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On The Relativistic Two-center Overlap Integrals of Arbitrary Half-Integral Spin Particles

Keyfi Yarım Spinli Parçacıklar için Rölativistik İki-Merkezli Örtme İntegrali

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Abstract

The relativistic $\Psi^{\alpha s}$-exponential-type spinor orbitals are defined for use in algebraic solution of the Dirac equation of particles with arbitrary half-integral spin s, s=1/2,3/2,5/2,… . The analytical expression given for the two-center overlap integrals over Slater-type spinör orbitals of spin s=1/2 particles through the $\Psi^{\alpha s}$-exponential-type spinor orbitals, is generalized for any half-integral spin. The relativistic two-center overlap integrals are expressed in terms of non-relativistic two-center overlap integrals over the Guseinov's Ψ^{α}-exponential-type orbitals where α=1,0,-1,-2,-3,… . In this study, the relativistic molecular auxiliary functions approximation derived in a previous paper by the author in [Physical Review E 2015; 91(2): 023303] is used for accurate calculation of these integrals. The calculations are performed for spin s, s=1/2, s=3/2 and α=3,2,1,0,-1,-2,-3 for each value of spin. The coupling feature between lower- and upper-components of $\Psi^{\alpha s}$-exponential-type spinor orbitals ensure that the kinetic-balance condition is fulfilled. It is shown that, the suggested relativistic basis spinors in the present study available to be used for algebraic solution of the generalized Dirac equation.

Keywords: Half-integral spin particles, $\Psi^{\alpha s}$-Exponential-Type Orbitals, Overlap Integrals, Multi-Center Integrals

Öz

Rölativistik $\Psi^{\alpha s}$-exponansiyel-tipli spinor orbitalleri, keyfi yarım spine s, s=1/2,3/2,5/2,… sahip parçacıkların Dirac denkleminin cebirsel çözümünde kullanılmak üzere tanımlanır. Spini s=1/2 olan parçacıklar için Slater-tipli spinör orbitalleri ile analitik ifadesi verilen bu örtme integralleri, $\Psi^{\alpha s}$-exponansiyel-tipli spinor orbitalleri yardımı ile herhangi yarım-spine sahip parçacıkların için genelleştirilir. Rölativistik iki-merkezli örtme integralleri Guseinov tarafından önerilen Ψ^{α}-exponansiyel-tipli orbitallerin rölativistik olmayan iki-merkezli örtme integrali cinsinden ifade edilir. Bu çalışmada, yazar tarafından daha önce [Physical Review E 2015; 91(2): 023303]'de önerilmiş olan rölativistik yardımcı fonksiyonlar yaklaşımı iki-merkezli integrallerin hassas hesaplanması amacı ile kullanılır. Hesaplamalar, spini s, s=1/2, s=3/2 ve herbir spin değeri için α=3,2,1,0,-1,-2,-3 olmak üzere gerçekleştirilir. $\Psi^{\alpha s}$-exponansiyel-tipli spinor orbitallerinin çiftlenim özelliği kinetic-denge koşulunun sağlanmış olduğunu garanti eder. Bu çalışmada özerilen baz spinörlerinin keysi yarım-spine sahip parçacıkların Dirac denkleminin cebirsel çözümünde kullanılabileceği gösterilir

Anahtar Kelimeler: Yarım-Spin Parçacıklar, $\Psi^{\alpha s}$-Exponansiyel-Tipli Orbitaller, Örtme İntegrali, Çok-Merkezli İntegraller

1. Introduction

The fundamental and most accurate method so far known for electronic structure calculation of atoms and molecules is so called Hartree-Fock self-consistent field approximation (HF-SCF) (Hartree 1928a, Hartree 1928b, Fock 1930a, Fock 1930b). Studies targeting very large molecules use the density functional theory (DFT) (Hohenberg and Kohn 1964) or the Monte-Carlo method (MC) (Hetherington 1984). These methods were developed later on based on the HF-SCF approximation. Yet, necessity of performing HF method for precise calculations of quantum mechanical systems is obvious (Drake and Yan 1994, Yan and Drake 1995, Yan et al. 1998, Wang et al. 2011, Ruiz 2004, Puchalski and Pachucki 2006, Pachucki 2010, Pachucki 2012a, Pachucki 2012b, Pachucki 2013). The elements of matrix form representation of HF equations (Roothaan 1951) are expressed in terms of multi-center integrals. These integrals are constituted with initially determined basis orbitals which are generally classified according to power of the natural exponential function in the radial part of their contents.

