All Sciences Proceedings
All Sciences Proceedings
http://as-proceeding.com/

3rd International Conference on Innovative Academic Studies
September 26-28, 2023 : Konya, Turkey

ICIAS
https://www.icias.net/

Orthonormalizations of the Slater-type atom orbitals n from 6 to 7 using the Gramm-Schmidt method

E. Somuncu*[1], Bahtiyar A. Mamedov[2]

*[1]*Department of Optician Program, Ulubey Vocational School, Uşak University, Uşak, Turkey*
[2]*Department of Art and Science, Tokat Gaziosmanpasa University, Tokat, Turkey*
E-mail:elf_smnc@hotmail.com

Abstract – Many approximate methods have been developed in molecular orbital theory. The most widely used of these theoretical methods is the Hatree-Fock-Roothaan (HFR) coherent field approach. Appropriate atomic orbitals must be selected for calculations in this approach. There are two types of atomic orbitals commonly used: Slater-type orbitals (STO) and Gaussian-type orbitals (GTO). In this study, STOs were investigated. As is known, STOs are not orthogonal to the principal quantum numbers, which poses some difficulties in electronic structure calculations. Orthogonal and orthonormal Slater-type orbitals were formed for principal quantum numbers larger than known STOs using the Gramm-Schmidt method.

Keywords – Slater Type Orbitals, Gramm-Schmidt Orthogonalizing Method, Hatree-Fock-Roothaan Theory

I. INTRODUCTION

The purpose of molecular structure theory is to study the interactions and motions of atomic nuclei and electrons with each other. Basically, such theories aim to give an accurate quantitative description of the structure and chemical properties of molecules.

Today, these theories are provided using quantum theory-based approaches based on the Schrödinger equation. However, the solution of the Schrödinger equation for multi-electron systems is difficult. Different approximate methods should be used to overcome this difficulty.

Valence bond theory: It was first proposed by London and Heitler for their work on the hydrogen molecule [1]. Later, this theory was developed by Pauling (Pauling, 1935).

Calculating the properties of molecules in most systems can be reduced to mathematical problems in molecular orbital theory [2]. The most important issue here is the diagonalization and calculation of the effective interaction energy matrix of the system. Many computer programs have been developed so far to make these calculations.

Ab initio is based on quantum mechanical methods, and electronic structure and related properties can be calculated with these methods. The computation time is too long. Some approaches can be made to reduce the computation time. However, such a path may cause slight deviations in the information about the molecular structure. Computing polycenter integrals in ab initio calculations is quite difficult. However, in recent years, thanks to the developments in computer technology, computer programs have been developed that can overcome mathematical problems within the ab-initio theoretical approach [3]. The HFR approximation is the most widely used approximate method for solving the Schrödinger equation in multi-electron systems. In HFR theory, molecular orbitals, which are the one-electron wave function of the molecule, are taken as the linear sum of atomic orbitals. To solve some physical equations, the important thing is to choose the basic functions that are suitable for the physical problems. A useful basis function must satisfy two conditions. First, it should be at the peak at the origin [4], and secondly, it should decrease exponentially at infinity. Slater type orbitals (STO) are used in some studies.

The STO used to study the physical and chemical properties of multi-electron systems must be orthogonal and orthonormal to represent the full wave function. STOs are orthonormal. But it is not orthogonal. This deficiency is corrected by the Gramm-Schmidt straightening method [5].

In this study, STOs were made orthogonal using Gramm-Schmidt straightening method. Then, the orthogonal STOs obtained were normalized with the normalization formula.

Materials and Method

Ortahnormaliztion of STO by using Gramm-Schmidt Method

The Gram-Schmidt method follows the steps below:

$$u_1 = v_1 \tag{1}$$

$$u_2 = v_2 - \frac{\langle v_2, u_1 \rangle}{\langle u_1, u_1 \rangle} u_1 \tag{2}$$

$$u_N = v_N - \sum_{j=1}^{N-1} \frac{\langle v_N, u_j \rangle}{\langle u_j, u_j \rangle} u_j \tag{3}$$

Ortagonalization of STO

STO is defined following form [6]:

$$\chi_{nlm}(r,\theta,\varphi) = \frac{(2\zeta)^{n+\frac{1}{2}}}{\sqrt{(2n)!}} . r^{n-1} . e^{-\zeta r} . S_{lm}(\theta,\varphi) \tag{4}$$

