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COMPUTATION OF ONE-CENTER OVERLAP, NUCLEAR ATTRACTION AND KINETIC ENERGY INTEGRALS OVER NONINTEGRAL-*n* SLATER-TYPE ORBİTALS

Y. YAKAR[1], M.Ö. SEZER[2]

[1]*Department of Physics, Faculty of Science and Arts, Sakarya University, Sakarya, TURKEY*
[2]*Department of Physics, Faculty of Science and Arts, Selçuk University, Konya, TURKEY*

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ABSTRACT

One-center nuclear attraction and kinetic energy integrals are defined in terms of overlap integrals with nonintegral-*n* Slater-type orbitals. Stirling's series used to overcome the difficulty introduced by the presence of nonintegral quantum numbers in the overlap integrals. Our results are satisfactory lower and large quantum numbers.

KEYWORDS : Slater-type orbitals, nuclear attraction and kinetic energy integrals.

1. INTRODUCTION

It is important to calculate of the multicenter integrals which are seen in *ab-initio* molecular calculations. Because of nature with multicenter, operator and basis functions are defined at the different center, calculation of the integrals even in not relativistic situation is rather difficult. In *ab-initio* calculations usually use two type basis functions. One of them is Gaussian-type basis functions, and the other is exponential-type basis functions. Gaussian-type orbitals (GTOs) are used widely in molecular calculations because two GTOs at a different center can be defined easily in terms of any GTO at a new center. The main advantage of the Gaussian functions is that multicenter molecular integrals can be evaluated easily. However, the usage of GTOs is not without problem in large scale calculations. But, GTOs do not represent the correct behavior of the wave function at the nuclei and at large distances of the nuclei. Compared to GTOs, exponential-type orbitals (ETOs), usually Slater-type orbitals (STOs), have the advantage that they can represent the two properties of the exact wave function: at the nuclear centers, the exact wave function must fulfill the cusp conditions and at large distance it should decrease exponentially[1]. We note the correct representations of the cusp is necessary for

rapid convergence of variational energy calculation. Consequently, for problems in which the long part of the wave function or its behavior in the neighborhood of the nuclei is important, it is desirable to use STOs which describe the physical situation more accurately than GTOs. However, the calculation of multicenter integrals over STOs is rather difficult and very dull. This situation is a more serious problem for larger molecules. Most of multicenter integrals seen while investigating of physical properties of atoms and molecules by Hartree-Fock method can be defined in terms of overlap integrals. Therefore, many researchers have put in a great deal of effort to develop new methods for effective calculation of the overlap integrals [2-5]. Most existing programs for overlap integrals over STOs assume that the principal quantum number n is a positive integer and cannot be used in the case of nonintegral values of n. However, it is well-known that nonintegral-n STOs provide a more flexible basis for molecular calculations than integer-n STOs [6]. Thus, it is of interest to consider the principal quantum number n as an adjustable or variational parameter as for instance the scaling parameter [7,8].

The calculation of molecular integrals with nonintegral-n STOs can be found in the older literature. Saturno and Parr [9] and Snyder [10] have employed these functions in calculations on atoms and for the methane molecule. Parr and Joy [11] have suggested the use of Slater functions of nonintegral principal quantum numbers and applied them to the hydrogen molecule. Geller [12] has also proposed some formulas for the calculation of overlap integrals over nonintegral-n STOs. Silverstone [6] also developed some formulas for two-center overlap integrals with nonintegral-n STOs by the Fourier transform convolution technique. He has expressed the overlap integral in terms of one-dimensional integrals whose integrands are the product of two Fourier transform radial functions and spherical Bessel function. However, the formulas developed by this author contain complicated differential operators and are rather difficult to program for arbitrary quantum numbers and scaling parameters. In this study, Gamma functions which depend on nonintegral-n into the analytical expression of overlap, nuclear attraction and kinetic energy integrals have been expanded with respect to Stirling series.

2. DEFINITIONS AND TYPES OF INTEGRALS

We will use complex Slater-type orbitals with possible nonintegral values of the principal quantum number n. The STOs designated by χ are given by

$$\chi_{n\ell m\zeta}(r\theta\phi) = \left[\frac{(2\zeta)^{2n+1}}{\Gamma(2n+1)}\right]^{1/2} e^{-\zeta r} Y_{\ell m}(\theta\phi), \tag{1}$$

where $n\ell m$ is the orbital quantum numbers, ζ is the scaling parameter, $\Gamma(z)$ donates the Gamma function[13] and $Y_{\ell m}(\theta\phi)$ shows the complex spherical harmonic functions. In this study, we have used the complex spherical harmonic functions in Condon-Shortly phase condition as follows