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They are referred to as Gaussian-type orbitals (GTO) (Boys and Egerton 1950) and exponential-type orbitals (ETO) (Hylleraas 1929, Slater 1930a, Löwdin and Shull 1956, Guseinov 2002) (please see also references therein). The radial part of the GTO have the following form,

$$R_n(\zeta) = r^n e^{-\zeta r^2} \tag{1}$$

where, are the principal quantum numbers. ζ is the orbital parameter. From the non-relativistic point of view i.e., Schrödinger equation, the reason for the suitability of GTO in molecular calculations is that the molecular integrals easily be evaluated. Correct representation of the wave-function at the limit (in the neighborhood or at large distance of the nuclei, cusp condition) (Kato 1957, Agmon 1982) is however, one of the feature that need to be fulfilled for rapid convergence of solution via algebraic approximation (Reinhardt and Hoggan 2009). In the light of this fact, the exponential-type orbitals (ETO) with the following form,

$$R_n(\zeta) = r^n e^{-\zeta r} \tag{2}$$

should also be considered as a basis because they suit to these limit cases better than GTO (Bouferguene et al. 1996, Rico et al. 2001). On the other hand, the problem of molecular integrals evaluation becomes more laborious. Compared to the GTO, this makes the ETO disadvantageous in terms of computation time. The significance of ETO where the theoretical results expected to be in complete agreement with experimental data. Importance of such consistency considerably increases in relativistic calculations (Drake G. W. 2002, Yan and Drake 2002, Wang et al. 2014, Puchalski and Pachucki 2008, Puchalski et al. 2010, Korobov 2002). From the relativistic point of view i.e., the Dirac equation, the Gaussian-type orbitals are naturally satisfying the so called *kinetic-balance* condition (Lee and McLean 1982, Stanton and Havriliak 1984) if of course, the nuclei considered as finite-sized (Pomeranchuk and Smorodinsky 1945, Zeldovich and Popov 1972). The choice for initial basis function is associated with the definition of the nucleus (Ishikawa et al. 1985). The cusp no longer valid. The disadvantage of using GTO in matrix form representation solution of the Dirac equation is that quantum electrodynamics (QED) effects can only be taken into account perturbatively (Shytov et al. 2007). Defining the model of nucleus as point-like, this means using exponential-type function as a spinors basis, allows direct solution of the Dirac equation without any approximation but this requires coupling between large- and small-components of the used basis function (Bağcı and Hoggan 2016, Bağcı 2020).

Any function as radial part for the basis orbital can actually, be used in the variational Hartree-Fock method (Slater 1930b, Kutzelnigg 2012). The choice depends to the properties of the system and it is admissible as long as the domain for the energy spectrum of the Schrodinger or the Dirac equation is taken into account (Gitman et al. 2012). For electrons moving around a central Coulomb potential the best way to determine the radial basis function is that simplification of the wave-function obtained from and exact solution. In this case exact solution of the Schrödinger or the Dirac equation for the hydrogen-like systems. The Slater-type orbitals (STO, $\chi - STO$) (Slater, 1930a), are derived by simplification of Laguerre polynomials in hydrogen-like wave-functions. They are the simplest and well-known type of ETO (Avery and Avery 2015). They are however, not orthogonal with respect to principal quantum number. The orthogonality property has a critical role in evaluation of molecular the three- and four-center integrals. These integrals have no closed form relations. The necessity of using orbital or charge density $[\rho_{pq} = \chi_p(r_a)\chi_q^*(r_b)]$ translation via complete orthonormal ETO arise due to there is no so far known an alternative approximation. Here, $\{pq\}$ represent the quantum numbers. The translation method involve series whose convergence may be increased if Guseinov's complete orthonormal sets of $\psi^\alpha -$ ETO (Guseinov 2002) is used (Figure 1).

The indices α by Guseinov himself defined as a new quantum number. The claim is that, ψ^α-ETO correspond to the total centrally symmetric potential which contains the core attraction potential and the Lorentz potential of the field produced by the particle itself. The accordingly, is called to as the frictional quantum number (Guseinov 2007, Guseinov 2012). The Lambda functions (Hylleraas 1929) and Coulomb-Sturmians (Löwdin and Shull 1956) are also obtained from certain integer values of $\alpha, \alpha = 0, \alpha = 1$ respectively.

The relations of Lambda and Coulomb-Sturmians with other ETO basis sets are described in (Guseinov 2002) and in (Filter and Steinborn 1980, Trivedi and Steinborn 1982, Weniger 1985). Since the indices α free from any constraint yet the ψ^α-ETO are still complete and orthonormal in any value of α, various series expansion relations can be constructed and their convergence can be tested in the both relativistic and non-relativistic molecular integrals evaluation procedure. This provide further advantage in quantum mechanical electronic structure calculations (Guseinov and Aksu 2008, Aksoy et al. 2013; Guseinov

