

### 33 Application of Gaussian Wave Functions for 1s States in Helium and Helium Like Atoms

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#### Abstract

Properties of Gaussian like orbital wave function and Slater like orbital wave function for Helium atom and Helium like ions was studied. This included energy, the radial distribution function, the shape of the wave function near the nucleus and the orbital exponent. For Gaussian the values of the orbital exponent and the constants varied using linear combination of four Gaussian functions to approximate the radial component of atomic orbital, the obtained result is better than universal result.

#### Theory

Slater-type orbital (STOs) in normalization form can be written as ; [1]

$$\frac{(2\varepsilon/a_0)^{n+\frac{1}{2}}}{[(2n)!]^{\frac{1}{2}}} r^{n-1} e^{-\varepsilon r/a_0} \dots\dots\dots(1)$$

where

$\frac{(2\varepsilon/a_0)^{n+\frac{1}{2}}}{[(2n)!]^{\frac{1}{2}}}$  is the normalization constant,  $\varepsilon$  is the orbital exponent and  $n$  is the principle quantum number.

The normalized radial factor in the hydrogen like wave function for 1s can be defined as [1];

$$R_{1s} = \frac{1}{\pi^{\frac{1}{2}}} \left(\frac{z}{a}\right)^{\frac{3}{2}} e^{-\frac{zr}{a}} \dots\dots\dots(2)$$

where  $z$  is the atomic number.

In atomic unit, the radial function for hydrogen atom takes the following form:

$$R_{1s} = \frac{1}{\pi^{\frac{1}{2}}} e^{-r} \dots\dots\dots(3)$$

And the function for Helium can be written as;

$$R_{1s} = \left(\frac{\beta}{\pi}\right)^{\frac{1}{2}} e^{-\beta r} \dots\dots\dots(4)$$

where  $\beta$  is the effective nuclear charge.

Another approach for describing atomic orbital is by using Gaussian type basis functions, which have the form

$$g_{ijk}(r) = N x^i y^j z^k e^{-\alpha r^2} \dots\dots\dots(5)$$

where,  $x$ ,  $y$ , and  $z$  are the position coordinates measured from the nucleus of an atom,  $i$ ,  $j$ , and  $k$  are taking positive integers, and  $\alpha$  is an orbital exponent. An S-type function (zero order Gaussian) is generated by setting  $i = j = k = 0$ ; a P-type function (first order Gaussian) is generated by setting one of the integers  $i$ ,  $j$  or  $k$  to 1 and the remaining two to 0, [2].

Gaussian functions lead to integrals that are easily evaluated with the exception of so-called semi-empirical models, which do not actually entail evaluation of large numbers of difficult integrals. All practical quantum chemical models now used Gaussian functions [2].

Given the different radial dependence of STOs and Gaussian functions, it is not obvious at first glance that Gaussian function is an appropriate choice for STOs.

In practice, instead of taking individual Gaussian functions as a member of the basis set, a normalized linear combination of Gaussian functions with fixed coefficient is optimized either by seeking minimum atom energies or by comparing calculated and experimental results for "representative" molecules. These linear combinations are called constructed functions, as the following one [2];

$$g_{3N}(r) = c_1 \left(\frac{2\alpha_1}{\pi}\right)^{\frac{3}{4}} e^{-\alpha_1 r^2} + c_2 \left(\frac{2\alpha_2}{\pi}\right)^{\frac{3}{4}} e^{-\alpha_2 r^2} + c_3 \left(\frac{2\alpha_3}{\pi}\right)^{\frac{3}{4}} e^{-\alpha_3 r^2} \dots\dots\dots(6)$$

In 1950 Boys [3] proposed the use of Gaussian type functions instead of STOs to approximate the radial component of atomic orbital. Such functions had been used independently by McWeeny [4, 5] who later [6] obtained the Gaussian approximation to

Slater orbital of 1s, 2s, and 2p types. However the Gaussian approach was applied to calculation of atomic and molecular electronic structures and properties. After 1973 with the appearance of the computer program [5] the Gaussian methodology was established as the standard approach for the future [7].