$$Y_{\ell m} = (2\pi)^{-1/2} P_{\ell|m|}(\cos\theta) e^{im\phi} \ , \tag{2}$$

where $P_{\ell|m|}(\cos\theta)$ are normalized associated Legendre functions defined as

$$P_{\ell|m|}(Cos\,\theta) = \frac{1}{2^{\ell}} \left[\frac{2\ell+1}{2} \frac{(\ell-|m|)!}{(\ell+|m|)!} \right]^{1/2} (1 - Cos^2\theta)^{|m|/2} \sum_{k=0}^{\frac{\ell-|m|}{2}+\frac{1}{4}\left[(-1)^{\ell-|m|}-1\right]} (-1)^k \frac{(2\ell-2k)!}{k!\,(\ell-k)!\,(\ell-|m|-2k)!} (Cos\,\theta)^{\ell-|m|-2k}. \tag{3}$$

With respect to postulate interested in the expectation value of quantum mechanics, if the operator $\hat{F}$ equivalents to any physical observable of atoms and molecule, the expectation value of this observable are given as follows

$$\overline{F} = \int_{\tau} \left[\chi_{n\ell m\zeta}(r\theta\phi) \right]^{*} \hat{F}\ \chi_{n'\ell'm'\zeta'}(r\theta\phi)\, d\tau \ , \tag{4}$$

where $\hat{F}$ is the operator which equivalents to the F observable.

2.1. OVERLAP INTEGRALS WITH NONINTEGRAL-*n* STOs

From expressing the expectation value given with Eq.(4), the overlap integral is defined as follows

$$S_{n\ell m\zeta}^{n'\ell'm'\zeta'} = \int_{\tau} \left[\chi_{n\ell m\zeta}(r\theta\phi) \right]^{*} \chi_{n'\ell'm'\zeta'}(r\theta\phi)\, d\tau \ . \tag{5}$$

Using Eq.(1) into Eq.(5), we can obtained explicitly the overlap integrals :

$$S_{n\ell m\zeta}^{n'\ell'm'\zeta'} = \left[\frac{(2\zeta)^{2n+1}(2\zeta')^{2n'+1}}{\Gamma(2n+1)\Gamma(2n'+1)} \right]^{1/2} \frac{\Gamma(n+n'+1)}{(\zeta+\zeta')^{(n+n'+1)}} \delta_{\ell\ell'}\delta_{mm'} . \tag{6}$$

2.2. NUCLEAR ATTRACTION INTEGRAL WITH NONINTEGRAL-*n* STOs

The nuclear attraction integral in atomic units is given by

$$V_{n\ell m\zeta}^{n'\ell'm'\zeta'} = \int_{\tau} \left[\chi_{n\ell m\zeta}(r\theta\phi) \right]^{*} \left(\frac{-Z}{r} \right) \chi_{n'\ell'm'\zeta'}(r\theta\phi)\, d\tau, \tag{7}$$

where Z denotes the nuclear charge. The nuclear attraction integral given by Eq.(7) can be expressed in terms of overlap integral as follows

$$V_{n\ell m\zeta}^{n'\ell'm'\zeta'} = -Z \left(\frac{\zeta+\zeta'}{n+n'} \right) S_{n\ell m\zeta}^{n'\ell'm'\zeta'} . \tag{8}$$

2.3. KINETIC ENERGY INTEGRAL WITH NONINTEGRAL-*n* STOs

The kinetic energy integrals in atomic units defined as

$$T_{n\ell m\zeta}^{n'\ell'm'\zeta'} = \int_{\tau}\left[\chi_{n\ell m\zeta}(r\theta\phi)\right]^{*}\left(-\frac{\nabla^2}{2}\right)\chi_{n'\ell'm'\zeta'}(r\theta\phi)\,d\tau\,, \tag{9}$$

can be expressed in terms of overlap integrals. We use

$$T_{n\ell m\zeta}^{n'\ell'm'\zeta'} = -\frac{\zeta'^2}{2}\left\{S_{n\ell m\zeta}^{n'\ell'm'\zeta'} - 2\left(\frac{2n'}{2n'-1}\right)^{1/2} S_{n\ell m\zeta}^{n'-1\ell'm'\zeta'} + \frac{4(n'+\ell')(n'-\ell'-1)}{\sqrt{2n'(2n'-1)}(2n'-2)(2n'-3)} S_{n\ell m\zeta}^{n'-2\ell'm'\zeta'}\right\} \tag{10}$$

As illustrated in Eq.(8) kinetic energy integrals can be reduced to the calculation of integrals having the form of overlap integrals defined by Eq.(5).

