

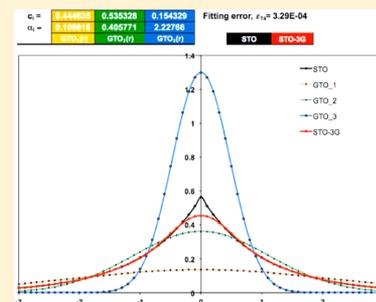
Gaussian-Type Orbitals versus Slater-Type Orbitals: A Comparison

Alexandre L. Magalhães*

Requimte/Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, Rua do Campo Alegre s/n, 4169-007 Porto, Portugal

Supporting Information

ABSTRACT: The advantages of Gaussian-type orbitals (GTO) over Slater-type orbitals (STO) in quantum chemistry calculations are clarified here by means of a holistic approach. The popular Microsoft Office Excel program was used to create an interactive application with which students are able to explore the features of GTO, including automatic calculations and graphical displays. The simple case of the ground state wave function of the hydrogen atom is analyzed, for which the mathematical expressions are easily obtained by the students. The present work can be used also as a classroom guide for the particular topic of GTO, usually taught in introductory courses to atomic and molecular structure.



KEYWORDS: Physical Chemistry, Upper-Division Undergraduate, Quantum Chemistry, Computational Chemistry

INTRODUCTION

Modern undergraduate curricula in chemistry and biochemistry usually include courses in Computational Chemistry. This is a consequence of the importance that this area has gained in recent decades, as expressed by the Chemistry Nobel prize awarded in 1998 and 2013 to computational chemists. After a first contact with quantum mechanical foundations in the first year of university, the students are ready to be introduced to basic approximation techniques for the solution of the Schrödinger equation. Nowadays, quantum chemistry calculations may seem too easy to run as a wide range of commercial and freeware program packages are available. They are usually very user-friendly and have appealing graphical interfaces, which may induce the students to use them as “black box” tools. Most beginners in science courses immediately reveal that attitude, which we have to dispel by gradually showing them the mathematical background of the methods. On the other hand, computers and other technological devices are part of the student’s everyday life, and they are always keen to use them. Modern courses in computational chemistry have to reach the right balance between teaching the formal mathematical foundations of methodologies and running “black box” computer applications, in order to keep the interest of students.

Here, we introduce a Microsoft Office Excel application, which allows the students to explore the features of Gaussian-type orbitals (GTOs) as opposed to those of Slater-type orbitals (STOs). Therefore, an interactive application is presented in which the simple case of the ground state wave function of the hydrogen atom is analyzed, using mathematical expressions easily obtained by the students. The present work can be employed as a classroom guide for the particular topic of GTOs, usually taught in introductory courses to atomic and molecular structure.

METHODS

The sequence of the topics presented here aims to drive the student through a learning path in which the characteristics and usefulness of GTOs are successively apprehended, by comparison with STOs. Nowadays, it is well established that providing students with a wide diversity of study tools definitely improves the learning process. Therefore, for each one of the topics, a few highly visual and interactive exercises were planned. To accomplish this goal, an application was built with the Microsoft Office Excel¹ program, which is very popular among students. It comprises nine different spreadsheets to be used in several activities, and it is available for download in the Supporting Information. Only the functions corresponding to the 1s hydrogen atomic orbital will be considered for the sake of simplicity. They were all designed to be highly interactive, and the cell formulas used in calculations and plots can be easily edited, which is an enormous pedagogical support for beginners in this field.

The theoretical concepts that are needed to follow the exercises suggested in this work can be found in almost all introductory textbooks to Computational Chemistry and a few specific references.^{2–7} Nevertheless, a summary of the relevant aspects of the theory is presented as Supporting Information.

RESULTS

Fitting a GTO to a STO

The first exercise is supported by the spreadsheet application *STO_vs_GTO*, which concerns the comparison of the two types of functions, defined as

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Table 1. Coefficients, Exponents, Least-Squares Errors, and Electronic Energies for STO-KG Contracted Functions of H Atom Ground State

K	Least-Squares Fit ⁸				Energy Optimized ¹²			
	α_i	c_i	ϵ_{1s}	E/hartree	α_i	c_i	ϵ_{1s}^a	E/hartree
2	0.151623	0.678914	3.16×10^{-3}	-0.48116 ^a	1.332480	0.2744085	6.70×10^{-3}	-0.48581
	0.851819	0.430129			0.2015287	0.8212254		
3	0.109818	0.444635	3.31×10^{-4}	-0.49491	4.500225	0.07047866	1.25×10^{-3}	-0.49698
	0.405771	0.535328			0.6812745	0.4078893		
	2.22766	0.154329			0.1513748	0.6476689		
5	0.0744527	0.193572	6.88×10^{-6}	-0.49951	34.05432	0.006026783	1.29×10^{-4}	-0.49981
	0.197572	0.482570			5.122332	0.04503430		
	0.578648	0.331816			1.164455	0.2019221		
	2.07173	0.113541			0.3271926	0.5030515		
	11.3056	0.0221406			0.1030649	0.3854084		
Exact								-0.50000

