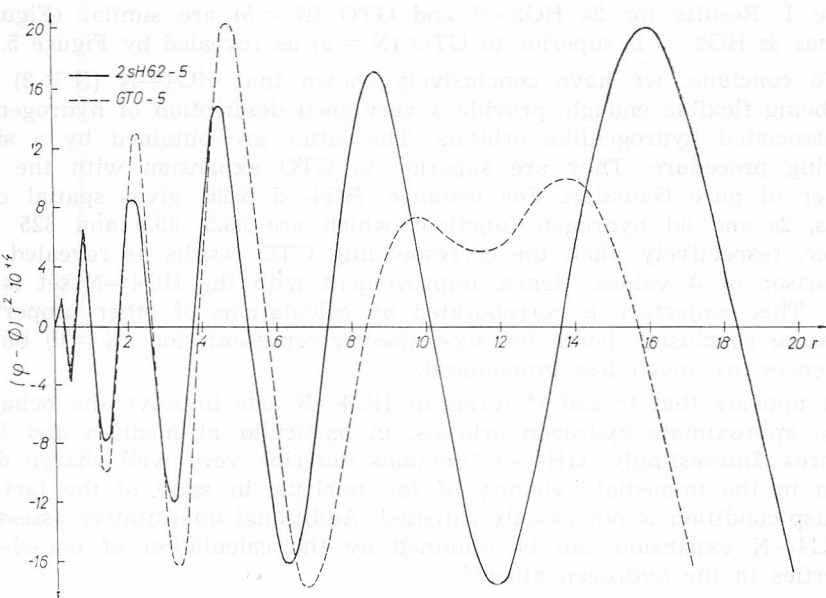


Figure 4. Comparison of radial residues for 2sH orbital represented by 2s HG2-5 and 1s GTO-5 basis set function (in a. u.).

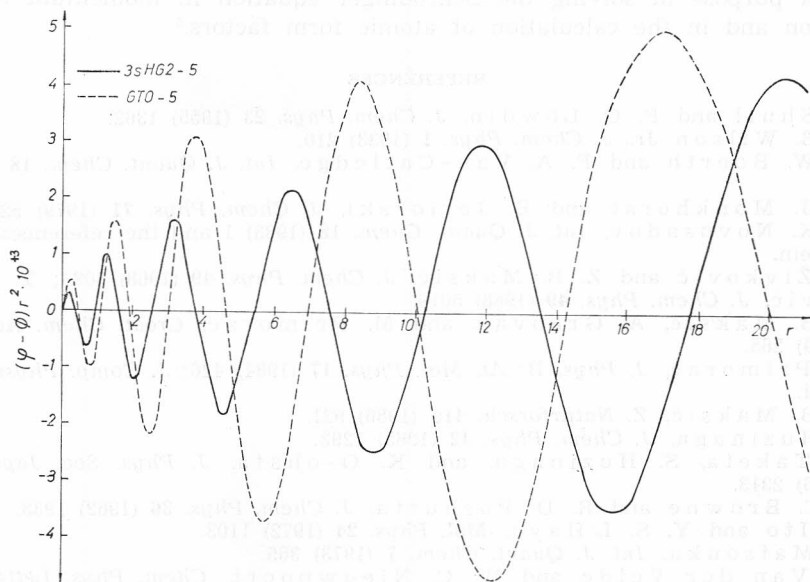


Figure 5. Comparison of radial residues for 3sH approximated by 3s HG2-5 and 1s GTO-5 expressions (in a. u.).

Figure 1. Results for 2s HG2—5 and GTO (N = 5) are similar (Figure 4) whereas 3s HG2—5 is superior to GTO (N = 5) as revealed by Figure 5.

To conclude, we have conclusively shown that HG4—N (N ≥ 2) basis sets, being flexible enough, provide a very good description of hydrogen and the associated hydrogenlike orbitals. The latter are obtained by a simple rescaling procedure. They are superior to GTO expansion with the same number of pure Gaussian. For instance, HG4—5 basis gives spatial errors for 1s, 2s and 3d hydrogen functions which are 83.5, 35.9 and 325 times smaller, respectively, than the corresponding GTO results as revealed by a comparison of Δ values. Hence, improvement with the HG4—N set is dramatic. This conjecture is corroborated by calculations of other properties.²⁸ The same conclusion holds for six-Gaussian representation (N = 6) but the differences are much less pronounced.

