Internet Electronic Journal of Molecular Design **2004**, *3*, 83–92 ISSN 1538–6414
BIOCHEM Press http://www.biochempress.com

Inter*net* Electronic Journal of
Molecular Design

February 2004, Volume 3, Number 2, Pages 83–92

Editor: Ovidiu Ivanciuc

Special issue dedicated to Professor Nenad Trinajstić on the occasion of the 65th birthday
Part 8

Guest Editor: Douglas J. Klein

Molecular Three–Center Electronic Integrals Over Slater–Type Orbitals Evaluated Using Nonlinear Transformations

Hassan Safouhi[1] and Lilian Berlu[2]

[1] Faculté Saint–Jean/University of Alberta. 8406, 91street. Edmoton (AB), Canada T6C 4G9
[2] Laboratoire SEESIB, UMR 6504. Université Blaise Pascal, 63177 Aubière Cedex, France

Received: October 16, 2003; Revised: January 13, 2004; Accepted: February 18, 2004; Published: February 29, 2004

Citation of the article:
H. Safouhi and L. Berlu, Molecular Three–Center Electronic Integrals Over Slater–Type Orbitals Evaluated Using Nonlinear Transformations, *Internet Electron. J. Mol. Des.* **2004**, *3*, 83–92, http://www.biochempress.com.

Internet Electronic Journal of Molecular Design

BioChem Press
http://www.biochempress.com

Molecular Three–Center Electronic Integrals Over Slater–Type Orbitals Evaluated Using Nonlinear Transformations[#]

Hassan Safouhi[1,]* and Lilian Berlu[2]

[1] Faculté Saint–Jean/University of Alberta. 8406, 91street. Edmoton (AB), Canada T6C 4G9
[2] Laboratoire SEESIB, UMR 6504. Université Blaise Pascal, 63177 Aubière Cedex, France

Received: October 16, 2003; Revised: January 13, 2004; Accepted: February 18, 2004; Published: February 29, 2004

Internet Electron. J. Mol. Des. **2004**, *3* (2), 83–92

Abstract

Motivation. Molecular three–center electronic integrals over Slater–type orbitals are required for *ab initio* and density functional theory (DFT) molecular structure calculations. They occur in many millions of terms, even for small molecules and require rapid and accurate evaluation.

Method. In this work, we present a very efficient approach based on properties of Bessel and sine functions and on nonlinear transformations for accurate numerical evaluation of integrals under consideration.

Results. Numerical results are obtained for three–center nuclear and three–center two–electron Coulomb and hybrid integrals over Slater–type orbitals for HCN, C_2H_2, Zn_3, BH_3, and CH_4 molecules. We also performed the same calculations using existing codes to show the accuracy of the new algorithm.

Conclusions. The results obtained in this work illustrate the efficiency of the algorithm based on the $S\overline{D}$ approach, which will lead to a definitive suite of *ab initio* Slater software.

Keywords. Molecular electronic integrals; Slater type orbitals; B functions; nonlinear transformations; convergence accelerators; numerical integration.

Abbreviations and notations

STO, Slater–type orbital
ETO, exponential–type orbital
GTO, Gaussian–type orbital

1 INTRODUCTION

Three–center nuclear attraction, hybrid and three–center two–electron Coulomb integrals contribute to the total energy of the molecule which is required to a precision sufficient for small fractional changes to be evaluated reliably. In practice, the precision threshold for the total energy is of order 10^{-3} atomic units and therefore individual integrals must be accurate to 10^{-8} to 10^{-10} au.

STOs [1,2] are chosen for the expansion of atomic orbitals. These functions have a dominating position among ETOs, due to the fact that their analytical expression is very simple. STOs are better

---

[#] Dedicated to Professor Nenad Trinajstić on the occasion of the 65th birthday.
* Correspondence author; phone: 1–780–485–8631; fax: 1–780–465–8760; E–mail: hassan.safouhi@ualberta.ca.

suited than GTOs to represent electron wave functions near the nucleus and at long range, provided that multicenter integrals using such functions could be computed efficiently.

STOs can be expressed as finite linear combinations of B functions [3,4,5]. The Fourier transforms of these B functions are exceptionally simple [6,7] and well adapted to the Fourier transform method [8,9], which led to analytical expressions for multicenter electronic integrals over B functions. These analytical expressions involve two–dimensional integral representations, which present severe numerical and computation difficulties. The integrand of the inner semi–infinite integral is a very oscillating function due to the presence of spherical Bessel function.