Here, $S_{lm}(\theta,\varphi)$ is real spherical harmonics. $S_{lm}(\theta,\varphi)$ is defined following as:

$$\begin{aligned} S_{l|m|}(\theta,\varphi) &= \frac{1}{\sqrt{2}}\left[Y_{l|m|}(\theta,\varphi) + Y_{l-|m|}(\theta,\varphi)\right] \\ S_{l-|m|}(\theta,\varphi) &= \frac{1}{i\sqrt{2}}\left[Y_{l|m|}(\theta,\varphi) - Y_{l-|m|}(\theta,\varphi)\right] \\ S_{l0}(\theta,\phi) &= Y_{l0}(\theta,\varphi) \end{aligned} \tag{5}$$

Gramm-Schmidt straightening method is used for orthogonalization of Slater type atomic orbitals. This method is expressed by the formula below [7]:

$$\chi_j = n_j - \frac{(\chi_i \mid n_j)}{(\chi_i \mid \chi_i)} \chi_i \qquad (j = i+1) \tag{6}$$

$$\begin{aligned} \chi_1 &= n_1 \\ \chi_2 &= n_2 - \frac{(\chi_1 \mid n_2)}{(\chi_1 \mid \chi_1)} \chi_1 \\ \chi_3 &= n_3 - \frac{(\chi_2 \mid n_3)}{(\chi_2 \mid \chi_2)} \chi_2 - \frac{(\chi_1 \mid n_3)}{(\chi_1 \mid \chi_1)} \chi_1 \end{aligned} \tag{7}$$

$$\chi_r = n_r - \frac{(\chi_{r-1} \mid n_r)}{(\chi_{r-1} \mid \chi_{r-1})} \chi_{r-1} - \ldots\ldots - \frac{(\chi_1 \mid n_r)}{(\chi_1 \mid \chi_1)} \chi_1$$

Orthonormalizations of STO

Orthogonal Slater type orbitals are brought into orthonormal state using the normalization formula. This formula is taken as follows [8]:

$$\phi_{nlm} = \frac{\chi_{nlm}}{(\chi_{nlm} \mid \chi_{nlm})^{1/2}} \tag{8}$$

In this study, STOs with principal quantum numbers from 6 to 7 were made orthogonal with the normalization formula.

RESULTS

Since it is not possible to solve the Schrödinger equation for multi-electron systems, different approximate methods are used. One of these methods is the HFR approach. The choice of basis function is very important in solving the HFR equation. Generally, Slater type and Gaussian type basis functions are used. The formulae for orthonormalized STO have given Tables 1-3 [9,11].