It appears that r^2 and r^4 terms in HG4—N sets improve the behaviour of the approximate hydrogen orbitals, in particular at medium and larger distances. Interestingly, GH4—5 functions describe very well charge distribution in the immediate vicinity of the nucleus, in spite of the fact that the cusp condition is not exactly satisfied. Additional quantitative assessment of HG4—N expansion can be obtained by the calculation of one-electron properties in the hydrogen atom.²⁸

Hydrogen orbitals could be useful for a description of valence orbitals in heavier atoms because STO orbitals do not perform very well for higher quantum numbers n. The same holds for polarization functions which describe charge reorganization upon formation of chemical bonds and play an important role in anions. Hence, a mixed STO-inner and HO-outer shell combined basis set might be advantageous. Hydrogen orbitals may also serve a purpose in solving the Schrödinger equation in momentum representation and in the calculation of atomic form factors.⁵

REFERENCES

1. H. Shull and P. O. Löwdin, *J. Chem. Phys.* **23** (1955) 1362.
2. E. B. Wilson Jr., *J. Chem. Phys.* **1** (1933) 210.
3. D. W. Boerth and F. A. Van-Catledge, *Int. J. Quant. Chem.* **18** (1980) 973.
4. H. J. Monkhorst and B. Jeriorski, *J. Chem. Phys.* **71** (1979) 5268.
5. B. K. Novosadov, *Int. J. Quant. Chem.* **18** (1983) 1 and the references cited therein.
6. T. Živković and Z. B. Maksić, *J. Chem. Phys.* **49** (1968) 3083; T. Živković, *J. Chem. Phys.* **49** (1968) 5019.
7. Z. B. Maksić, A. Graovac, and M. Primorac, *Croat. Chem. Acta* **52** (1979) 265.
8. M. Primorac, *J. Phys. B: At. Mol. Phys.* **17** (1984) 426; *J. Comp. Physics*, in print.
9. Z. B. Maksić, *Z. Naturforsch.* **41a** (1986) 921.
10. S. Huzinaga, *J. Chem. Phys.* **42** (1965) 1293.
11. H. Taketa, S. Huzinaga, and K. Oohata, *J. Phys. Soc. Japan* **21** (1966) 2313.
12. J. C. Browne and R. D. Poshusta, *J. Chem. Phys.* **36** (1962) 1933.
13. H. Ito and Y. S. L'Haya, *Mol. Phys.* **24** (1972) 1103.
14. O. Matsouka, *Int. J. Quant. Chem.* **7** (1973) 365.
15. G. Van der Velde and W. C. Nieuwpoort, *Chem. Phys. Letters* **13** (1972) 409.
16. B. I. Dunlap, J. W. D. Connolly, and J. R. Sabin, *Int. J. Quant. Chem. S* **11** (1977) 81.

17. S. H. Lamson and R. P. Messmer, *J. Chem. Phys.* **76** (1982) 3102, *Chem. Phys. Letters* **98** (1983) 72.
18. R. Colle and D. Salvetti, *Theoret. Chim. Acta* **53** (1979) 55; R. Montagnani, P. Riani, and O. Salvetti, *ibid.* **62** (1983) 329; R. Montagnani and O. Salvetti, *ibid.* **64** (1984) 371.
19. J. W. Mintmire and C. T. White, *Int. J. Quant. Chem. S* **17** (1983) 609.
20. A. F. Ruysink and A. Vos, *Acta Cryst. A* **30** (1974) 497.
21. A. Golebiewski and J. Mrozek, *Int. J. Quant. Chem.* **7** (1973) 623; *ibid.* **7** (1973) 1020.
22. F. Bondi, O. Salvetti, and A. Golebiewski, *Int. J. Quant. Chem.* **12** (1977) 29.
23. J. Katriel and G. Adam, *J. Chem. Phys.* **51** (1969) 3709; *J. Katriel, Chem. Phys. Letters* **3** (1969) 1624.
24. M. Primorac, Ph. D. Thesis, Zagreb University, 1986.
25. K. Kovačević, Ph. D. Thesis, Zagreb University, 1988.
26. R. Fletcher, *Comp. J.* **13** (1970) 317.
27. R. F. Stewart, *J. Chem. Phys.* **52** (1970) 431.
28. M. Primorac, K. Kovačević, and Z. B. Maksić, *J. Mol. Structure Theochem*, **202** (1989) 75.
29. F. L. Pilar, *Elementary Quantum Chemistry*, Mc Graw-Hill, New York, 1968.
30. S. Huzinaga, *J. Chem. Phys.* **42** (1964) 1293.

SAŽETAK

Hermite-Gaussov razvoj vodikovih orbitala

Miljenko Primorac, Krešimir Kovačević i Zvonimir B. Maksić

Vodikove orbitale 1s, 2s, 2p, 3s, 3p, 3d, 4s, 4p i 4d razvijene su u redove Hermite-Gaussovih(HG) funkcija primjenom metode najmanjih kvadrata. HG približenje četvrtog stupnja daje vrlo točan opis vodikovih orbitala. Ovaj postupak mogao bi biti vrlo djelotvoran za teške atome, pri rješavanju Schrödingerove jednadžbe u impulsnoj reprezentaciji i pri računanju faktora raspršenja X-zraka.