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# Convergence Improvement of Two–electron Four–center Coulomb and Exchange Integrals Over Slater–type Orbitals

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# Convergence Improvement of Two–electron Four–center Coulomb and Exchange Integrals Over Slater–type Orbitals[#]

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**Abstract**

**Motivation.** Two–electron four–center Coulomb and exchange integrals the rate limiting step of *ab initio* molecular structure calculations. These integrals contribute to the total energy of the molecule, which is required to a precision sufficient for small fractional changes to be evaluated reliably.

**Method.** The Fourier transform method combined with nonlinear transformations for improving convergence of highly oscillatory integrals is used to develop an efficient algorithm for a fast numerical evaluation of molecular integrals over Slater type orbitals.

**Conclusions.** Numerical results are obtained for HCN, $C_2H_2$, $Zn_3$, $BH_3$, $CH_4$ and $SF_6$ molecules. They are all highly accurate and they show that the approach used in this work, which we previously used for the numerical evaluation of three–center nuclear attraction, three–center two–electron Coulomb and hybrid integrals, should lead to a suite of *ab initio* Slater software.

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

**Abbreviations and notations**

| | |
|---|---|
| ETO, exponential–type orbitals | STO, Slater–type orbitals |
| GTO, Gaussian–type orbitals | |

## 1 INTRODUCTION

Previous work on accurate and fast numerical evaluation of molecular integrals over STOs continues with the present contribution. Among the integrals required to develop electronic structure theory over STOs [1,2] are the four–center two–electron Coulomb and exchange integrals. These integrals are without any doubt, the most difficult integrals occurring in molecular structure calculations. These integrals over STOs can be expressed in terms of integrals over the so–called B functions [3–7]. By applying the Fourier transform method [8,9], one can express the molecular integrals over B functions in terms of three–dimensional integral representations [9]. These integral

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representations are the principal source of the difficulties occurring in the numerical evaluation of the molecular integrals.

Recently, we developed an efficient and rapid algorithm based on the Fourier transform method and on the $S\overline{D}$ approach [10,11]. Recurrence relations were developed for a better control of the degree of accuracy [12,13]. This approach was efficiently applied to the three–center nuclear attraction, three–center two–electron Coulomb and hybrid integrals with linear and nonlinear systems [14]. In this work, we performed calculations for the two–electron four–center Coulomb and exchange integrals for a series of molecules. Values obtained using the ADGGSTNGINT code developed by Rico *et al*. [15] are also listed in the numerical tables.

## 2 DEFINITIONS AND BASIC FORMULAE

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]:

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

where $\hat{k}_{n-\frac{1}{2}}(\zeta r)$ stands for the reduced Bessel function, which satisfies the following relations:

$$\hat{k}_{n+\frac{1}{2}}(x)=(2n-1)\hat{k}_{n-\frac{1}{2}}(x)+x^{2}\hat{k}_{(n-1)-\frac{1}{2}}(x) \tag{3}$$

and

$$\left(\frac{d}{xdx}\right)^{m}\left[\frac{\hat{k}_{n+\frac{1}{2}}(x)}{x^{2n+1}}\right]=(-1)^{m}\left[\frac{\hat{k}_{n+m+\frac{1}{2}}(x)}{x^{2(n+m)+1}}\right] \tag{4}$$

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

$$J=\left\langle \chi_{n_1,l_1}^{m_1}(\xi_1,r_1-R_1)\chi_{n_3,l_3}^{m_3}(\xi_3,r_2-R_3)\left|\frac{1}{|r_1-r_2|}\right|\chi_{n_2,l_2}^{m_2}(\xi_2,r_1-R_2)\chi_{n_4,l_4}^{m_4}(\xi_4,r_2-R_4)\right\rangle \tag{5}$$