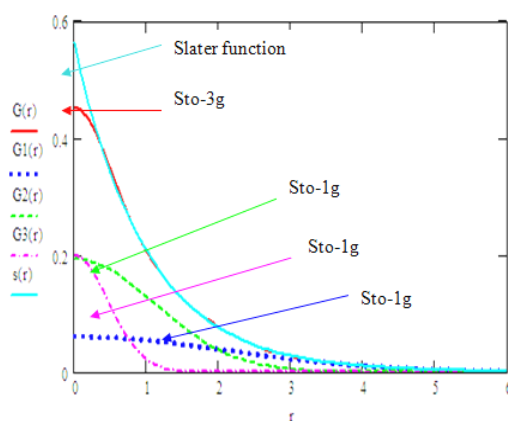
All integrals that are required to solve the Schrödinger equation, using a Gaussian basis, can be reduced to the standard form. Much effort has been devoted over the intervening years [8-10] to the design of efficient computational procedures and much faster integration routines have been developed by P.W.Gill [11]. The spread sheet was used for more than one Gaussian functions to the model Slater functions accurately in 1999 [7].

Table (1) and Figs.(1 and 2) show respectively the fitting for linear combination of three and four Gaussian functions proposed by Hehre, Stewart, and Pople with Slater functions for the hydrogen 1s atomic orbital [12]. We can see that although the region near the nucleus is not fit well, in the bonding region beyond 0.5  $a_0$ , the trends of fitting is very good and the fitting near the nucleus can be improved by using more Gaussian functions [2].

**Table (1)**

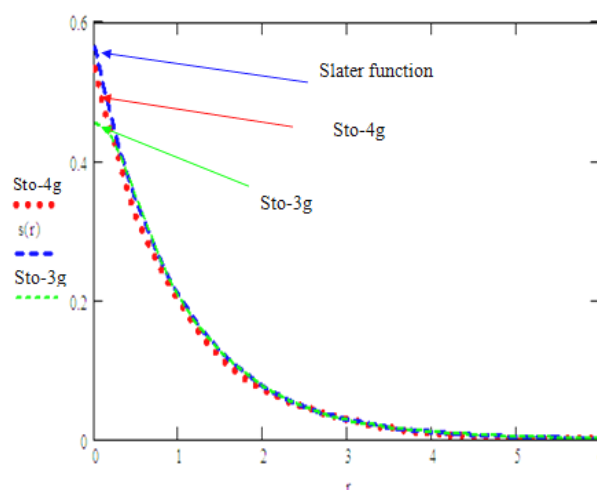
**The Gaussian sets proposed by Hehre, Stewart, and Pople for the representation of the Slater functions for the Hydrogen 1s atomic orbital [7].**

$\Phi$	$1s\alpha$	$c$
<b>Sto-3g</b>	0.109818	0.444635
	0.405771	0.535328
	2.22766	0.154329
<b>Sto-4g</b>	0.080187	0.291626
	0.265204	0.532846
	0.954620	0.260141



**Fig. (1).**

Fig.(1) The linear combination of three Gaussian functions proposed by Hehre, Stewart, and Pople and Slater function for the hydrogen 1s atomic orbital where Sto-3g mean linear combination of three Gaussian functions respectively.



**Fig.(2).**

Fig.(2) The linear combination of four Gaussian functions proposed by Hehre, Stewart, and Pople with Slater function for the hydrogen 1s atomic orbital where Sto-3g, Sto-4g mean linear combination of three Gaussian, four Gaussian respectively.

### Calculations

The energy for the Gaussian wave function and the Slater type orbital wave function was calculated for Helium sequence using variational calculation which requires the evaluation of the following integrals:[1]

$$E = \frac{\int_0^\infty \psi H \psi d\tau}{\int_0^\infty \psi \psi d\tau} \dots\dots\dots(7)$$

Since  $\psi$  is normalized then equation (7) becomes

$$E = \int_0^\infty \psi H \psi d\tau \dots\dots\dots(8)$$

The Hamiltonian operator H for 2-particle system can be defined as [1]

$$H = (-\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}) \dots\dots\dots(9)$$

The calculated energy for Gaussian wave function may be expressed as [1].

$$E(\beta) = 3\beta - 8\frac{(2)^{\frac{1}{2}}}{\pi}(\beta\pi)^{\frac{1}{2}} + \frac{2}{\pi}(\beta\pi)^{\frac{1}{2}} \dots\dots\dots(10)$$

For Slater type orbital wave function [1].

$$E(\beta) = \beta^2 - 4\beta + \frac{5}{8}\beta \dots\dots\dots(11)$$

where the first term in eq.(11) represents the kinetic energy for the two electrons, the second term is the coulombic potential energy for the two electron and the third term is the coulombic repulsion between the two electrons.