^aCalculated in this work.

$$\chi_{1s}^{\text{STO}} = \left(\frac{\zeta^3}{\pi}\right)^{1/2} \exp(-\zeta r) \quad \text{and}$$

$$\chi_{1s}^{\text{GTO}} = \left(\frac{2\alpha}{\pi}\right)^{3/4} \exp(-\alpha r^2) \quad (1)$$

The χ_{1s}^{GTO} is a function familiar to first year students who have learned about it in statistics as the *normal distribution*. The user can input any positive value for the GTO exponent α , and assess the quality of the fitting to the $\zeta = 1$ STO, graphically and by calculation of the fitting error ϵ_{1s} as defined by Pople et al.:⁸

$$\epsilon_{1s} = \int (\chi_{1s}^{\text{GTO}} - \chi_{1s}^{\text{STO}})^2 dr \quad \text{or}$$

$$\epsilon_{1s} = \int_0^\infty (\chi_{1s}^{\text{GTO}} - \chi_{1s}^{\text{STO}})^2 4\pi r^2 dr \quad (2)$$

The fitting error 2 is estimated by means of a simple but effective integration technique, which is the Newton–Cotes formula of first order or the trapezoidal rule.⁹ We have considered the interval of integration $0.0 < r < 11.0$ (in au), subdivided into 110 segments of equal width 0.1, which are values that ensure enough accuracy to compare the performances of different GTOs.

Which is then the best value for α ?

By trying different values for α , one can realize how the quality of the overall fitting is affected. As a relatively simple exercise, students are invited to get the optimum α , i.e., the one that minimizes integral 2, by applying the Solver add-in optimization tool.¹⁰ One has to select the minimization mode of Solver, and set the target cell of ϵ_{1s} by changing the yellow cell of α_i . The optimum value for the GTO exponent, obtained with a convergence criterion of 0.000001, is $\alpha = 0.271062$, corresponding to a fitting error $\epsilon_{1s} = 0.0429957$ and energy $E = -0.4242E_{\text{H}}$.

As evident from the plot, regions farther from and closer to the nucleus have different fitting performances and, as we know, they contribute differently to the electron energy. Consequently, the best value of the exponent in terms of electron energy is not given exactly by minimizing eq 2 but rather by using the Rayleigh ratio upon the Variation theory:²

$$E_{1s} = \frac{\int (\chi_{1s}^{\text{GTO}})^* \hat{H} \chi_{1s}^{\text{GTO}} dr}{\int (\chi_{1s}^{\text{GTO}})^* \chi_{1s}^{\text{GTO}} dr} \quad (3)$$

The denominator of eq 3 is equal to unity as the GTO expression 1 is already normalized. In the numerator, the Hamiltonian for this radial symmetry problem is defined, in atomic units, as

$$\hat{H} = -\frac{1}{2}\nabla^2 - \frac{1}{r} \quad \text{with the Laplacian given by}$$

$$\nabla^2 = \frac{1}{r} \frac{\partial^2}{\partial r^2} (r) \quad (4)$$

Substituting GTO form 1 and the above Hamiltonian into expression 3, and defining the space in spherical coordinates, we get the expression:

$$E_\alpha \left(\frac{8\alpha^3}{\pi^3}\right)^{1/2} \int_0^\infty \left\{ e^{-\alpha r^2} \left[-\frac{1}{2r} \frac{\partial^2}{\partial r^2} (r e^{-\alpha r^2}) - \frac{e^{-\alpha r^2}}{r} \right] \right\}$$

$$r^2 dr \int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\phi \quad (5)$$

The radial symmetry of the system makes the integration in θ and ϕ to be equal to 4π . Using the values of the following definite integrals,¹¹

$$\int_0^\infty r^{2n} e^{-\alpha r^2} dr = \frac{1 \cdot 3 \cdot 5 \cdots (2n-1)}{2^{n+1} \alpha^n} \left(\frac{\pi}{\alpha}\right)^{1/2}$$

$$\int_0^\infty r^{2n+1} e^{-\alpha r^2} dr = \frac{n!}{2\alpha^{n+1}} \quad (6)$$

the expression for the energy as a function of α is obtained:

$$E_\alpha = \frac{3}{2}\alpha - 2\left(\frac{2\alpha}{\pi}\right)^{1/2} \quad (7)$$

The spreadsheet application includes the plot of expression 7, which shows the existence of a single minimum at $\alpha = 8/(9\pi)$. In fact, this optimum value can be verified by minimization of 7. This value corresponds to an electronic energy of $-0.4244E_{\text{H}}$, far from the exact value of $-0.5E_{\text{H}}$ for the 1s hydrogen atom. This is, thus, the best we can achieve in terms of energy (ca. 15% error) with a GTO wave function of the form 1. It is interesting to verify that, in reality, the value of α corresponding to the minimum energy does not imply the best fit from eq 2, $\epsilon_{1s} = 0.0434376$ as compared with $\epsilon_{1s} = 0.0429957$ obtained previously with $\alpha = 0.271062$.