The molecular integrals under consideration are to be evaluated via a numerical quadrature of integral representations in terms of nonphysical integration variables. These integral representations were derived with the help of the Fourier transformation method.

The semi–infinite integrals can be transformed into infinite series of integrals of alternating sign. These series are slowly convergent and this is why their use is prohibitively long for sufficient accuracy. The epsilon algorithm of Wynn or Levin's u transform, accelerate the convergence of infinite series but in the case of the semi–infinite integrals involved in the analytical expressions of molecular integrals, the calculation times for a sufficient accuracy still long. Therefore new numerical integration techniques are required.

Recently, we developed an efficient and rapid algorithm based on the $S\bar{D}$ approach [10,11]. It is shown that the $S\bar{D}$ approach is much more efficient and rapid compared with the alternative cited above. The application of the nonlinear $\bar{D}$ transformation of Sidi [12,13] is greatly simplified with the introduction of the $S\bar{D}$ approach. Recurrence relations were developed to control the degree of the accuracy and for a better stability of the algorithm [14,15].

In the present work, we performed calculation for HCN, C_2H_2, Zn_3, BH_3, and CH_4 molecules, to show that the progress represented by the $S\bar{D}$ approach is another useful step in developing software for evaluating molecular integrals over STOs.

2 Definitions and Properties

Slater–type orbital (STOs) are given by [1,2]:

$$\chi_{n,l}^{m}(\xi,r)=\sqrt{\frac{(2\xi)^{2n+1}}{(2n)!}}\,r^{n-1}e^{-\xi r}Y_{l}^{m}(\theta_r,\varphi_r) \tag{1}$$

where $Y_l^m(\theta_r,\varphi_r)$ stands for the spherical harmonic.

The B function is defined as follows [4,5]:

$$B_{n,l}^{m}(\xi,r)=\frac{(\xi r)^{l}}{2^{n+l}(n+l)!}\hat{k}_{n-\frac{1}{2}}(\xi r)Y_{l}^{m}(\theta_{r},\varphi_{r}) \tag{2}$$

where $\hat{k}_{n-\frac{1}{2}}(\zeta r)$ stands for the reduced Bessel function.

The three–center nuclear attraction integral over STOs is defined by :

$$I_{a}=\left\langle \chi_{n1,l1}^{m1}(\xi_{1},r)\left|\frac{1}{|r-R_{1}|}\right|\chi_{n2,l2}^{m2}(\xi_{2},r-R_{2})\right\rangle \tag{3}$$

The three–center two–electron Coulomb integral over STOs is defined by :

$$I_{r}=\left\langle \chi_{n1,l1}^{m1}(\xi_{1},r_{1}-R_{1})\chi_{n3,l3}^{m3}(\xi_{3},r_{2}-R_{3})\left|\frac{1}{|r_{1}-r_{2}|}\right|\chi_{n2,l2}^{m2}(\xi_{2},r_{1}-R_{1})\chi_{n4,l4}^{m4}(\xi_{4},r_{2}-R_{4})\right\rangle \tag{4}$$

The hybrid integral over STOs is defined by :

$$I_{h}=\left\langle \chi_{n1,l1}^{m1}(\xi_{1},r_{1}-R_{1})\chi_{n3,l3}^{m3}(\xi_{3},r_{2}-R_{1})\left|\frac{1}{|r_{1}-r_{2}|}\right|\chi_{n2,l2}^{m2}(\xi_{2},r_{1}-R_{1})\chi_{n4,l4}^{m4}(\xi_{4},r_{2}-R_{4})\right\rangle \tag{5}$$

3 Analytical and Numerical Evaluations of Molecular Integrals

STOs can be expressed as finite linear combination in terms of B functions. From this, it follows that the molecular integrals over STOs can be expressed as finite linear combinations of integrals over B functions.

The Fourier transformation method allowed the development of analytic expressions for molecular multicenter integrals over B functions [8,9]. The obtained analytic expressions turned out to be extremely difficult to evaluate because of the presence of two–dimensional integral representations. These integral representations are the principal source of severe numerical and computation difficulties in the evaluation of molecular integrals. The inner semi–infinite integrals, which are highly oscillatory because of the presence of spherical Bessel functions, are of the form :

$$\int_{0}^{\infty} h(x)\frac{\hat{k}(R\,\gamma(s,x))}{\gamma(s,x)^{n_\gamma}}j_{\lambda}(vx)\,dx \tag{6}$$

where h(x) is a non–oscillating function.