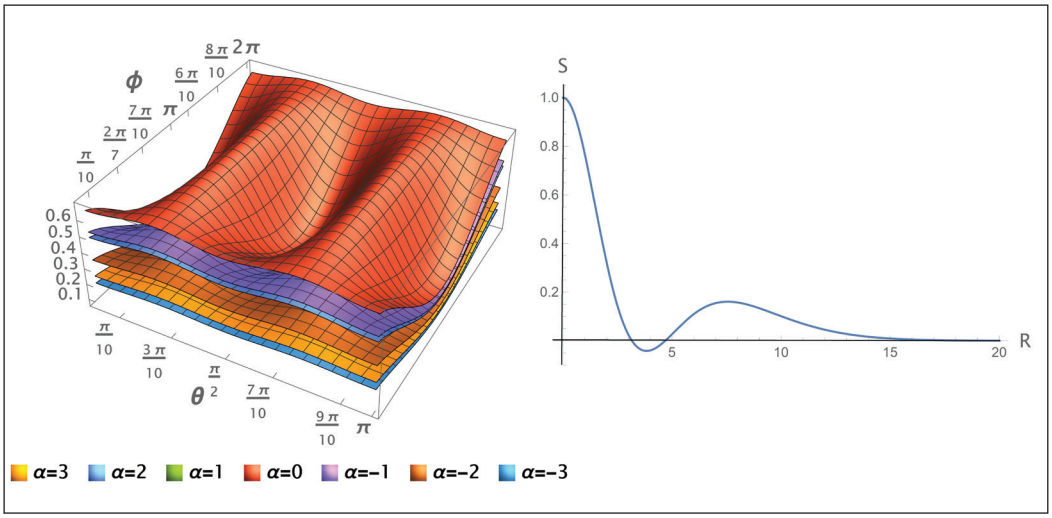

Figure 1. Results for the non-relativistic two-center overlap integrals over $\psi^{\alpha}-$ ETO in atomic units (a.u.) where, $nlm_l = 211, n'l'm_{l'} = 211,$ $\rho = 2, \tau = 0.$ Left hand- and right hand-side of the figure are results integrals depending on the rotational angles (Θ, Φ) and the inter-nuclear distance *R*, respectively.

et al. 2014). The non-relativistic Coulomb-Sturmians introduced as *good bases* (Bretin and Gazeau, 1982) for use in solution of the Dirac equation of higher half-spin particles moving around a Coulomb field. The relativistic two-center overlap integrals for $s = \frac{1}{2}$ using Dirac-Slater orbitals have calculated by Talman (2004). This calculation procedure by the author extended to the half-integral spin case in (Guseinov et al. 2012). In the present study, we consider to use the ψ^{α}-ETO for such systems because they are sets of complete orthonormal basis functions that make them naturally legitimate and more favorable. The radial parts of the ψ^{α}-ETO used in the present work for relativistic orbitals are the same and they are complete without the inclusion of the continuum. They ensure the variational stability (Schwarz and Wallmier 1982) for spin $s, s > \frac{1}{2}$. The relativistic calculations for multi-center integrals over ψ^{α}-ETO thus, allows easy for arbitrary values of spin with help of the ETO.

2.Definitions

The $(2s+1)$ large, and small-components of relativistic exponential-type spinor Ψ^{as}-ETSO basis sets are defined as (Guseinov 2007, Guseinov, 2009, Guseinov 2010, Guseinov 2012),

$$\Psi^{as}_{nljm}(\zeta,\vec{r}) = N_{nl}(\zeta)\begin{bmatrix}\Psi^{asL}_{nljm}(\zeta,\vec{r})\\ \Psi^{asS}_{nljm}(\zeta,\vec{r})\end{bmatrix}, \tag{3}$$

here, *L, S* represent the large- and small-components of the spinor orbitals, respectively. They are written below explicitly as,

$$\Psi^{asL}_{nljm}(\zeta,\vec{r}) = \begin{bmatrix}\Psi^{as0}_{nljm}(\zeta,\vec{r})\\ \Psi^{as2}_{nljm}(\zeta,\vec{r})\\ \vdots\\ \Psi^{as2s-1}_{nljm}(\zeta,\vec{r})\end{bmatrix}, \tag{4}$$

$$\Psi^{asS}_{nljm}(\zeta,\vec{r}) = \begin{bmatrix}\Psi^{as2s-1}_{\tilde{n}\tilde{l}jm}(\zeta,\vec{r})\\ \vdots\\ \Psi^{as2}_{\tilde{n}\tilde{l}jm}(\zeta,\vec{r})\\ \Psi^{as0}_{\tilde{n}\tilde{l}jm}(\zeta,\vec{r})\end{bmatrix}. \tag{5}$$

Note that, the notation used in this paper is similar with ones used in (Grant 2007, Niederle and Nikitin 2006) Now, for each component in the Eqs. (4, 5) we have,

$$\Psi^{as\lambda}_{nljm}(\zeta,\vec{r}) = \begin{bmatrix}A^{ls}_{jm}(\lambda)\psi^{\alpha}_{nlm(\lambda)}(\zeta,\vec{r})\\ B^{ls}_{jm}(\lambda)\psi^{\alpha}_{nlm(\lambda)}(\zeta,\vec{r})\end{bmatrix}, \tag{6}$$

$$\Psi^{as\lambda}_{nljm}(\zeta,\vec{r}) = \begin{bmatrix}A^{ls}_{jm}(\lambda)\psi^{\alpha}_{nlm(\lambda)}(\zeta,\vec{r})\\ B^{ls}_{jm}(\lambda)\psi^{\alpha}_{nlm(\lambda)}(\zeta,\vec{r})\end{bmatrix}, \tag{7}$$