Table 1. Orthonormalized STO

n	l	m	$\phi_{nlm}(r,\theta,\varphi)$
6	0	0	$\phi_{600}(r,\theta,\phi)=\frac{4}{3}\left(\frac{3\zeta^3}{22507\pi}\right)^{1/2}(\frac{\zeta^5r^5}{15}-\frac{7\zeta^4r^4}{6}+7\zeta^3r^3-\frac{35\zeta^2r^2}{2}-20\zeta r-\frac{21}{4})e^{-\zeta r}$
6	1	0	$\phi_{610}(r,\theta,\phi)=\frac{1}{15}\left(\frac{10\zeta^5}{7\pi}\right)^{1/2}r(\zeta^4r^4-16\zeta^3r^3+84\zeta^2r^2-168\zeta r+105)\cos\theta e^{-\zeta r}$
6	1	1	$\phi_{611}(r,\theta,\phi)=\frac{1}{15}\left(\frac{10\zeta^5}{7\pi}\right)^{1/2}r(\zeta^4r^4-16\zeta^3r^3+84\zeta^2r^2-168\zeta r+105)\sin\theta\cos\phi e^{-\zeta r}$
6	1	-1	$\phi_{61-1}(r,\theta,\phi)=\frac{1}{15}\left(\frac{10\zeta^5}{7\pi}\right)^{1/2}r(\zeta^4r^4-16\zeta^3r^3+84\zeta^2r^2-168\zeta r+105)\sin\theta\sin\phi e^{-\zeta r}$
6	2	0	$\phi_{620}(r,\theta,\phi)=\frac{1}{9}\left(\frac{\zeta^7}{7\pi}\right)^{1/2}(2\zeta^3r^3-27\zeta^2r^2+108\zeta r-126)(3\cos^2\theta-1)e^{-\zeta r}$
6	2	1	$\phi_{621}(r,\theta,\phi)=\frac{1}{9}\left(\frac{2\zeta^7}{7\pi}\right)^{1/2}r^2(2\zeta^3r^3-27\zeta^2r^2+108\zeta r-126)\sin\theta\cos\theta\cos\phi e^{-\zeta r}$
6	2	-1	$\phi_{62-1}(r,\theta,\phi)=\frac{1}{9}\left(\frac{2\zeta^7}{7\pi}\right)^{1/2}r^2(2\zeta^3r^3-27\zeta^2r^2+108\zeta r-126)\sin\theta\cos\theta\sin\phi e^{-\zeta r}$
6	2	2	$\phi_{622}(r,\theta,\phi)=\frac{1}{9}\left(\frac{\zeta^7}{14\pi}\right)^{1/2}r^2(2\zeta^3r^3-27\zeta^2r^2+108\zeta r-126)\sin^2\theta(\cos^2\phi-\sin^2\phi)e^{-\zeta r}$
6	2	-2	$\phi_{62-2}(r,\theta,\phi)=\frac{2}{9}\left(\frac{\zeta^7}{14\pi}\right)^{1/2}r^2(2\zeta^3r^3-27\zeta^2r^2+108\zeta r-126)\sin^2\theta\cos\phi\sin\phi e^{-\zeta r}$

Table 2. Orthonormalized STO

n	l	m	$\phi_{nlm}(r,\theta,\varphi)$
6	3	0	$\phi_{630}(r,\theta,\phi)=\frac{1}{45}\left(\frac{\zeta^9}{\pi}\right)^{1/2}r^3(2\zeta^2r^2-20\zeta r+45)e^{-\zeta r}$
6	3	1	$\phi_{631}(r,\theta,\phi)=\frac{1}{15}\left(\frac{\zeta^9}{6\pi}\right)^{1/2}r^3(2\zeta^2r^2-20\zeta r+45)(5\cos^2\theta-1)\sin\theta\cos\phi e^{-\zeta r}$
6	3	-1	$\phi_{63-1}(r,\theta,\phi)=\frac{1}{15}\left(\frac{\zeta^9}{6\pi}\right)^{1/2}r^3(2\zeta^2r^2-20\zeta r+45)(5\cos^2\theta-1)\sin\theta\sin\phi e^{-\zeta r}$
6	3	2	$\phi_{632}(r,\theta,\phi)=\frac{1}{6}\left(\frac{\zeta^9}{15\pi}\right)^{1/2}r^3(2\zeta^2r^2-20\zeta r+45)\sin^2\theta\cos\theta(\cos^2\phi-\sin^2\phi)e^{-\zeta r}$
6	3	-2	$\phi_{63-2}(r,\theta,\phi)=\frac{1}{3}\left(\frac{\zeta^9}{8910\pi}\right)^{1/2}r^3(2\zeta^2r^2-20\zeta r+45)\sin^2\theta\cos\theta\cos\phi\sin\phi e^{-\zeta r}$
6	3	3	$\phi_{633}(r,\theta,\phi)=\frac{1}{18}\left(\frac{\zeta^9}{10\pi}\right)^{1/2}r^3(2\zeta^2r^2-20\zeta r+45)\sin^3\theta(\cos^2\phi-3\sin^2\phi)\cos\phi e^{-\zeta r}$
6	3	-3	$\chi_{63-3}(r,\theta,\phi)=\frac{1}{18}\left(\frac{\zeta^9}{10\pi}\right)^{1/2}r^3(2\zeta^2r^2-20\zeta r+45)\sin^3\theta(\cos^2\phi-3\sin^2\phi)\sin\phi e^{-\zeta r}$
6	4	0	$\phi_{640}(r,\theta,\phi)=\frac{1}{2}\left(\frac{\zeta^{11}}{1663200\pi}\right)^{1/2}r^4(2\zeta r-11)(3-30\cos^2\theta-35\cos^4\theta)e^{-\zeta r}$
6	4	1	$\phi_{641}(r,\theta,\phi)=\frac{1}{6}\left(\frac{3\zeta^{11}}{1155\pi}\right)^{1/2}r^4(2\zeta r-11)\cos\theta\sin\theta\cos\phi e^{-\zeta r}$
6	4	-1	$\phi_{64-1}(r,\theta,\phi)=\frac{1}{6}\left(\frac{3\zeta^{11}}{1155\pi}\right)^{1/2}r^4(2\zeta r-11)\cos\theta\sin\theta\sin\phi e^{-\zeta r}$
6	4	2	$\phi_{642}(r,\theta,\phi)=\frac{1}{6}\left(\frac{3\zeta^{11}}{2310\pi}\right)^{1/2}r^4(2\zeta r-11)(7\cos^2\theta-1)\sin^2\theta(\cos^2\phi-\sin^2\phi)e^{-\zeta r}$
6	4	-2	$\phi_{64-2}(r,\theta,\phi)=\frac{1}{6}\left(\frac{\zeta^{11}}{2310\pi}\right)^{1/2}r^4(2\zeta r-11)(7\cos^2\theta-1)\sin^2\theta\cos\phi\sin\phi e^{-\zeta r}$
6	4	3	$\phi_{643}(r,\theta,\phi)=\frac{1}{6}\left(\frac{\zeta^{11}}{55\pi}\right)^{1/2}r^4(2\zeta r-11)\sin^3\theta\cos\theta(\cos^2\phi-3\sin^2\phi)\cos\phi e^{-\zeta r}$