Recently, we developed a very efficient, rapid and simple algorithm for the numerical evaluation of the above semi–infinite integrals [14,15]. This algorithm is based on the $S\overline{D}$ approach [10,11], which consists on transforming the semi–infinite integrals involving spherical Bessel functions into semi–infinite integrals involving the simple sine function as follows:

$$\frac{1}{v^{\lambda+1}}\int_0^{\infty}\left(\frac{d}{xdx}\right)^{\lambda}\left[x^{\lambda-1}h(x)\frac{\hat{k}(R\,\gamma(s,x))}{\gamma(s,x)^{n\gamma}}\right]\sin(\ vx\ )\,dx \tag{7}$$

The strong oscillations of the integrands are thus reduced. Once the semi–infinite integral involving the spherical Bessel function is transformed into a semi–infinite integral involving the sine function, we apply the nonlinear $\overline{D}$ transformation of Sidi [12,13] using Cramer's rule as suggested in [12].

The approximation of the semi–infinite integral (7) is given by:

$$S\overline{D}_n^{(2,j)}=\frac{1}{v^{\lambda+1}}\frac{\sum_{i=0}^{n+1}C_{n+1}^{i}(1+i+j)^{n}F(x_{i+j})/\left[x_{i+j}^{2}G(x_{i+j})\right]}{\sum_{i=0}^{n+1}C_{n+1}^{i}(1+i+j)^{n}/\left[x_{i+j}^{2}G(x_{i+j})\right]} \tag{8}$$

where the functions F(x) and G(x) are given by :

$$F(t)=\int_0^{t}\left(\frac{d}{xdx}\right)^{\lambda}\left[x^{\lambda-1}h(x)\frac{\hat{k}(R\,\gamma(s,x))}{\gamma(s,x)^{n\gamma}}\right]\sin(\ vx\ )\,dx \tag{9}$$

and

$$G(x)=\left(\frac{d}{xdx}\right)^{\lambda}\left[x^{\lambda-1}h(x)\frac{\hat{k}(R\,\gamma(s,x))}{\gamma(s,x)^{n\gamma}}\right] \tag{10}$$

For the computation of Eq. (8), we developed recurrence relations for both the numerator and the denominator [14]. This result led to a better control of the degree of accuracy and to a better stability of the algorithm [14,15].

Table 1. Exponents of STOs for a series of orbitals

Orbitals	Zn	S	B	C	N	F	H
1s	28.979194	15.396775	4.649767	5.636105	6.621925	8.593356	1.00000
2s	9.212368	4.468108	1.076139	1.346562	1.612481	2.154463	
2p	13.015418	5.987867	1.226030	1.581274	1.929475	2.561510	
3s	4.615722	1.723750					
3p	4.754359	1.684294					
3d	4.660219	1.584294					
4s	0.966290						

Table 2. The Geometry used for the molecular calculations

Molecules	Geometry	Cartesian Coordinates
	Linear	H(0.0, 0.0, –a)
HCN	H–C = a = 2.000 a.u.	C(0.0, 0.0, 0.0)
	C–N = b = 2.187 a.u.	N(0.0, 0.0, b)
		H^1(0.0, 0.0, –a–b/2)
	Linear	C^1(0.0, 0.0, –b/2)
C_2H_2	H–C = a = 2.002 a.u.	C^2(0.0, 0.0, b/2)
	C–C = b = 2.281 a.u.	H^2(0.0, 0.0, a+b/2)
	Equilateral Triangle, Planar	Zn^1(b, 0.0, 0.0)
Zn_3	Zn–Zn = a = 5.03593 a.u.	Zn^2(–b/2, a/2, 0.0)
	b = 2.90749 a.u.	Zn^3(–b/2, –a/2, 0.0)
		B (0.0, 0.0, 0.0)
	Equilateral Triangle, Planar	H^1(0.0, 0.0, a)
BH_3	B–H = a = 2.250 a.u.	H^2(b/2, 0.0, –a/2)
	b = 3.897 a.u.	H^3(–b/2, 0.0, –a/2)
		C (0.0, 0.0, 0.0)
	Regular Tetrahedron	H^1(b, b, b)
CH_4	C–H = a = 2.0665 a.u.	H^2(b,–b, –b)
	b = 1.1931 a.u.	H^3(–b,b, –b)
		H^4(–b,–b, b)