$$\begin{aligned}A^{ls}_{jm}(\lambda) &= \eta_t C^{ls}_{jm}(\lambda)\beta_{m(\lambda)}\\ B^{ls}_{jm}(\lambda) &= \eta_t C^{ls}_{jm}(\lambda+1)\beta_{m(\lambda+1)}\\ A^{ls}_{jm}(\lambda) &= -iC^{ls}_{jm}(2s-\lambda)\beta_{m(2s-\lambda)}\\ B^{ls}_{jm}(\lambda) &= -iC^{ls}_{jm}(2s-(\lambda+1))\beta_{m(2s-(\lambda+1))}\end{aligned} \tag{8}$$

where $m_l = m(\lambda) = m - s + \lambda, \beta(\lambda) = (-1)^{[|m(\lambda)|-m(\lambda)]},$

$0 \le \lambda \le 2s-1$

$t = 2(j-l) = \pm 1, \pm 3, ..., 2s, \eta_t = \frac{t}{|t|}, j \le s, -j \le m \le j,$

$l = j - \frac{1}{2}t, \tilde{n} = n + t, \tilde{l} = l + t = j + \frac{1}{2}t.$

$C^{ls}_{jm}(\lambda)$ are the modified Clebsch-Gordan coefficients. They are determined by (Wigner 1959; Condon and Shortley 1970),

$$\begin{aligned}C^{ls}_{jm}(\lambda) &= \langle lsm(\lambda)s-\lambda \,|\, lsjm\rangle\\ &= (-1)^{m(\lambda)+l-s}\sqrt{2j+1}\begin{pmatrix}l & s & j\\ m(\lambda) & s-\lambda & -m\end{pmatrix}\end{aligned} \tag{9}$$

here, $\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix}$ are the Wigner 3-j-symbols. The Racah formula is used for computation of them:

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = (-1)^{j_1-j_2-m_3}\sqrt{\nabla(j_1j_2j_3)}\sqrt{J_1J_2J_3}\sum_t \frac{(-1)^t}{J^t_{j_1m_1j_2m_2j_3m_3}} \tag{10}$$

$$\begin{aligned} J_1 &= (j_1+m_1)!(j_1-m_1)! \\ J_2 &= (j_2+m_2)!(j_2-m_2)! \\ J_3 &= (j_3+m_3)!(j_3-m_3)! \end{aligned} \tag{11}$$

$$\begin{aligned} J^t_{j_1m_1j_2m_2j_3m_3} &= (j_3+j_1+t+m_1)!(j_3-j_2+t+m_2)! \\ &(j_1+j_2-j_3-t)!(j_1-t-m_1)!(j_2-t-m_2)!, \end{aligned} \tag{12}$$

and, with, $\nabla(j_1j_2j_3)$ is a triangle coefficient (Shore and Menzel 1968) (Figure 2).

The non-relativistic scalar ψ^α-ETO functions used in the present paper defined as (Guseinov 2002),

$$\psi^\alpha_{nlm_l}(\zeta,\vec{r}) = (-1)^\alpha\left\{\frac{(2\zeta)^3(n-l-1)!}{(2n)^\alpha[(n+l+1-\alpha)!]^3}\right\}^{\frac{1}{2}} (2\zeta r)^l e^{-\zeta r}L^{2l+2-\alpha}_{n+l+1-\alpha}(2\zeta r)Y_{lm}(\theta,\varphi) \tag{13}$$

$Y_{lm}(\theta,\varphi)$ are the normalized complex or real spherical harmonics $(Y_{lm}\equiv S_{lm})$ that differs from Condon-Shortley phases by sign factor $(-1)^{ml}$, $L^p_q(x)$ are the generalized Laguerre polynomials (Abramowitz and Stegun 1972).

The ψ^α-ETO are orthonormal with respect to the weight function $\left(\frac{n}{\zeta r}\right)^\alpha$;

$$\int \psi^{\alpha*}_{nlm_l}(\zeta,\vec{r})\left(\frac{n}{\zeta r}\right)^\alpha \psi^\alpha_{n'l'm_{l'}}(\zeta,\vec{r})dV = \delta_{nn'}\delta_{ll'}\delta_{m_lm_{l'}} \tag{14}$$