The energy and D(r) for Helium sequence are shown in Tables (2 and 3) using Gaussian and Slater wave function respectively.

Figs. (3 and 4) show the wave function and D(r)) via r for Hartree-Fock wave function and Slater type orbital wave function respectively.

Figs. (5 and 6) show the wave function and D(r)) via r for Hartree-Fock wave function and Gaussian wave function respectively.

The optimized trial wave function (Gaussian and Slater) are compared with the Hartree-Fock wave function by the following radial distribution functions relation [3].

$$\begin{aligned} \phi(r) = & 0.75738e^{(-1.43r)} + 0.43658e^{(-2.4415r)} \\ & + 0.17295e^{(-4.0996r)} - 0.0273e^{(-6.4843r)} \\ & + 0.06675e^{(-7.978)} \dots\dots\dots(12) \end{aligned}$$

Then by using four Gaussian functions which have the form:

$$\begin{aligned} g_{4N}(r) = & c_1\left(\frac{2\alpha_1}{\pi}\right)^{\frac{3}{4}}e^{-\alpha_1r^2} + c_2\left(\frac{2\alpha_2}{\pi}\right)^{\frac{3}{4}}e^{-\alpha_2r^2} \\ & + c_3\left(\frac{2\alpha_3}{\pi}\right)^{\frac{3}{4}}e^{-\alpha_3r^2} + c_4\left(\frac{2\alpha_4}{\pi}\right)^{\frac{3}{4}}e^{-\alpha_4r^2} \dots\dots\dots(13) \end{aligned}$$

Fig. (7, 8) and Table (4) show the four Gaussian functions proposed in this work to represent the Slater functions for the hydrogen 1s atomic orbital.

**The units in all tables and graphs are the atomic units**

**Table (2)**  
*The calculated values of a1s and c.*

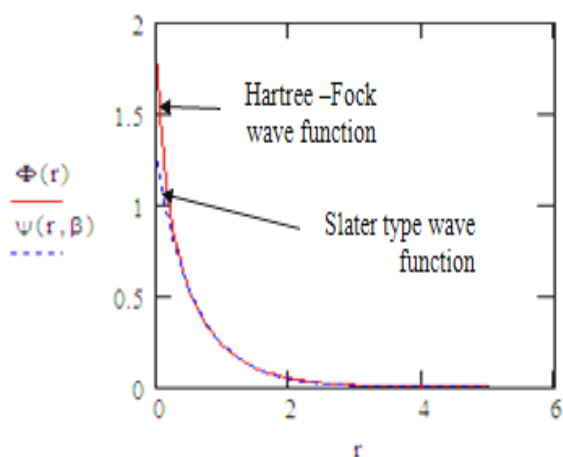
$\Phi$	<i>a1s</i>	<i>c</i>
<b>Sto-4g</b>	4583.9408965	0.0001066
	0.1706123	0.687439
	8.48995604	0.038478
	0.9210104	0.335034