4 RESULTS AND DISCUSSION

For the computation of the function G(x), we used useful properties of the reduced Bessel function which are given by :

$$\hat{k}_{n+\frac{1}{2}}(x)=(2n-1)\hat{k}_{n-\frac{1}{2}}(x)+x^2\hat{k}_{(n-1)-\frac{1}{2}}(x) \tag{11}$$

and

$$\left(\frac{d}{xdx}\right)^m\left[\frac{\hat{k}_{n+\frac{1}{2}}(x)}{x^{2n+1}}\right]=(-1)^m\left[\frac{\hat{k}_{n+m+\frac{1}{2}}(x)}{x^{2(n+m)+1}}\right] \tag{12}$$

For the computation of the function F(x), we transform the finite integral as follows :

$$F(x_i)=\sum_{l=0}^{i-1}\int_{x_l}^{x_{l+1}}\left(\frac{d}{xdx}\right)^{\lambda}\left[x^{\lambda-1}h(x)\frac{\hat{k}(R\gamma(s,x))}{\gamma(s,x)^{n_\gamma}}\right]\sin(\ vx\ )\,dx \tag{13}$$

For the numerical evaluation of each term of the finite sum in the right hand side of equation (13), we used the following procedure :

When $v \geq 1$, we used Gauss–Legendre quadrature of order 20.

Table 3. Values obtained for the three–center nuclear attraction integrals over STOs

Molecules	Integrals	Values
HCN	$\langle 1s^{N} \mid 1/R_{NH} \mid 1s^{C}\rangle$	0.381875917(–4)
	$\langle 2s^{N} \mid 1/R_{NH} \mid 1s^{C}\rangle$	0.343932422(–1)
	$\langle 2p_z^{N} \mid 1/R_{NH} \mid 1s^{C}\rangle$	–0.460301915(–1)
	$\langle 2p_z^{N} \mid 1/R_{NH} \mid 2p_z^{C}\rangle$	–0.846763083(–1)
	$\langle 2p_{+1}^{N} \mid 1/R_{NH} \mid 2p_{+1}^{C}\rangle$	0.908692109(–1)
C_2H_2	$\langle 1s^{C1} \mid 1/R_{C1H1} \mid 1s^{C2}\rangle$	0.588771147(–4)
	$\langle 1s^{C1} \mid 1/R_{C1H1} \mid 2s^{C2}\rangle$	0.360164917(–1)
	$\langle 2s^{C1} \mid 1/R_{C1H1} \mid 2s^{C2}\rangle$	0.197610020(0)
	$\langle 2p_z^{C1} \mid 1/R_{C1H1} \mid 2s^{C2}\rangle$	0.883417584(–1)
	$\langle 2p_z^{C1} \mid 1/R_{C1H1} \mid 2p_z^{C2}\rangle$	–0.663963358(–1)
	$\langle 2p_{+1}^{C1} \mid 1/R_{C1H1} \mid 2p_{+1}^{C2}\rangle$	0.104661604(0)
Zn_3	$\langle 3s^{Zn1} \mid 1/R_{Zn1Zn3} \mid 3s^{Zn2}\rangle$	0.256568979(–5)
	$\langle 3p_z^{Zn1} \mid 1/R_{Zn1Zn3} \mid 3p_z^{Zn2}\rangle$	0.208995809(–6)
	$\langle 3d_z^{Zn1} \mid 1/R_{Zn1Zn3} \mid 3d_z^{Zn2}\rangle$	0.182968766(–5)
BH_3	$\langle 1s^{B} \mid 1/R_{BH2} \mid 1s^{H1}\rangle$	0.360887086(–1)
	$\langle 2s^{B} \mid 1/R_{BH2} \mid 1s^{H1}\rangle$	0.188340741(0)
	$\langle 2p_z^{B} \mid 1/R_{BH2} \mid 1s^{H1}\rangle$	0.135277743(0)
CH_4	$\langle 1s^{C} \mid 1/R_{CH2} \mid 1s^{H1}\rangle$	0.358308926(–1)
	$\langle 2s^{C} \mid 1/R_{CH2} \mid 1s^{H1}\rangle$	0.226630147(0)
	$\langle 2p_z^{C} \mid 1/R_{CH2} \mid 1s^{H1}\rangle$	0.583812120(–1)

When $10^{-15} \leq v < 1$, we divided the finite interval $[x_i, x_{i+1}]$ into M subintervals, where $M = \min(v^{-2}, N)$. The finite integral, which occur in the right hand side of equation (13), can be re–written as :

$$\sum_{k=1}^{M} \int_{\tilde{x}_{k-1}}^{\tilde{x}_k} \left(\frac{d}{xdx}\right)^{\lambda} \left[x^{\lambda-1} h(x) \frac{\hat{k}(R\gamma(s,x))}{\gamma(s,x)^{n_\gamma}} \right] \sin(vx)\, dx \qquad (14)$$

For the evaluation of each finite integral involving in the above finite sum, we used Gauss–Legendre quadrature of order 20.