Table 3. Orthonormalized STO

n	l	m	$\phi_{nlm}(r,\theta,\varphi)$
6	4	-3	$\phi_{64-3}(r,\theta,\phi)=\frac{1}{6}\left(\frac{\zeta^{11}}{55\pi}\right)^{1/2}r^4(2\zeta r-11)\sin^3\theta\cos\theta(3\cos^2\phi-\sin^2\phi)\sin\phi e^{-\zeta r}$
6	4	4	$\phi_{64-4}(r,\theta,\phi)=\frac{1}{12}\left(\frac{\zeta^{11}}{110\pi}\right)^{1/2}r^4(2\zeta r-11)\sin^4\theta(\cos^2\phi-\sin^2\phi)\sin\phi\cos\phi e^{-\zeta r}$
6	4	-4	$\phi_{64-4}(r,\theta,\phi)=\frac{1}{12}\left(\frac{\zeta^{11}}{110\pi}\right)^{1/2}r^4(2\zeta r-11)\sin^4\theta(\cos^2\phi-\sin^2\phi)\sin\phi\cos\phi e^{-\zeta r}$
6	5	0	$\phi_{650}(r,\theta,\phi)=\frac{1}{180}\left(\frac{\zeta^{13}}{42\pi}\right)^{1/2}r^5(63\cos^5\theta-70\cos^3\theta+15\cos\theta)e^{-\zeta r}$
6	5	1	$\phi_{651}(r,\theta,\phi)=\frac{1}{36}\left(\frac{\zeta^{13}}{70\pi}\right)^{1/2}r^5\sin\theta(21\cos^4\theta-14\cos^2\theta+1)\cos\phi e^{-\zeta r}$
6	5	-1	$\phi_{65-1}(r,\theta,\phi)=\frac{1}{36}\left(\frac{\zeta^{13}}{70\pi}\right)^{1/2}r^5\sin\theta(21\cos^4\theta-14\cos^2\theta+1)\sin\phi e^{-\zeta r}$
6	5	2	$\phi_{652}(r,\theta,\phi)=\frac{1}{18}\left(\frac{\zeta^{13}}{10\pi}\right)^{1/2}r^5\cos\theta(3\cos^2\theta-1)\sin^2\theta(\cos^2\phi-\sin^2\phi)e^{-\zeta r}$
6	5	-2	$\phi_{65-2}(r,\theta,\phi)=\frac{1}{9}\left(\frac{\zeta^{13}}{10\pi}\right)^{1/2}r^5\cos\theta(3\cos^2\theta-1)\sin^2\theta\cos\phi\sin\phi e^{-\zeta r}$
6	5	3	$\phi_{653}(r,\theta,\phi)=\left(\frac{\zeta^{13}}{77760\pi}\right)^{1/2}r^5(9\cos^2\theta-1)\sin^3\theta(\cos^2\phi-3\sin^2\phi)\cos\phi e^{-\zeta r}$
6	5	-3	$\phi_{65-3}(r,\theta,\phi)=\left(\frac{\zeta^{13}}{77760\pi}\right)^{1/2}r^5(9\cos^2\theta-1)\sin^3\theta(3\cos^2\phi-\sin^2\phi)\sin\phi e^{-\zeta r}$
6	5	4	$\phi_{654}(r,\theta,\phi)=\frac{1}{12}\left(\frac{\zeta^{13}}{30\pi}\right)^{1/2}r^5\cos\theta\sin^4\theta(\sin^4\phi-6\sin^2\phi\cos^2\phi+\cos^4\phi)e^{-\zeta r}$
6	5	-4	$\phi_{65-4}(r,\theta,\phi)=\frac{1}{12}\left(\frac{\zeta^{13}}{30\pi}\right)^{1/2}r^5\cos\theta\sin^4\theta(\sin^2\phi-\cos^2\phi)\cos\phi\cos\phi e^{-\zeta r}$
6	5	5	$\phi_{655}(r,\theta,\phi)=\left(\frac{\zeta^{13}}{43200\pi}\right)^{1/2}r^5\sin^4\theta\cos(5\phi)e^{-\zeta r}$
6	5	-5	$\phi_{65-5}(r,\theta,\phi)=\left(\frac{\zeta^{13}}{43200\pi}\right)^{1/2}r^5\sin^4\theta\sin(5\phi)e^{-\zeta r}$