**Table (3)**  
*The energy and D(r) for Helium sequence using Gaussian wave function.*

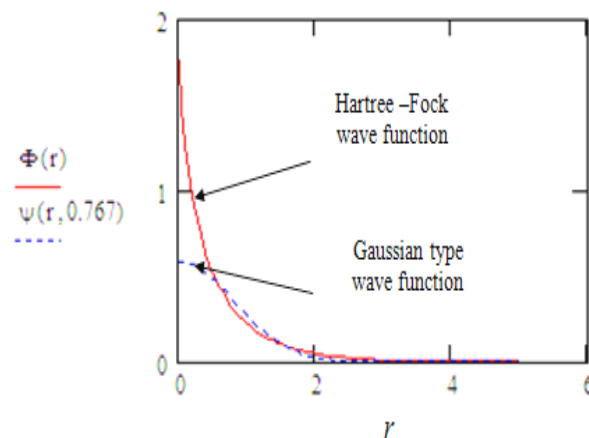
<i>z</i>	$\beta$	<i>E</i> ( $\beta$ )	<i>E rror</i>	<i>D</i> ( <i>r</i> )	<i>r</i>
2	0.767	-2.301	20%	0.081813	0.8
3	1.982	-5.945	18.3%	0.13153	0.5
4	3.762	-11.286	17.3%	0.18063	0.35
5	6.109	-18.326	16.8%	0.22986	0.3
6	9.021	-27.063	16.485%	0.27852	0.25
7	12.499	-37.497	16.27%	0.33032	0.2
8	16.543	-49.629	16.11%	0.35906	0.19
9	21.153	-63.459	16.005%	0.429	0.17

**Table (4)**  
**The energy and  $D(r)$  for Helium sequence using Slater type orbital.**

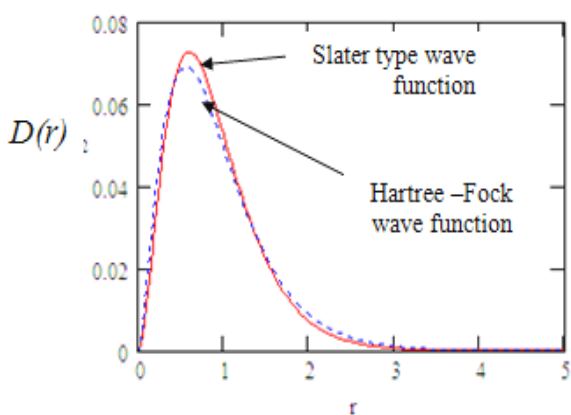
$z$	$\beta$	$E(\beta)$	$E\ error$	$D(r)$	$r$
2	1.8675	-2.8476	1.93%	0.08286	0.56
3	2.8675	-7.22266	0.77%	0.12353	0.35
4	3.8675	-13.59766	0.44%	0.1666	0.26
5	4.8675	-21.97266	0.255%	0.20958	0.21
6	5.8675	-32.34766	0.176%	0.252	0.18
7	6.8675	-44.72266	0.134%	0.29558	0.15
8	7.8675	-59.09766	0.108%	0.33875	0.13



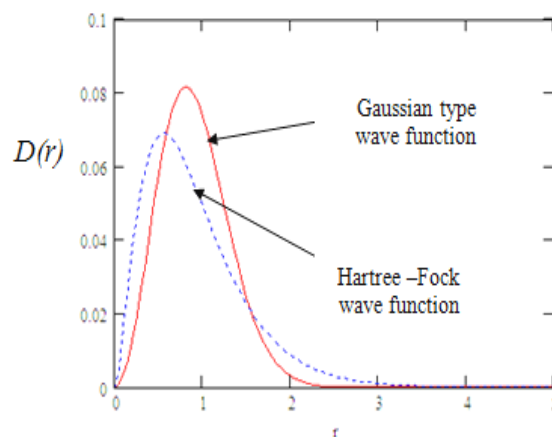
**Fig.(3) The Hartree-Fock wave function and Slater type orbital wave function via  $r$  for He atom.**



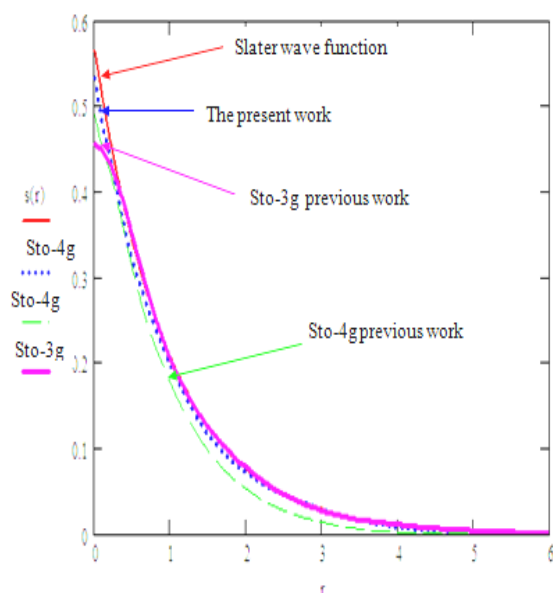
**Fig.(5) Hartree-Fock wave function and Gaussian wave function via  $r$  for He atom.**