The value of M was determined after a series of numerical tests on different values of v. In the case of three–center nuclear attraction integrals $N = 100$, and in the case of hybrid and three–center two–electron Coulomb integrals $N = 200$.

Table 1 contains values of screening parameters that occur in the analytic expression of STOs. Table 2 contains the geometry used for the calculations that we performed in the present work. Table 3 contains values obtained for three–center nuclear attraction integrals over STOs. Table 4 contains values obtained for hybrid integrals over STOs. Table 5 contains values obtained for two–electron three–center Coulomb integrals over STOs. In Tables 4 and 5, ValuesSTOnG are obtained using ADGGSTNGINT code developed by Rico *et al.* [17].

Table 4. Values obtained for the hybrid integrals over STOs

Molecules	Integrales	Values	Values STOnG
HCN	$<1s^N\ 1s^N \vert\ 1s^N\ 1s^c>$	0.189680244(–3)	0.189611087(–3)
	$<2s^N\ 2s^N \vert\ 1s^N\ 1s^c>$	0.887205039(–4)	0.887224163(–4)
	$<2p_z^N\ 2p_z^N \vert\ 1s^N\ 1s^c>$	0.111238306(–3)	0.110883723(–3)
	$<2p_{+1}^N\ 2p_{+1}^N \vert\ 1s^N\ 1s^c>$	0.953438610(–4)	0.955261424(–4)
	$<2p_z^N\ 2p_z^N \vert\ 1s^N\ 2p_z^c>$	0.924888121(–1)	0.924884562(–1)
	$<2p_{+1}^N\ 2p_{+1}^N \vert\ 1s^N\ 2p_z^c>$	0.918988732(–1)	0.918985099(–1)
C_2H_2	$<1s^{H1}\ 1s^{H1} \vert\ 1s^{H1}\ 1s^{C1}>$	0.394551433(–1)	0.394551427(–1)
	$<1s^{H1}\ 1s^{H1} \vert\ 1s^{H1}\ 2s^{C1}>$	0.336441046(0)	0.336441060(0)
	$<1s^{H1}\ 1s^{H1} \vert\ 1s^{H1}\ 2p_z^{C1}>$	–0.331044695(0)	–0.331044702(0)
	$<1s^{C1}\ 1s^{C1} \vert\ 1s^{C1}\ 1s^{C2}>$	0.191531264(–3)	0.191349811(–3)
	$<1s^{C1}\ 1s^{C1} \vert\ 1s^{C1}\ 2p_z^{C2}>$	–0.263608734(0)	–0.263607524(0)
	$<2p_z^{C1}\ 1s^{C1} \vert\ 1s^{C1}\ 2p_z^{C2}>$	–0.248837120(–2)	–0.248839248(–2)
	$<2p_z^{C1}\ 2p_z^{C1} \vert\ 1s^{C1}\ 2p_z^{C2}>$	–0.869945452(–1)	–0.869943801(–1)
	$<2p_z^{C1}\ 2p_z^{C1} \vert\ 2p_z^{C1}\ 2p_z^{C2}>$	–0.199708012(0)	–0.199708010(0)
Zn_3	$<4s^{Zn1}\ 4s^{Zn1} \vert\ 4s^{Zn1}\ 4s^{Zn2}>$	0.118817489(0)	0.118817489(0)
	$<4s^{Zn1}\ 4s^{Zn1} \vert\ 4s^{Zn1}\ 4s^{Zn2}>$	–0.327900521(–3)	–0.327844315(–3)
	$<3p_z^{Zn1}\ 3d_z^{Zn1} \vert\ 3p_z^{Zn1}\ 3d_z^{Zn2}>$	–0.113150435(–6)	–0.105624731(–6)
BH_3	$<1s^B\ 1s^B \vert\ 1s^B\ 1s^{H1}>$	0.159929779(0)	0.159928754(0)
	$<2s^B\ 2s^B \vert\ 2s^B\ 1s^{H1}>$	0.233221831(0)	0.233221808(0)
	$<2p_z^B\ 2p_z^B \vert\ 2p_z^B\ 1s^{H1}>$	0.240407770(0)	0.240407770(0)
CH_4	$<1s^C\ 1s^{H1} \vert\ 1s^{H1}\ 1s^{H1}>$	0.361522242(–1)	0.361522237(–1)
	$<2s^C\ 1s^{H1} \vert\ 1s^{H1}\ 1s^{H1}>$	0.325746729(0)	0.325746742(0)
	$<2p_z^C\ 1s^{H1} \vert\ 1s^{H1}\ 1s^{H1}>$	0.186412471(0)	0.186412475(0)