3. The Two-center Overlap Integrals of Ψ^{as}_{nljm} ETSO in Terms of Non-Relativistic Overlap Integrals

According to Refs. (Talman 2004; Guseinov et al. 2012; Niederle and Nikitin 2006) the two-center overlap of 2(2*s*+1)-component Ψ^{as}_{nljm} ETSO in terms of ψ^α ETO determined by;

$$\begin{aligned} S^{\alpha s}_{nljm,n'l'j'm'}(\rho,\tau) &= \int \Psi^{\alpha s\dagger}_{nljm}(\zeta,r\vec{a})\Psi^{\alpha s}_{n'l'j'm'}(\zeta',r\vec{b})dV \\ &= N_{nl}(\zeta)N_{n'l'}(\zeta') \\ \times\sum_{\lambda=0}^{2s}&\left[\wedge^{\alpha s}_{nljm,n'l'j'm'}(\rho,\tau)+\Omega^{\alpha s}_{\bar{n}\bar{l}jm,\bar{n}'\bar{l}'j'm'}(\rho,\tau)\right], \end{aligned} \tag{15}$$

where, $\rho=\frac{R}{2}(\zeta+\zeta'),\tau=\frac{\zeta-\zeta'}{\zeta+\zeta'}$. $\wedge^{as}_{nljm,n'l'j'm'}(\rho,\tau)$ and $\Omega^{as}_{\bar{n}\bar{l}jm,\bar{n}'\bar{l}'j'm'}(\rho,\tau)$ are the two-center overlap integrals for elements of the large- and small-components of Ψ^{as}_{nljm} -ETSO, respectively. They are expressed as follows,

$$\begin{aligned} \wedge^{as}_{nljm,n'l'j'm'}(\rho,\tau) &= \int \Psi^{as\lambda\dagger}_{nljm}(\zeta,r\vec{a})\Psi^{as\lambda}_{n'l'j'm'}(\zeta',r\vec{b})dV \\ &= \eta_t n_{t'}\{[C^{ls}_{jm}(\lambda)\beta_{m(\lambda)}C^{l's}_{j'm'}(\lambda)\beta_{m'(\lambda)}]S^\alpha_{nljm(\lambda),n'l'j'm'(\lambda)}(\rho,\tau)\} \\ &+[C^{ls}_{jm}(\lambda+1)\beta_{m(\lambda+1)}C^{l's}_{j'm'}(\lambda+1)\beta_{m'(\lambda+1)}]S^\alpha_{nljm(\lambda+1),n'l'j'm'(\lambda+1)}(\rho,\tau), \end{aligned} \tag{16}$$

$$\begin{aligned} \Omega^{as}_{nljm,n'l'j'm'}(\rho,\tau) &= \int \Psi^{as\lambda\dagger}_{nljm}(\zeta,r\vec{a})\Psi^{as\lambda}_{n'l'j'm'}(\zeta',r\vec{b})dV \\ &= \eta_t n_{t'}\left\{\begin{matrix}[C^{ls}_{jm}(2s-\lambda)\beta_{m(2s-\lambda)}C^{l's}_{j'm'}(2s-\lambda)\beta_{m'(2s-\lambda)}]\\ S^\alpha_{nljm(2s-\lambda),n'l'j'm'(2s-\lambda)}(\rho,\tau)\end{matrix}\right\} \\ &+[C^{ls}_{jm}(2s-(\lambda+1))\beta_{m(2s-(\lambda+1))}C^{l's}_{j'm'}(2s-(\lambda+1))\beta_{m'(2s-(\lambda+1))}] \\ &\times S^\alpha_{nljm(2s-(\lambda+1)),n'l'j'm'(2s-(\lambda+1))}(\rho,\tau) \end{aligned} \tag{17}$$

The non-relativistic $S^\alpha_{nlm,n'l'm_{l'}}(\rho,\tau)$ overlap integrals occurring in Eqs. (15-17) are defined in molecular coordinate system as (Guseinov, 1985; Guseinov and Şahin, 2010),

$$\begin{aligned} S^\alpha_{nlm,n'l'm_{l'}}(\rho,\tau) &= \int \psi^{\alpha*}_{nlml}(\zeta,r\vec{a})\psi^\alpha_{n'l'm_{l'}}(\zeta',r\vec{b})dV = \\ &= \sum_{v=0}^{\min(l,l')} T^*_{lm_l,l'm_{l'}}(\Theta,\Phi)S^\alpha_{nlv,n'l'v}(\rho,\tau) \end{aligned} \tag{18}$$

$S^\alpha_{nlv,n'l'v'}(\rho,\tau)$ are the two-center overlap integrals over ψ^α-ETO in the lined-up molecular coordinate system. Three are several ways of computation that we know they give accurate results for the $S^\alpha_{nlv,n'l'v'}(\rho,\tau)$. Expressing the ψ^α