Product of GTOs or STOs

The spreadsheet application *product_2_GTO* displays the graphical result of the product of two Gaussian functions. It allows the user to choose the center and the exponent of each GTO, and confirm graphically that the product results always in a new GTO function (see the mathematical demonstration in Supporting Information). One can also verify that the greater the distance between the centers of the GTOs, the smaller the product. Those general characteristics can be extrapolated to more than two functions; the present application offers the possibility to test the product of three GTOs (*product_3_GTO*).

For comparison, it is also possible to work with STOs in separate Excel spreadsheets (*product_2_STO* and *product_3_STO*) and observe that the product never results in another STO unless the original functions are all centered at the same point.

Optimizing STO-KG

Defining the contracted function,

$$\chi_{\mu}^{\text{STO}} = \sum_i^K c_i \chi_{1s}^{\text{GTO}}(\alpha_i) \quad (8)$$

is to find the best values for the contraction coefficients c_i and GTO exponents α_i , according to a certain criterion. The first one used by Pople et al.⁸ was to minimize a least-squares fitting error of type 2. Later, new sets of parameters were defined by minimizing the electronic energy of the atom ground state.¹² Table 1 is adapted from those pioneering works and concerns the values for the hydrogen atom 1s orbital.

The spreadsheet applications STO-KG show the result of contracted functions with $K = 2, 3$, and 5 , given the values of c_i and α_i as input. It is interesting to note that the higher the number of primitives used, the more accurate the contracted function will be, i.e., the smaller the value of the fitting error ϵ_{1s} , despite the fact that the first derivative at the nucleus remains always nil.

As shown in Table 1, this criterion does not ensure the best energy function. We have used the Excel application to calculate the fitting error obtained with the minimum energy exponents provided by Pople et al.,¹² and the results are collected in Table 1. As observed previously, the energy minimization method shows higher values for ϵ_{1s} .

As an additional exercise, the Solver can be used to find the contracted function that minimizes the fitting error ϵ_{1s} . The simplest case of $K = 2$ is less affected by convergence instabilities, and consequently, the corresponding spreadsheet is the only one prepared to that exercise. The user has to set the target cell of ϵ_{1s} by changing the values of the colored cells of c_i and α_i , under the normalization condition, i.e., forcing the *Norm. condition* cell to keep the value 1. As usual in most iterative processes, the convergence is not guaranteed, and it depends on the initial values. For instance, starting with the values $c_1 = 0.1$, $c_2 = 0.1$, $\alpha_1 = 1.3$, and $\alpha_2 = 1.0$, the Pople results in Table 1 are well reproduced.⁸

The present spreadsheet application can be used also to find the best linear combination of any given pair of fixed GTOs, on the basis of minimization of ϵ_{1s} . As an illustration, one can use the two exponents of STO-2G contracted function suggested by Pople et al.,¹² namely, $\alpha_1 = 1.332480$ and $\alpha_2 = 0.2015287$, and apply the Solver tool. In this exercise, only the cells corresponding to the linear coefficients are allowed to vary,

under the normalization condition. The process converges rapidly to $c_1 = 0.289616$ and $c_2 = 0.810237$, thus slightly different from Pople's values, but with a smaller associated error $\epsilon_{1s} = 6.40 \times 10^{-3}$.

Calculating the Energy Optimized Coefficients of STO-2G

The spreadsheet application *2-fold-secular determinant* includes an exercise to find the minimum energy wave function of the H atom ground state for the simplest case of a trial function (8) with $K = 2$.