Table 5. Values obtained for the two–electron three–center Coulomb integrals over STOs

Molecules	Integrals	Values	Values STOnG
HCN	$<1s^N\ 1s^N \vert\ 1s^C\ 1s^H>$	0.350683920(–1)	0.350683917(–1)
	$<2s^N\ 2s^N \vert\ 1s^C\ 1s^H>$	0.340387248(–1)	0.340387246(–1)
	$<2p_z^N\ 2p_z^N \vert\ 1s^C\ 1s^H>$	0.391235521(–1)	0.391235519(–1)
	$<2p_{+1}^N\ 2p_{+1}^N \vert\ 1s^C\ 1s^H>$	0.323982101(–1)	0.323982100(–1)
	$<2p_z^N\ 2p_z^N \vert\ 2p_z^C\ 1s^H>$	–0.108226943(0)	–0.108226943(0)
	$<2p_z^N\ 2p_{+1}^N \vert\ 2p_{+1}^C\ 1s^H>$	–0.590789136(–2)	–0.590789136(–2)
	$<2p_{+1}^N\ 2p_{+1}^N \vert\ 2p_z^C\ 1s^H>$	–0.100877778(0)	–0.100877777(0)
C_2H_2	$<1s^{H1}\ 1s^{H1} \vert\ 1s^{C1}\ 1s^{C2}>$	0.580191754(–4)	0.580191863(–4)
	$<1s^{H1}\ 1s^{H1} \vert\ 1s^{C1}\ 2s^{C2}>$	0.340731246(–1)	0.340731242(–1)
	$<1s^{H1}\ 1s^{H1} \vert\ 2s^{C1}\ 2s^{C2}>$	0.189880723(0)	0.189880723(0)
	$<1s^{H1}\ 1s^{H1} \vert\ 2p_z^{C1}\ 2s^{C2}>$	0.965493985(–1)	0.965493984(–1)
	$<1s^{H1}\ 1s^{H1} \vert\ 2p_z^{C1}\ 2p_z^{C2}>$	–0.747697058(–1)	–0.747697057(–1)
	$<1s^{H1}\ 1s^{H1} \vert\ 2p_{+1}^{C1}\ 2p_{+1}^{C2}>$	0.103010386(0)	0.103010385(0)
Zn_3	$<3s^{Zn1}\ 3s^{Zn1} \vert\ 3s^{Zn2}\ 3s^{Zn3}>$	0.256043336(–5)	0.254437595(–5)
	$<3p_z^{Zn1}\ 3p_z^{Zn1} \vert\ 3p_z^{Zn2}\ 3p_z^{Zn3}>$	0.207524636(–6)	0.206357464(–6)
	$<3d_z^{Zn1}\ 3d_z^{Zn1} \vert\ 3d_z^{Zn2}\ 3d_z^{Zn3}>$	0.184579771(–5)	0.183796183(–5)
BH_3	$<1s^B\ 1s^B \vert\ 1s^{H1}\ 1s^{H2}>$	0.107790849(0)	0.107790849(0)
	$<2s^B\ 2s^B \vert\ 1s^{H1}\ 1s^{H2}>$	0.784265327(–1)	0.784265327(–1)
	$<2p_z^B\ 2p_z^B \vert\ 1s^{H1}\ 1s^{H2}>$	0.839837472(–1)	0.839837472(–1)
CH_4	$<1s^C\ 1s^C \vert\ 1s^{H1}\ 1s^{H2}>$	0.153132818(0)	0.153132818(0)
	$<2s^C\ 2s^C \vert\ 1s^{H1}\ 1s^{H2}>$	0.121381978(0)	0.121381978(0)
	$<2p_z^C\ 2p_z^C \vert 1s^{H1}\ 1s^{H2}>$	0.126914672(0)	0.126914672(0)