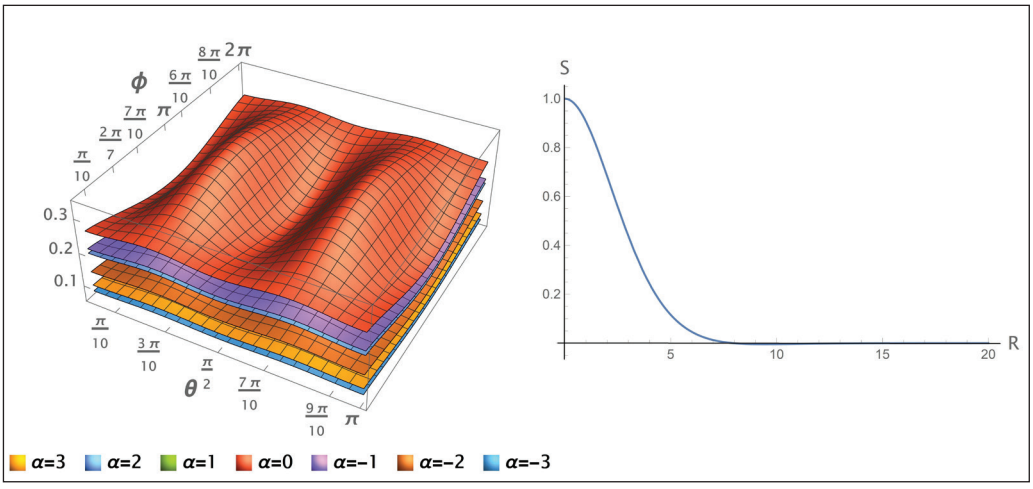

Figure 2. Results for the relativistic two-center overlap integrals over Ψ^{as}-ETO in atomic units (a.u.) where, $s=\frac{1}{2}, nljm = 21\frac{1}{2}\frac{1}{2'}$, $n'l'j'm' = 21\frac{1}{2}\frac{1}{2}, \rho = 2,$ $\tau = 0.$ Left hand- and right hand-side of the figure are results integrals depending on the rotational angles (Θ,Φ) and the inter-nuclear distance R, respectively.

-ETO in terms of χ-STO using the following formulae,

$$\psi^{\alpha}_{nlm_l}(\zeta,\vec{r}) = \sum_{n'=l+1}^{n} \omega^{\alpha l}_{nn'} \chi n' l m_l(\zeta,\vec{r}),$$

then utilizing from the numerical integration procedure suggested by the author (Bağcı and Hoggan 2014) to improve the accuracy in Guseinov's approach (2007) is one of them. Here, $\omega^{\alpha l}_{nn'}$ are the expansion coefficients. Direct calculation of $S^{\alpha}_{nlv,n'l'v}(\rho,\tau)$ via relationships given in (Guseinov and Şahin 2010) is the other one. In both through the prolate spheroidal coordinates

$$1 \le \mu \le \infty, -1 \le v \le 1, 0 \le \varphi \le 2\pi,$$
$$\mu = \frac{r_a + r_b}{R}, v = \frac{r_a - r_b}{R}, R = r\vec{a} - r\vec{b} \quad ,$$

the analytical expressions are reduced product of angular momentum coefficients and so called the molecular auxiliary functions which their simple form here, are given as (Guseinov 1970, Pople and Beveridge 1970),

$$Q^{q}_{NN'}(\rho,\tau) = \int_{1}^{\infty}\int_{-1}^{1} (\mu v)^{q} (\mu+v)^{N} (\mu-v)^{N'} e^{-\rho\mu-\rho\tau v} d\mu dv, \tag{20}$$

where, $\{q,N,N'\} \in Z, \{\rho,\tau\} \in R$. The domain of the parameters allow to take advantage of the binomial series expansion for $(\mu+v)^{N}(\mu-v)^{N'}$ and reduce the analytical evaluation for the Eq. (20) to the integrals which have the following form:

$$M^{1}_{a}(p) = \int_{1}^{\infty} x^{a} e^{-ax} dx,\ M^{2}_{a}(p) = \int_{-1}^{-1} x^{a} e^{-ax} dx. \tag{21}$$

These auxiliary functions are the special case of relativistic molecular auxiliary functions defined by the author via transformation of the relativistic two-center two-electron Coulomb energy associated with a charge density into a kinetic energy-like integrals using the Poisson equation in (Bağcı and Hoggan 2015) (please see also references therein). The resulting expression was obtained by expanding the potential in the set of Slater-type functions with noninteger values of principal quantum numbers. In this case the domain for the parameters expand. They now, free to take any real values (see the appendix for detail). This generalized form of the Eq. (20) can be calculated either numerical or analytical through the methods given again by the author in (Bağcı and Hoggan 2014, Bağcı and Hoggan 2015) and in a series of papers in (Bağcı and Hoggan 2018, Bağcı et al. 2018, Bağcı and Hoggan 2020), respectively. An Efficient method for evaluation of the rotation angular functions $T^{v*}_{lm_l,l'm_{l'}}(\Theta,\Phi)$ derived recently (Guseinov 2011). This method is an improvement to a previous work (Guseinov 1985). It is used for both real and complex spherical harmonics:

$$T^{kL}_{lm_l,l'm_{l'}} = \begin{cases} D^{kL}_{lm_l,l'm_{l'}}, for\ complex\ SH \\ D^{kL}_{lm_l,l'm_{l'}}, for\ real\ SH \end{cases} \tag{22}$$

$$D^{kL}_{lm_l,l'm_{l'}} = \frac{2}{1+\delta_{k0}} C^{ll'L}_{-kk0} C^{ll'L}_{-ml m_{l'} M} \left(\frac{4\pi}{2L+1}\right)^{\frac{1}{2}}, \tag{23}$$

