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Accurate evaluation of overlap integrals of Slater type orbitals with noninteger principal quantum numbers using complete orthonormal sets of Ψ^{α}- exponential type orbitals

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In this paper, by the use of complete orthonormal sets of Ψ^{α} exponential-type orbitals (Ψ^{α}-ETOs, $\alpha = 1, 0, -1, -2, \ldots$), the series expansion formulas in line-up coordinate systems are established for the overlap integrals with noninteger n^* Slater-type orbitals (NISTOs) in terms of overlap integrals over integer n Slater-type orbitals (ISTOs). The suggested approach guarantees a highly accurate calculation of the noninteger n^* overlap integrals with arbitrary values of parameters. The results of computer calculations presented are in a complete agreement with those obtained in the literature using the alternative procedure.

KEY WORDS: Slater type orbitals, exponential type orbitals, overlap integrals, noninteger principal quantum numbers

1. Introduction

The calculation of overlap integrals over STOs is of fundamental importance in the development of *ab initio* and semi-empirical methods for the study of the electronic structure and properties of molecular systems. The most existing programs for overlap integrals over integer n STOs cannot be used in the case of nonintegral values of n. However, it is well-known that the noninteger n STOs provide a more flexible basis for molecular calculations than integer n STOs [1–7]. Thus, it is of interest to develop the efficient (fast and accurate) algorithms

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for performing the computation of overlap integrals over non integer n^{th} Slater-type orbitals (NISTOs). Our aim in this work is to elaborate a general algorithm for the calculation of overlap integrals over NISTOs using the complete orthonormal sets of Ψ^{α}-ETOs presented in [8].

2. Definition

The overlap integrals over NISTOs are defined as

$$S_{n^*lm,n'^*l'm}\left(\zeta,\zeta';\vec{R}\right)=\int\chi^*_{n^*lm}\left(\zeta,\vec{r}_a\right)\chi_{n'^*l'm}\left(\zeta',\vec{r}_b\right)\,\mathrm{d}V. \tag{1}$$

Here, the normalized NISTOs with nonintegral value of principal quantum number are determined as

$$\chi_{n^*lm}\left(\zeta,\vec{r}\right)=(2\zeta)^{n^*+\frac{1}{2}}\left[\Gamma(2n^*+1)\right]^{-1/2}r^{n^*-1}e^{-\zeta r}S_{lm}\left(\theta,\varphi\right), \tag{2}$$

where n^* is a noninteger principal quantum number and S_{lm} is a complex or real spherical harmonic; ζ is the screening constant and $\Gamma(x)$ is the gamma function [9]. The normalized ISTOs can be obtained from equation (2) for $n^*=n$ where n is an integer:

$$\chi_{nlm}\left(\zeta,\vec{r}\right)=(2\zeta)^{n+\frac{1}{2}}\left[(2n)!\right]^{-\frac{1}{2}}r^{n-1}e^{-\zeta r}S_{lm}\left(\theta,\varphi\right). \tag{3}$$

3. Series expansion relations in terms of overlap integrals over integer *n* STOs

With the calculation of overlap integrals over NISTOs, equation (1), we shall require the formulas for the expansion of NISTOs in terms of integer n Slater-type orbitals (ISTOs). For this purpose we utilize the one-center expansion formulas for NISTOs in terms of ISTOs obtained with aid of complete orthonormal sets of Ψ^{α} exponential-type orbitals (Ψ^{α}-ETOs) [8]:

$$\chi_{n^*lm}\left(\zeta,\vec{r}\right)=\lim_{N\to\infty}\sum_{\mu=l+1}^{N}V^{\alpha N}_{n^*l,\mu l}(t)\chi_{\mu lm}\left(\zeta',\vec{r}\right), \tag{4}$$

where $\alpha=1,0,-1,-2,\ldots$ and $t=(\zeta-\zeta')/(\zeta+\zeta')$. Here, the expansion coefficients $V^{\alpha N}$ are determined as follows:

$$V^{\alpha N}_{n^*l,n'l}(t)=\sum_{\mu=l+1}^{N}\Omega^{\alpha l}_{n'\mu}(N)\frac{\Gamma(n^*+\mu-\alpha+1)}{\left[\Gamma(2n^*+1)\Gamma(2\mu-2\alpha+1)\right]^{1/2}}\times(1+t)^{n^*+\frac{1}{2}}(1-t)^{\mu-\alpha+\frac{1}{2}}, \tag{5}$$

$$\Omega_{n\kappa}^{\alpha l}(N) = \left[\frac{[2(k-\alpha)]!}{(2\kappa)!}\right]^{1/2} \sum_{\mu=\max(n,\kappa)}^{N} (2\mu)^{\alpha} \omega_{\mu n}^{\alpha l} \omega_{\mu\kappa}^{\alpha l}, \tag{6}$$

$$\omega_{n\mu}^{\alpha l} = (-1)^{\mu-l-1} \left[\frac{(\mu+l+1)!}{(2n)^{\alpha}(\mu+l+1-\alpha)!} F_{\mu+l+1-\alpha}(n+l+1-\alpha) \times F_{\mu-l-1}(n-l-1) F_{\mu-l-1}(2\mu)\right]^{1/2}. \tag{7}$$

We notice that in the case of integer values of n^* $(n^* = n)$ the coefficients $V_{n^*l,\mu l}^{\alpha N}(t)$ for $t = 0$ are reduced to the Kronecker symbol, i.e.,

$$V_{n^*l,\mu l}^{\alpha N}(0) = \delta_{n\mu}\delta_{nN}. \tag{8}$$

In order to evaluate the integral (1) we use equation (4) for the one-center expansion of NISTOs in terms of ISTOs. Then, it is easy to obtain the following expressions through the overlap integrals over ISTOs with the same and different screening constants, respectively:

$$S_{n^*lm,n'^*l'm}(p,t) = \lim_{N,N'\to\infty} \sum_{\mu=l+1}^{N} \sum_{\mu'=l'+1}^{N'} V_{n^*l,\mu l}^{\alpha N}(t) V_{n'^*l',\mu'l'}^{\alpha N'} S_{\mu lm,\mu'l'm}\left(p',0\right), \tag{9}$$

$$S_{n^*lm,n'^*l'm}(p,t) = \lim_{N,N'\to\infty} \sum_{\mu=l+1}^{N} \sum_{\mu'=l'+1}^{N'} V_{n^*l,\mu l}^{\alpha N} V_{n'^*l',\mu'l'}^{\alpha N'} S_{\mu lm,\mu'l'm}(p,t), \tag{10}$$

where $p = \frac{R}{2}(\zeta+\zeta')$, $p' = R\zeta'$, $V_{n^*l,\mu l}^{\alpha N} \equiv V_{n^*l,\mu l}^{\alpha N}(0)$, $S_{n^*lm,n'^*l'm}(p,t) \equiv S_{n^*lm,n'^*l'm}\left(\zeta,\zeta';R\right)$, and $S_{nlm,n'l'm}(p,t) \equiv S_{nlm,n'l'm}\left(\zeta,\zeta';R\right)$. The overlap integrals $S_{nlm,n'l'm}(p,t)$ between the normalized ISTOs occurring in equations (9) and (10) are defined as

$$S_{nlm,n'l'm}(p,t) = \int \chi_{nlm}^{*}(\zeta,\vec{r}_a)\chi_{n'l'm}\left(\zeta',\vec{r}_b\right)\, \mathrm{d}V. \tag{11}$$

For the calculation of overlap integrals over ISTOs, equation (11), in our previous works [10, 11] the sets of recurrence relations and analytical formulas were presented. This algorithm is especially useful for the computation of overlap integrals for large quantum numbers of ISTOs appearing in the series expansion formulas for the multicenter multielectron molecular integrals.

The overlap integrals with NISTOs, equations (9) and (10), can be calculated by the use of computer programs for the overlap integrals over ISTOs presented in [10–13].

Table 1
The comparative values of the two-center overlap integrals over NISTOs in lined-up coordinate systems for various values of parameters and $N = N' = 17$.

