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Calculation of two-center nuclear attraction integrals of Slater type orbitals with noninteger principal quantum numbers using Guseinov's one-center expansion formulas and Löwdin-α radial function

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ABSTRACT

In this work, by the use of Guseinov's one-center expansion formulas and Löwdin-α radial function, the series expansion relations in molecular coordinate system are established for the two-center nuclear attraction integrals of noninteger n^* Slater type orbitals in terms of basic two-center nuclear attraction integrals over integer n Slater functions. The Löwdin α-radial function convoluted with the Guseinov's one-center expansion formulas is one of the most important ingredients for accurate and efficient implementation of electronic structure calculation methods regardless of Hartree–Fock–Roothaan (HFR) method. The proposed algorithm shows better performance in arbitrary quantum numbers, screening constants and location of orbitals leading to significantly reduced run times.

1. Introduction

The accurate calculation of multicenter molecular integrals over Slater type orbitals with noninteger principal quantum numbers (NISTOs) plays an important role in the development of ab initio and semi-empirical methods for the studying properties of the atoms and molecules [1,2]. It is well known that the STOs give more accurate results because they fulfill a cusp condition and have correct asymptotic behavior. Many authors have worked on evaluating multicenter molecular integrals over STOs with integer principal quantum numbers (ISTOs) including the Fourier transform [3–5], the B-function [6,7] and Guseinov's symmetrical and unsymmetrical one-range addition methods [8,9], etc. Unfortunately, the literature on the evaluation of multicenter molecular integrals over NISTOs in HFR theory is not very abundant [10,11]. Recently, efficient approximation formulae for multicenter molecular integrals over NISTOs have been proposed [12]. By the use of complete orthonormal sets of Ψ^{α}-exponential type orbitals (Ψ^{α}-ETOs, $\alpha = 2,1,0,-1,-2,\ldots$) the NISTOs can be expressed in terms of ISTOs [13,14]. With this spirit in mind, we calculate the two-center nuclear attraction integrals over NISTOs using the convolution between a Guseinov's one-center expansion formula and a Löwdin-α radial function which makes the offered algorithm faster and more accurate than the other known algorithms. In addition, some numerical tests have been performed for the computation of the two-center nuclear attraction integrals over NISTOs.

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2. Theory

The two-center nuclear attraction integrals over NISTOs are defined as:

$$J_{n^*lm,n^{*\prime}l^\prime m^\prime}(\zeta,\zeta^\prime,\vec{R}) = \int \chi^*_{n^*lm}(\zeta,\vec{r}_a)\frac{1}{r_b}\chi_{n^{*\prime}l^\prime m^\prime}(\zeta^\prime,\vec{r}_a)dV, \tag{1}$$

where $\vec{R} \equiv \vec{R}_{ab} = \vec{r}_a - \vec{r}_b$ and,

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

Here, the $S_{lm}(\theta,\varphi)$ are the complex ($S_{lm} \equiv Y_{lm}$) or real spherical harmonics. We notice that the definition of phases in this work for the complex spherical harmonics ($Y^*_{lm} = Y_{l-m}$) differs from the Condon–Shortley phases [15] by the sign factor $(-1)^m$.

For the calculation of integrals (1), we use the following one-center expansion formula suggested by Guseinov [16,17]:

$$\chi_{n^*lm}(\zeta,\vec{r}) = \lim_{N\to\infty}\sum_{n''=l+1}^{N} V^{\alpha N}_{n^*l,n''l}\chi_{n''lm}(\zeta,\vec{r}), \tag{3}$$

where $\alpha = 2,1,0,-1,-2,\ldots$ The normalized ISTOs $\chi_{nlm}(\zeta,\vec{r})$ and expansion coefficients $V^{\alpha N}$ occurring in Eq. (3) are determined by:

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

$$V^{\alpha N}_{n^*l,n'l} = \sum_{n''=l+1}^{N}\Omega^{\alpha l}_{n'n''}(N)\frac{\Gamma(n^*+n''-\alpha+1)}{[\Gamma(2n^*+1)\Gamma(2n''+1)]^{1/2}} \tag{5}$$

$$\Omega^{\alpha l}_{n\kappa}(N) = \sum_{n'=\max(n,\kappa)}^{N}(2n')^{\alpha}\omega^{\alpha l}_{n'n}\omega^{\alpha l}_{n'\kappa} \tag{6}$$

$$\omega^{\alpha l}_{nn'} = (-1)^{n'-l-1}\left[\frac{(n'+l+1)!}{(2n)^{\alpha}(n'+l+1-\alpha)!}F_{n'+l+1-\alpha}(n+l+1-\alpha)F_{n'-l-1}(n-l-1)F_{n'-l-1}(2n')\right]^{1/2}. \tag{7}$$

Taking into account Eq. (3) in (1) we obtain the following relation in terms of two-center nuclear attraction integrals with ISTOs:

$$J_{n^*lm,n^{*\prime}l^\prime m^\prime}(\zeta,\zeta^\prime;\vec{R}) = \lim_{N,N^\prime\to\infty}\sum_{n''=l+1}^{N}\sum_{n'''=l^\prime+1}^{N^\prime} V^{\alpha N}_{n^*l,n''l}V^{\alpha N^\prime}_{n^{*\prime}l^\prime,n'''l^\prime}J_{n''lm,n'''l^\prime m^\prime}(\zeta,\zeta^\prime;\vec{R}), \tag{8}$$

where $J_{nlm,n^\prime l^\prime m^\prime}(\zeta,\zeta^\prime;\vec{R})$ are the two-center nuclear attraction integrals over ISTOs determined by:

$$J_{nlm,n^\prime l^\prime m^\prime}(\zeta,\zeta^\prime;\vec{R}) = \int \chi^*_{nlm}(\zeta,\vec{r}_a)\frac{1}{r_b}\chi_{n^\prime l^\prime m^\prime}(\zeta^\prime,\vec{r}_a)dV. \tag{9}$$

For the evaluation of this integral we use the Guseinov's one-center charge density expansion formula [17–19]. Then, we obtain:

$$J_{nlm,n^\prime l^\prime m^\prime}(\zeta,\zeta^\prime;\vec{R}) = \sum_{v=|l-l^\prime|}^{l+l^\prime}\sum_{\sigma=-v}^{v} W_{nlm,n^\prime l^\prime m^\prime,\mu v\sigma}(\zeta,\zeta^\prime;z)J_{\mu v\sigma}(z,\vec{R}). \tag{10}$$

Here, $J_{nlm}(\zeta,\vec{R})$ are the basic two-center nuclear attraction integrals defined by:

$$J_{nlm}(\zeta,\vec{R}) = \frac{1}{\sqrt{4\pi}}\int \chi^*_{nlm}(\zeta,\vec{r}_a)\frac{1}{\vec{r}_b}dV \tag{11}$$

See Refs. [12,17] for the exact definition of the quantity $W_{nlm,n^\prime l^\prime m^\prime,\mu v\sigma}(\zeta,\zeta^\prime;z)$.

For the calculation of basic two-center nuclear attraction integral we use the Löwdin's radial function method set out in Refs. [20–22]. Then, we obtain:

$$J_{nlm}(\zeta,\vec{R}) = 2^n\sqrt{\frac{2\pi}{\zeta(2n)!}}\sum_{i=0}^{n+l}\sum_{j=0}^{n} j!C^{nl0}_0(i,j)\times\left[\sum_{k=0}^{j}\frac{1}{(j-k)!}(R\zeta)^{i+j-l-k-1}((-1)^i-(-1)^{j-k-1}) - 2e^{-\zeta R}(R\zeta)^{i-l-1}\right]S_{lm}(\theta,\varphi). \tag{12}$$

For the rapid and accurate calculation of the $C^{nlm}_{l^\prime}(i,j)$ coefficients recently we have proposed a new algorithm using binomial coefficients [23].