$$D^{kL}_{lm_l,l'm_{l'}} = \frac{(-1)^{\delta_{m_{l'}-|m_{l'}|}} (-i)^{\delta_{m_{l'}-|m_{l'}|}}}{2[(1+\delta_{m_l})(1+\delta_{m_{l'}}]^{\frac{1}{2}}} (D^{kL}_{l|m_l|,l'|m_{l'}|} + D^{kL}_{l-|m_l|,l'|m_{l'}|}$$
$$+\varepsilon m_l D^{kL}_{l-|m_l|,l'|m_{l'}|} + \varepsilon m_{l'} D^{kL}_{l|m_l|,l'-|m_{l'}|} + \varepsilon m_l \varepsilon m_{l'} D^{kL}_{l-|m_l|,l'-|m_{l'}|}. \tag{24}$$

4. Results and Discussions

The calculation method suggested in this study is used evaluation of the relativistic molecular integrals arise in algebraic solution of the Dirac equation for particles in a central Coulomb field. The wave-equation accordingly restricted to kinematic role. This is due to fully adequate formalism that describe higher spin field not available yet. The literature besides no longer insist in forming the Lagrangian formalism. The higher spin particles Dirac equation instead, is generalization of the Dirac equation correspond to the representation $\left(\frac{1}{2},0\right)\times\left(0,\frac{1}{2}\right)$ to representation $(s,0)\times(0,s)$.

The $2(2s+1)$-component formalism used in the present study according to the above approximation, depend on both Minkowski space coordinates and some continuous variables corresponding to spin degrees of freedom. A more detailed discussion on the wave-function for the half-integral spin Dirac equation of a charged particle moving around the Coulomb potential can be found in (Niederle and Nikitin 2006, Gazeau 1980). The conclusion we have reached from these works is that the Coulomb-Sturmian functions can be used for solution of the Dirac-like equations. The relativistic Coulomb-Sturmians are obtained based on the Sturm-Liouville problem. They are the solution of the second order Dirac-Coulomb differential equation (Szmytkowski 1997). It is however, for the higher spin Dirac-like equation more proffered to use their non-relativistic counterpart (Bretin and Gazeau 1982). They are a sub-set of the $\Psi^{\alpha s}_{nljm}$-ETSO while $\alpha = 1$. The $\Psi^{\alpha s}_{nljm}$-ETSO accordingly are proposed for use in the present paper. A method guarantees highly accurate calculation for the relativistic molecular integrals over ψ^{α}-ETO is derived based on the recent papers published by the author (Bağcı and Hoggan 2014) (Bağcı and Hoggan 2015, Bağcı and Hoggan 2018, Bağcı, et al. 2018, Bağcı and Hoggan 2020). These integrals may arise in the matrix form representation of the Dirac-like equation. As a sample, a detailed discussion is made for two-center overlap integrals. They are defined in terms of overlap integrals over non-

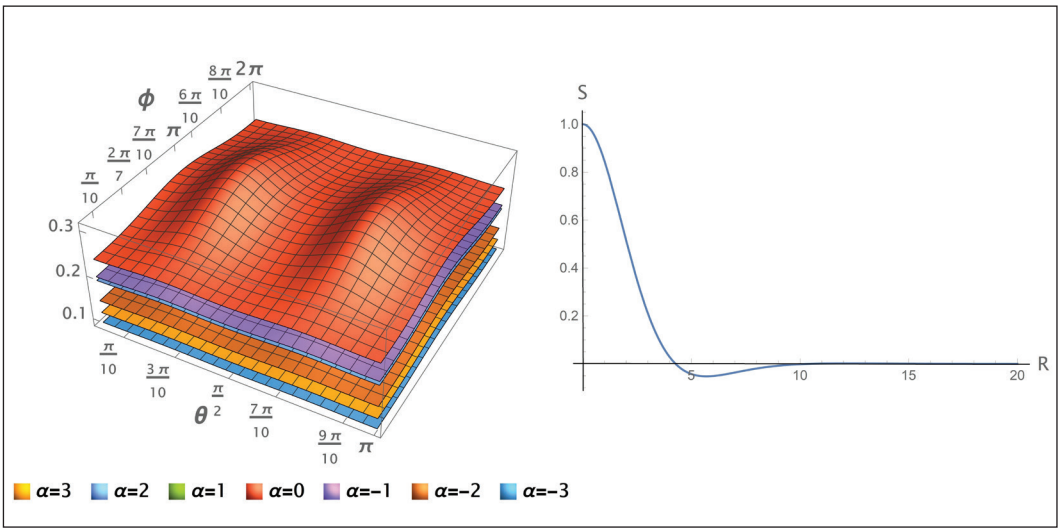

Figure 3. Results for the relativistic two-center overlap integrals over Ψ^{as} -ETO in atomic units (a.u.) where, $s=\frac{3}{2}, nljm=21\frac{3}{2}\frac{3}{2'}$, $n'l'j'm'=21\frac{3}{2}\frac{3}{2}, \rho=2,$ $\tau=0.$ Left hand- and right hand-side of the figure are results integrals depending on the rotational angles (Θ,Φ) and the inter-nuclear distance R, respectively.

relativistic scalar ψ^{α} -ETO. Note that, a computer program for fast and accurate calculation of relativistic molecular auxiliary functions and overlap integrals recently, has been written (Bağcı and Hoggan 2020) in *Julia* programming language. We plan to present this computer program code in future.