3. RESULTS AND CONCLUSIONS

The calculation of overlap integrals having different quantum numbers and scaling parameters in a more accurate and less time consuming manner has gained great importance in the field of atomic and especially large molecular studies. So far, many theoretical works have been performed for calculation of overlap integrals over STOs, and in these works, principal integer quantum number has been employed. However, there is too few studies taking into account of nonintegral principal quantum numbers.

In determining the various physical parameters of atoms or molecules, instead of real atomic orbitals, the ones constructed from linear combination of Slater-type atomic orbitals have been generally used. In other words, for the purpose of simulating the real atomic orbitals, the base functions consisting of many STOs having nonintegral principal quantum numbers are employed. Because there have been too many basis functions in multicenter integrals in the atomic and molecular calculations, the procedure becomes lengthy and time consuming. But, it is possible to define the real atomic orbitals by using a less number STOs including nonintegral-*n*. Moreover, it is more convenient employ these wave functions in computing of multicenter integrals. The main problem here, arises from the numerical computations of factorial functions which have nonintegral principal quantum numbers. This problem can be overcome by using the Stirling's series that converges more rapidly, instead of above mentioned functions. It is possible to use the Maclaurin expansion for the numerical evaluation of the Gamma function (see ref[13], p. 604). However, Stirling's series for large integer positive values gives much more rapid convergence. In addition, Stirling's series gives also rather well convergence for the nonintegral positive values. The calculated values of overlap, nuclear attraction and kinetic energy integrals for random chosen quantum numbers and screening constants are given in Table 1, 2 and 3 respectively in atomic units. Unfortunately, because of the unavailability of literature values of overlap integrals,

nuclear attraction and kinetic energy integrals with noninteger-n STOs, except for Kogas et.al.[14] which their results are given as four-digits for overlap intgerals, it was not possible for us to compare our values are reproduced. In our study, the integral results have been given as ten-digits. In computing the analytical expressions obtained for one center integrals, Pentium III-933 PC and Lahey Fortran 77 Programming language have been employed.

Table 1. Overlap Integrals with Non-Integer n STOs in a.u.

n	ℓ	m	ζ	n'	ℓ'	m'	ζ'	$S_{n\ell m\zeta}^{n'\ell'm'\zeta'}$
0.995312	0	0	18.509594	2.079508	0	0	2.719940	1.7553137240E-2
								1.8E-2[a]
1.827215	1	1	6.798603	2.411421	1	1	2.119813	2.9536938856E-1
								2.95E-1[a]
2.644286	1	0	1.905761	2.830987	1	0	6.744730	3.3287274814E-1
								3.33E-1[a]
2.648836	1	1	1.147838	3.100865	1	1	4.519049	3.0705216034E-1
								3.07E-1[a]
2.035171	2	0	2.715351	2.567643	2	0	10.287745	4.3453578567E-1
								4.35E-1[a]
2.395357	2	1	6.629406	2.139111	2	1	1.410602	2.6660002039E-1
								2.67E-1[a]
5.34	3	2	0.2468	8.6	3	2	12.4361	1.8496531010E-6
12.67	8	6	1.6328	8.74	8	6	0.8611	7.9867378361E-1

[a] Ref.[14]

Table 2. Nuclear attraction integrals with Non-Integer n STOs in a.u.

n	ℓ	m	ζ	n'	ℓ'	m'	ζ'	$V_{n\ell m\zeta}^{n'\ell'm'\zeta'}$
0.9985	0	0	1.4258	2.0745	0	0	8.0621	-27.1189591164
4.2	1	1	0.1	4.2	2	1	0.1	-3.8094784851E-1
5.246	2	2	5.6819	3.942	2	2	2.0796	-6.9272438933
6.5	3	1	0.75	4.8	2	1	10.42	-3.0026188120E-4
2.8	1	0	15.22	8.8	0	0	3.4167	-2.4312156844E-3

Table 3. Kinetic energy integrals with Non-Integer n STOs in a.u.

n	ℓ	m	ζ	n'	ℓ'	m'	ζ'	$T_{n\ell m\zeta}^{n'\ell'm'\zeta'}$
0.9985	0	0	1.4258	2.0745	0	0	8.0621	2.0691580520
4.2	1	1	0.1	4.2	2	1	0.1	1.3191262606E-3
5.246	2	1	5.6819	3.942	2	1	2.0796	1.2923950025
6.5	3	2	0.75	4.8	3	2	10.42	-1.5552491709E-4
2.8	1	0	15.22	8.8	1	0	3.4167	-4.8849905865E-4

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