The numerical results listed in Tables 3–5 are obtained with HCN, C_2H_2, Zn_3, BH_3, and CH_4 molecules. The molecular integrals over STOs are expressed as finite linear combinations of integrals over the so–called B functions. These integrals over B functions are transformed into analytical expressions in terms of the semi–infinite integrals given by Eq. (6) [8,9]. The $S\overline{D}$ approach was used for the numerical evaluation of these semi–infinite integrals. Note that this approach was demonstrated to be more accurate and more rapid compared with alternatives using the $\overline{D}$ transformation [13], Levin's *u* transform [18] or the epsilon algorithm of Wynn [19].

For the computation of $S\overline{D}_n^{(2,j)}$, we used the recurrence relations developed in [14], which allowed a better control of the degree of accuracy, that we set to 10 correct decimals in the present work. For the numerical evaluation of Gaunt coefficients which occur in the analytic expressions of the molecular integrals, we used the subroutine GAUNT.F developed by Weniger [16]. The spherical harmonics $Y_l^m(\theta_r,\varphi_r)$ are computed using the recurrence formulae presented in [16].

The numerical results obtained in the present work are in complete agreement with those obtained using ADGGSTNGINT code developed by Rico *et al.* [17] (more than 7 similar decimals in Table 4 and more than 9 similar decimals in Table 5). Numerical results obtained for three–center nuclear attraction integrals over B functions [14] are in complete agreement with those obtained by Grotendorst et al. [9]. A comparison with values obtained using the Alchemy package [20] for three–center nuclear attraction integrals over STOs showed that in most cases we obtained 10 similar decimals [14].

The abbreviations $2p_z$, $2p_{+1}$, $3p_z$ and $3d_z$ refer to orbitals defined with the quantum numbers: $n = 2$, $l = 1$, $m = 0$, $n = 2$, $l = 1$, $m = 1$, $n = 3$, $l = 1$, $m = 0$ and $n = 3$, $l = 2$, $m = 0$ respectively. Numbers in parentheses represent powers of 10. All the calculations were performed on a PC–Workstation with an Intel Xeon Processor with 2.4GHz.

4 CONCLUSIONS

Three–center nuclear attraction, hybrid and three–center two–electron Coulomb integrals over STOs are expressed as finite linear combination of integrals over the so–called B functions. With the help of the Fourier transform method, one can express the molecular integrals under consideration in terms of semi–infinite integrals. These semi–infinite integrals turned out to be highly oscillatory and difficult to evaluate to a high pre–determined accuracy.

It was shown that these semi–infinite integrals are suitable to apply the $S\overline{D}$ approach. The spherical Bessel function is replaced by the simple sine function, and this helped the extrapolation process.

A very simple algorithm is now developed and it is now shown to be very efficient. Great simplifications are obtained with the help of the recurrence relations satisfied by the terms that occur in the expression of the approximations $S\bar{D}_n^{(2,j)}$. The numerical and computational study showed that the use of $S\bar{D}$, combined with quadrature rules can also give accurate results in certain regions corresponding to the case where the value of v is very small.

Numerical results are obtained for HCN, C_2H_2, Zn_3, BH_3, and CH_4 molecules. All are precise. These results confirm that this $S\bar{D}$ approach, represents another most significant advance on the road to routine precise and rapid evaluation of these molecular electronic integrals.