The expansion and one-range addition theorem are now available to be used for multi-center integrals of $2(2s+1)$-component Ψ^{as}_{nljm} -ETO. The method of computation for relativistic molecular integrals over Ψ^{as}_{nljm} -ETSO require a proof that satisfactory accuracy is obtained for molecular auxiliary functions. For this the molecular two-center overlap integrals over scalar χ -STO should be calculated at first. Then, it would be quite sufficient using the relationship given in the Eq. (19). This is for representing the ψ^{α} -ETO in terms of χ -STO. Since this task completed by the author, necessity of an additional investigation for accurate calculation of the two-center overlap integrals is obviously eliminated. Instead here, we investigate the behavior two-center overlap integrals depending on rotation angles (Θ,Φ) and inter-nuclear distance R to see whether the relativistic two-center overlap integrals fulfill the orthogonality property or not. The results are presented in the Figures. 1, 2 and 3. In the Fig. 1 the results non-relativistic scalar ψ^{α} -ETO, in the Figures 2 and 3 the results for relativistic Ψ^{as}_{nljm} -ETSO with spin $s, s=\frac{1}{2}$ and $s=\frac{3}{2}$ are given, respectively. At the left (Fig. 1a and Fig. 2a) and right (Fig. 1b and Fig 2b) hand-side of these figures the results are given for angular momentum quantum number $l, l=1, l=2$. It can be seen from these figures that the expected density distributions for the given angular momentum quantum number $l=1$ are obtained (Fig. 1a and Fig. 2a). From the figures we can see that for all the orthogonality property is satisfied (Fig. 1b and Fig. 2b). These results are enough to have conclusion that the Ψ^{as}_{nljm} -ETSO can be used for solution of the Dirac equation with half-integral spin.

5. Appendix

The general, relativistic form of the molecular auxiliary functions of the Eq. (20) in prolate spheroidal coordinates have the following form (Bağcı and Hoggan 2015),

$$\begin{Bmatrix} P^{n_1 q}_{n_2 n_3 n_4}(p_{123}) \\ Q^{n_1 q}_{n_2 n_3 n_4}(p_{123}) \end{Bmatrix} = \frac{p_1^{n_1}}{(n_4-n_1)_{n_1}} \int_1^{\infty}\int_{-1}^{1} (\mu v)^q (\mu+v)^{n_2} (\mu-v)^{n_3} \times \begin{Bmatrix} P[n_4-n_1, p_1 f^k_{ij}(\mu,v)] \\ Q[n_4-n_1, p_1 f^k_{ij}(\mu,v)] \end{Bmatrix} e^{-p_2\mu - p_3 v} d\mu dv \quad (A.1)$$

here, $\{q,n_1\}\in Z, \{n_1,n_2,n_3\}\in R, p_{123}$ $=\{p_1,p_2,p_3\}, p_1>0, p_2>0, -p_2\le p_3\le p_2. P, Q$ are the normalized complementary incomplete and the normalized incomplete gamma functions;

$$P[a,z]=\frac{\gamma(a,z)}{\Gamma(a)}, \quad Q[a,z]=\frac{\Gamma(a,z)}{\Gamma(a)}, \quad (A.2)$$

with, $\gamma(a,z)$ and $\Gamma(a,z)$ are incomplete gamma functions.

$$\gamma(a,z)=\int_0^z t^{a-1}e^{-t}dt, \qquad \Gamma(a,z)=\int_z^{\infty} t^{a-1}e^{-t}dt, \quad (A.3)$$

$\Gamma(a)$ is the complete gamma function,

$$\Gamma(a)=\Gamma(a,z)+\gamma(a,z) \quad (A.4)$$

And the Pochammer's symbol $(a)_n$ is defined as,

$$(a)_n=\frac{\Gamma(a+n)}{\Gamma(a)}. \quad (A.5)$$

$f^k_{ij}(\mu,v)$ is the irreducible representation of an interaction potential.,

$$f_{ij}^{k}(\mu,v)=(\mu v)^{k}(\mu+v)^{i}(\mu-v)^{j}. \quad \text{(A.6)}$$

For Coulomb potential it has a form that, $f_{10}^{0}(\mu,v)=\mu+v$.

6. Aknowledgement

This work is dedicated in memory of Professor Israfil Guseinov who was my PhD thesis advisor. He well adapted his great experience on mathematical analysis for use in quantum chemistry especially when exponential-type orbitals are considered as a basis sets. His works on this field for me in fact, is still a source of inspiration to find an effective and practical solution for a mathematical expression that came to impasse. He unfortunately, passed away in February of last year.

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