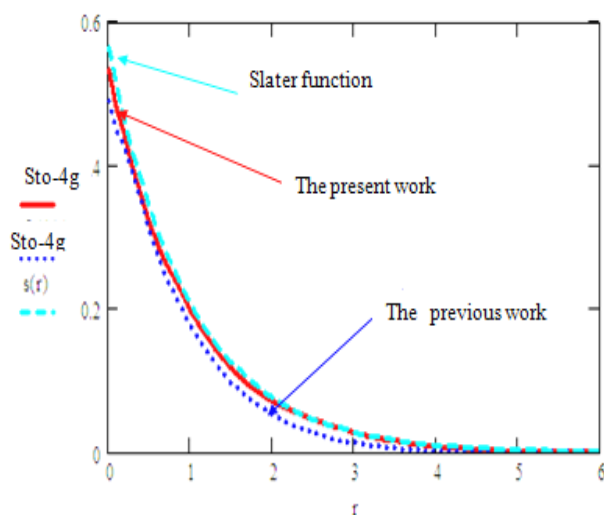
**Fig.(4)  $D(r)$  via  $r$  for Hartree-Fock wave function and Slater type orbital wave function for He atom.**



**Fig.(6)  $D(r)$  via  $r$  for Hartree-Fock wave function and Gaussian wave function for He atom.**



**Fig.(7) The linear combination of three and four Gaussian functions proposed by Hehre, Stewart, and Pople with Slater function for the hydrogen 1s atomic orbital compared with the present work.**



**Fig.(8) The linear combination of four Gaussian functions proposed by Hehre, Stewart, and Pople with Slater function for the hydrogen 1s atomic orbital compared with the present work.**

### Discussion

1. The energy of the Helium sequence was calculated using variational method for two types of wave functions, Slater type orbital and Gaussian type orbital. The results are shown in Tables (3) and (4). From these results one can conclude that STO<sub>s</sub> gives energies nearer to the experimental than Gaussian functions.

- The energy error, listed in Tables (3) and (4), decreases as  $Z$  increases because the nucleon–electron attraction predominates the electron–electron repulsion.
- Figs. (5) and (6) show that a Gaussian function does not have the desired cusp at the nucleus and hence gives a poor representation of an atomic orbital for small values of  $r$ .
- Because the Gaussian function leads to integrals that are easily evaluated, all practical quantum chemical models now make use of Gaussian functions. The STO<sub>s</sub> approximated by a linear combination of Gaussian functions have different  $\alpha$  values whereas that represented by a single Gaussian function has one  $\alpha$  value, this is why the Gaussian function is applicable for Quantum Chemistry.
- The proposed method gives a better fitting, as shown in Figs. (7) and (8), compared with previous methods shown in Figs. (1) and (2). One can see that although the region near the nucleus is not fit well, but the bonding region (beyond  $0.5 a_0$ ) is very well fitted. However, the fitting near the nucleus can be improved by using more Gaussian functions.

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#### الخلاصة

تم دراسة الخصائص الموجية لكاسين وسليتر لذرة الهليوم وشبيهة ذرة الهليوم، ومن هذه الخصائص دالة التوزيع القطرية والطاقة وشكل الدوال قريبة من النواة وكذلك قيم معامل الاوربتال. كما تم صياغة دوال كاسين ذات الجمع الخطي لاربعة حدود لكي تكون مقاربة لدالة سليتر في المناطق القريبة من النواة بعد تغيير قيم معاملات الاوربتال والثوابت لكي يطابق الخط البياني لدالة كاسين الخط البياني لدالة سليتر وكانت النتائج افضل من النتائج المنشورة عالميا.