5 REFERENCES

[1] J. C. Slater, Atomic shielding constants, *Phys. Rev.* **1930**, *36*, 57.
[2] J. C. Slater, Analytic atomic wave functions, *Phys. Rev.* **1932**, *42*, 33.
[3] Shavitt, The Gaussian function in calculation of statistical mechanics and quantum mechanics, Methods in Computational Physics.2. Quantum.Mechanics, edited by B. Alder, S. Fernbach, M. Rotenberg, (Academic Press, New York), **1963**.
[4] Filter and E. O. Steinborn, Extremely compact formulas for molecular one–electron integrals and Coulomb integrals over Slater–type orbitals, *Phys. Rev. A* **1978**, *18*, 1.
[5] E. O. Steinborn and E. Filter, Translations of fields represented by spherical–harmonics expansions for molecular calculations. III. Translations of reduced Bessel functions, Slater–type s–orbitals, and other functions, *Theor. Chim. Acta*. **1975**, *38*, 273.
[6] J. Weniger, Reduzierte Bessel–Funktionen als LCAO–Basissatz: Analytische und numerische Untersuchungen, Ph.D. thesis, Universität Regensburg, 1982.
[7] E. J. Weniger and E. O. Steinborn, The Fourier transforms of some exponential–type functions and their relevance to multicenter problems, *J. Chem. Phys.*, **1983**,*78*, 6121.
[8] P. Trivedi and E. O. Steinborn, Fourier transform of a two–center product of exponential–type orbitals. Application to one– and two–electron multicenter integrals, *Phys. Rev. A*. **1983**, *27*, 670.
[9] J. Grotendorst and E. O. Steinborn, Numerical evaluation of molecular one– and two–electron multicenter integrals with exponential–type orbitals via the Fourier–transform method, *Phys. Rev. A*. **1988**, *38*, 3857.
[10] H. Safouhi, The properties of sine, spherical Bessel and reduced Bessel functions for improving convergence of semi–infinite very oscillatory integrals: The evaluation of three–center nuclear attraction integrals over B functions, *J. Phys. A : Math. Gen.* **2001**, *34*, 2801.
[11] H. Safouhi, An extremely efficient approach for accurate and rapid evaluation of three–center two–electron Coulomb and hybrid integral over B functions, *J. Phys. A : Math. Gen.* **2001**, *34*, 881.
[12] A. Sidi, Extrapolation methods for oscillating infinite integrals, *J. Inst. Maths. Applics*. **1980**, *26*, 1.
[13] A. Sidi, Computation of infinite integrals involving Bessel functions of arbitrary order by the $\bar{D}$–transformation, *J. Comp. Appl. Math.* **1997**, *78*, 125.
[14] L. Berlu and H. Safouhi, An extremely efficient and rapid algorithm for a numerical evaluation of three–center nuclear attraction integrals over Slater type functions, *J. Phys. A : Math. Gen.* **2003**. *In press*.
[15] L. Berlu and H. Safouhi, A new algorithm for accurate and fast numerical evaluation of hybrid and three–center two–electron Coulomb integrals over Slater type functions, *J. Phys. A : Math. Gen.* **2003**. *In press*.
[16] E. J. Weniger and E. O. Steinborn. Programs for the coupling of spherical harmonics, *Comput. Phys. Commun.* **1982**, *25*, 149.
[17] J. Fernàndez Rico, R. Lòpez, I. Ema and G. Ramìrez, Calculation of many centre two–electron molecular integrals with STO, *Comp. Phys. Commun.* **1997**, *105*, 216.
[18] D. Levin, Development of non–linear transformations for improving convergence of sequences, Int. J. Comput. Math. **1973**, *B 3*, 371.
[19] P. Wynn, On a device for computing the $e_m(S_n)$ transformation, Math. Tables Aids Comput. **1956**, *10*, 91.
[20] M. Yoshimine, B. H. Lengsfield, P. S. Bagus, A. D. McLean and b. Liu, *Alchemy II* (International Business Machines, San Jose, from MOTECC–90), **1990**.

Biographies

Hassan Safouhi is assistant professor of mathematics at the Faculté Saint–Jean/University of Alberta. After obtaining a Ph.D. degree in applied mathematics from the University Blaise Pascal, Dr. Safouhi undertook postdoctoral research with Prof. André Joyal at the University of Québec at Montréal. More recently, Dr. Safouhi has collaborated on projects with the group "Theoretical Chemistry" of the University Blaise Pascal. Dr. Safouhi is dedicated to the development of new mathematical techniques for a rapid and accurate numerical evaluation of molecular multicenter integrals over Slater–type orbitals.

Lilian Berlu obtained a diploma of advanced studies in computational and theoretical chemistry at the University Henri Poincaré, under the supervision of Prof. Rivail. L. Berlu started a Ph.D. thesis on molecular integrals involved in nuclear magnetic shielding calculations over Slater–type orbitals at the University Blaise Pascal. He will defend his thesis the 6th of november 2003. This year L. Berlu spent three–months at the Faculté Saint–Jean/University of Alberta where he did research training under the supervision of Prof. Safouhi. Since that time L. Berlu and Prof. Safouhi have closely collaborated on the development of new optimized algorithms for a complete SCF *ab initio* molecular calculations over Slater–type orbitals using nonlinear transformations.