The Rayleigh ratio (3) that results from the application of the variation method may be simplified to

$$E = \frac{c_1^2 H_{11} + c_2^2 H_{22} + 2c_1 c_2 H_{12}}{c_1^2 + c_2^2 + 2c_1 c_2 S_{12}} \quad (9)$$

Taking into account the symmetry of this particular system, we have

$$H_{ij} = H_{ji} = \int \chi_{1s}^{\text{GTO}}(\alpha_i) \hat{H} \chi_{1s}^{\text{GTO}}(\alpha_j) d\tau \quad (10)$$

$$H_{ii} = \int \chi_{1s}^{\text{GTO}}(\alpha_i) \hat{H} \chi_{1s}^{\text{GTO}}(\alpha_i) d\tau \quad (11)$$

$$S_{ij} = S_{ji} = \int \chi_{1s}^{\text{GTO}}(\alpha_i) \chi_{1s}^{\text{GTO}}(\alpha_j) d\tau \quad (12)$$

All these elements can be easily evaluated using Hamiltonian (4) and definite integrals (6). The overlap integrals S_{ij} are equal to unity, $S_{11} = S_{22} = 1$, as we are using normalized GTOs (1). All the canonical forms of the elements H_{11} , H_{22} , H_{12} , and S_{12} , which depend on the input values of α_1 and α_2 , are accessible by the user in the respective spreadsheet cells.

Minimizing the energy expression 9 with respect to the coefficients c_1 and c_2 , and keeping the GTO exponents α_1 and α_2 fixed, leads to the secular equations whose corresponding determinant should vanish in order to get the nontrivial solutions. That condition results in a quadratic equation whose lowest root is the best energy one can obtain for the atom ground state, using a linear combination of two GTO with predefined and fixed exponents α_1 and α_2 .

$$aE^2 + bE + c = 0$$

$$\text{where } a = 1 - S_{12}; \quad b = 2H_{12}S_{12} - H_{11} - H_{22};$$

$$c = H_{11}H_{22} - H_{12}^2 \quad (13)$$

The three coefficients of the equation, a , b , and c , are calculated in separated cells, and the two roots are shown, as well. The spreadsheet identifies the lowest root, with which the secular equations are defined and, consequently, the c_1/c_2 ratio. Using the equation of the normalization condition the values of coefficients c_1 and c_2 are finally obtained.

As a first exercise with this spreadsheet, one may use Table 1 to enter the exponents found by Pople et al.¹² ($\alpha_1 = 1.332480$ and $\alpha_2 = 0.2015287$) and verify the correct values of the energy and expansion coefficients. Another interesting exercise is to enter the least-squares fit exponents suggested earlier by Pople et al.⁸ ($\alpha_1 = 0.151623$ and $\alpha_2 = 0.851819$). The coefficients found, $c_1 = 0.710925$ and $c_2 = 0.393837$, are not exactly those obtained by the authors ($c_1 = 0.678914$ and $c_2 = 0.430129$, see Table 1) due to the different minimization criteria used. The corresponding energies are $E = -0.48199E_{\text{H}}$ and $E = -0.48116E_{\text{H}}$ for the former and latter cases, respectively. The associated fitting errors, computed with the STO-2G spread-

sheet, are $\varepsilon_{1s} = 0.00409$ and $\varepsilon_{1s} = 0.00316$, respectively, which reveals once again that a least-squares fit wave function does not ensure the minimum in the electronic energy.

The Solver may be used also in this spreadsheet to find the values of exponents α_1 and α_2 , and corresponding coefficients c_1 and c_2 , that minimize the energy of the trial function. The user has to set the target cell of E , by changing the values of the two colored cells of α_i . The method converges rapidly to Pople's exponents in Table 1¹² if, for instance, the previous values of Pople et al.⁸ ($\alpha_1 = 0.151623$ and $\alpha_2 = 0.8518199$) are given as input.

CONCLUSIONS

Computational programs have already been shown to be invaluable pedagogical instruments for introducing fundamental topics of computational chemistry at the undergraduate level.^{13–17} This work focuses on the differences between Slater and Gaussian basis set of atomic functions. Using nothing more than the popular Microsoft Office Excel program, the main features of GTOs are explored and compared with STOs. This interactive application allows the user to input the values for the exponents and coefficients of combination of GTOs in STO-KG minimal basis, and then to explore graphically and by calculus some mathematical features. Among the activities available in the Microsoft Office Excel application, it is important to stress the product of two or three GTOs or STOs, the fitting of a GTO or STO-KG contracted function to a pure STO, or the calculation of the energy-minimized coefficients of a linear combination of two GTOs. Using the Solver add-in tool, it is shown that different optimized contracted functions are obtained with the STO fitting error and the electronic energy minimization criteria. In this work, the student has the opportunity to unveil some secrets of basis sets in computational chemistry by means of a simple and familiar program, and that training could be a valuable contribution to a more rational use of advanced quantum packages.

ASSOCIATED CONTENT

Supporting Information

A Microsoft Excel application, with nine different interactive exercises, is provided as an indispensable tool to this article. The relevant topics of quantum theory, which support the exercises developed in this work, are summarized as auxiliary material. This material is available via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

*E-mail: almagalh@fc.up.pt

Notes

The authors declare no competing financial interest.

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