								Equations (9) and (10) in Turbo Pascal 7.0	Equations (9) and (10) in Mathematica 5			
n^*	l	$n'*$	l'	m	p	p'	t	$\alpha = 0$	$\alpha = 0$	$\alpha = 1$	$\alpha = -1$	Reference [6]
7.3	4	7.3	4	4	2	1	0.5	1.01734314959344E-01	1.017343148889628E-01	1.017343260081906E-01	1.0173435184322346E-01	1.101734314960E-01
3.8	0	5.5	0	0	2.31	1.54	11/33	2.90802046505438E-01	2.908020459831434E-01	2.908020430948767E-01	2.90802093240919E-01	2.90802069369E-01
5.7	1	3.8	1	1	2.38	1.82	4/17	8.66889506331727E-01	8.668895066998231E-01	8.668895064966607E-01	8.668895066998231E-01	8.66889476942E-01
7.7	4	6.6	4	4	6	7.5	−0.25	2.34831461718284E-01	2.3483146019118006E-01	2.3483145709511305E-01	2.348314694545564E-01	2.34831448531E-01
4.1	2	3.7	2	2	10.25	9	5/41	2.93541966880792E-02	2.935419701322025E-02	2.9354189813759587E-02	2.93541978255766E-02	2.93217486171E-02
4.6	3	3.7	2	2	4	2.8	0.3	3.36298814615661E-01	3.362988647194424E-01	3.3629890916449356E-01	3.3629882528623E-01	
7.2	6	7.8	6	6	8	7.84	0.02	1.80791756875938E-01	1.8079441278114533E-01	1.80794413147871E-01	1.8079441276532351E-01	
8.7	4	8.8	5	4	0.008	0.0048	0.4	−4.50210194347972*E*-04	−4.5021019516522707E-04	−4.502101948196665E-04	−4.5021019298838096E-04	
13.2	7	11.5	7	6	0.06	0.054	0.1	9.84040136524412E-01	9.840401364384664E-01	9.840401364380328E-01	9.840401364358113E-01	
15.5	10	12.8	10	10	0.06	0.054	0.1		9.96889730182741E-01	9.96889728830528E-01	9.968897287341084E-01	
15.5	14	15.8	14	14	0.06	0.054	0.1		8.237701856862741E-01	8.237129583400589E-01	8.237530045411975E-01	

Table 2
Convergence of the series expansion relations for overlap integrals over NISTOs as a function of summation limits for $N = N'$.

N	Equation (9) for $S_{5.711,3.811}(2.38, 4/17)$	Equation (10) for $S_{13.276,11.576}(0.06, 0.1)$
11	0.8668894475103913	0.9840682484939571
12	0.866889464207532	0.9840407293306768
13	0.8668894874545716	0.9840401363432201
14	0.8668895007016616	0.9840401350076602
15	0.8668895055602754	0.9840401363152588
16	0.8668895066908764	0.9840401364339384
17	0.8668895066998231	0.9840401364384664

4. Numerical results and discussion

In this study, we proposed a new technique for the efficient computation of overlap integrals with noninteger n^* STOs, based on the usage of complete sets of Ψ^{α}-ETOs. An analysis of the numerical aspects and several numerical tests confirmed that the convergence and the numerical stability of the relevant formulas are guaranteed. Besides having an excellent convergence rate, the proposed method is perfectly general, valid for arbitrary values of quantum numbers, screening constants and internuclear distances. On the basis of formulae (9) and (10) we constructed a program for the computation of overlap integrals over NISTOs using Turbo Pascal 7.0 language and Mathematica 5.0 international mathematical software. One can determine the accuracy of computer results obtained in this work for the overlap integrals over NISTOs using different sets of Ψ^{α}-ETOs. The examples of computer calculation for the overlap integrals over NISTOs are shown in table 1. As can be seen from table 1 that the calculated values of overlap integrals over NISTOs for $\alpha = 1, 0, -1$ show a good rate of convergence with the literature for the arbitrary values of parameters. Greater accuracy is attainable by the use of more terms in the series expansion formulas (9) and (10). The better accuracies can be obtained, if required, by the use of large number of summation terms.

Table 2 lists partial summations corresponding to progressively increasing upper summation limits of equations (9) and (10) for $N = N'$. We see from table 2 that the equations (9) and (10) display the most rapid convergence to the numerical result, with eleven digits stable and correct by the 17th terms in the infinite summations.

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