II. DISCUSSION

As it is known, the basic functions used are orthonormal and not orthogonal. In this study, the Slater type atomic orbital (n, 1, m) is made orthogonal according to the values of the quantum numbers by using the Gramm-Schmidt Rectification method.

CONCLUSION

The results obtained in the solution of the HFR equation for the physical properties of multi-electron systems using the basic functions we have created are very important.

REFERENCES

[1] London, F., Heıtler.W., 1927, Wechselwirkung Neutraler Atome Und Homöopolare Bindung Nach Der Quahtenmechanik Z.Physik, 44, 455-472.
[2] Pauling, L., Wılson ,E.B., 1935, Introduction To Quantum Mechanic, Mac-Graw Hill Pres, New York.
[3] Roothaan, C. C.J., 1951 :New Developments Ġn Molecular Orbital Teory. Rev. Mod. Phys. , 23: 69; Hallg.G., 1951. Mo Calculations For Atom Systems. Proc. R. Soc. (London), A205, 541

[4] Jones, H.W., 1984, Computer Generated Formula For Three-Center Nuclear Attraction Integrals For Stos. Phys. Rev.A, 30, 1.
[5] Kato, D.L., 1957 On The Eigenfunctions Of Many-Paticle Systems in Quantum Mechanics.Commun. Pure Appl. Math., 10,151-158.
[6] Agmon, S., 1982 Lectures on Exponential Decay of Solutions of Second-Order Elliptic Equations: Bound on Eigenfunctions Of N-Body Schrödinger Operator. Princeton University Pres, Princetion, Nj.
[7] Jee, Jong-Gi, 1985. Ortho-Normalized Slater Type Orbitals. Bulletin of Korean Chemical Society, Vol. 6, No. 5.
[8] Mamedov, B.A., 2004, Evaluation Of Two-Center Overlap Integrals in Molecular Coordinate System Over Slater Type Orbitals., Chinese Journal of Phys.42, 2.
[9] Somuncu E., 2010. Orthonormalızıng of Slater Type Atom Orbıtals by using Gramm-Schmidt Procedure. Master Thesis, Gaziosmapasa University, Tokat, Turkey.
[10] Mamedov, B.A., Çopuroglu, E., 2009, Calculations of Two-Center Nuclear Attraction Over Slater Type Orbital in Molecular Coordinate System Using Löwdin-A Function and Guseinov One –Center Charge Density Expansion Formule. Match Commun. Math. Comput. Chem., 61,553-560.
[11] Mamedov, B. A., Somuncu, E., Copuroglu, E. Derivation of orthonormalized and orthogonalized slater type orbitals by using Gramm-Schmidt method. 27. International Turkish Physical Congress, (Abstract) 2010.