## 3 Analytical Development of Coulomb Integrals Over STOs

The molecular integral over STOs (5) can be expressed as finite linear combination of integrals over B functions. By applying the Fourier transform method, one can express the molecular integrals under consideration in terms of three–dimensional integral representations. The inner semi–infinite integral is a highly oscillatory integral, due to the presence of spherical Bessel functions. This semi–infinite integral is given by:

$$\int_0^\infty x^{n_x} \frac{\hat{k}_{\nu_1}(R_1\gamma_1(s,x))}{\gamma_1(s,x)^{n_{\gamma_1}}} \frac{\hat{k}_{\nu_2}(R_2\gamma_2(t,x))}{\gamma_2(t,x)^{n_{\gamma_2}}} j_\lambda(vx)\,dx \tag{6}$$

It is shown [16] that the above semi–infinite integral satisfies all the conditions to apply nonlinear $\overline{D}$ transformation of Sidi [17,18]. This method was shown to be more accurate and efficient compared with the approaches using Gauss–Laguerre quadrature, Levin's *u* transform [19] or the epsilon algorithm of Wynn [20]. However, the application of the $\overline{D}$ transformation presents severe numerical and computation difficulties. The $S\overline{D}$ approach, which was recently introduced by Safouhi [10], led to great simplifications in the application of the $\overline{D}$ transformation. This approach consists on transforming the semi–infinite integrals involving spherical Bessel functions into semi–infinite integrals involving the simple sine function, which are given by:

$$\frac{1}{v^{\lambda+1}} \int_0^\infty \left(\frac{d}{xdx}\right)^{\lambda} \left[x^{n_x+\lambda-1} g(x)\right] \sin(vx)\,dx \tag{7}$$

where:

$$g(x) = \frac{\hat{k}_{\nu_1}(R_1\gamma_1(s,x))}{\gamma_1(s,x)^{n_{\gamma_1}}} \frac{\hat{k}_{\nu_2}(R_2\gamma_2(t,x))}{\gamma_2(t,x)^{n_{\gamma_2}}} \tag{8}$$

It is shown that the semi–infinite integral involving the sine function (7) satisfies all the conditions to apply the $\overline{D}$ transformation. The properties of the sine function in particular the fact that its zeros are equidistant allowed the use of Cramer's rule [12], for evaluating the approximation of the semi–infinite integral (7):

$$S\overline{D}_n^{(2,j)} = \frac{1}{v^{\lambda+1}} \frac{\sum_{i=0}^{n+1} C_{n+1}^{i} (1+i+j)^n F(x_{i+j}) / \left[x_{i+j}^2 G(x_{i+j})\right]}{\sum_{i=0}^{n+1} C_{n+1}^{i} (1+i+j)^n / \left[x_{i+j}^2 G(x_{i+j})\right]} \tag{9}$$

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

$$F(x) = \int_0^x \left(\frac{d}{xdx}\right)^{\lambda} \left[x^{n_x+\lambda-1} g(x)\right] \sin(vx)\,dx \tag{10}$$

and

$$G(x) = \left(\frac{d}{xdx}\right)^{\lambda} \left[x^{n_x+\lambda-1} g(x)\right] \tag{11}$$

Recurrence relations were developed for, an efficient computation of Eq. (9), a better control of the degree of accuracy and for a better stability of the algorithm [12,13].

**Table 1.** Slater type orbital exponents

| 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 | | | | | | |

## 4 RESULTS AND DISCUSSION

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

$$F(x_i) = \sum_{l=0}^{i-1} \int_{x_l}^{x_{l+1}} \left(\frac{d}{xdx}\right)^{\lambda} \left[x^{n_x+\lambda-1} g(x)\right] \sin(vx)\,dx \tag{12}$$

For the numerical evaluation of each term of the finite sum in the right hand side of Eq. (12), we used the procedure described in [14]. For the computation of the function $G(x)$ (11), we used Leibnitz formulae combined with Eqs. (3) and (4). The subroutine GAUNT.F developed by Weniger [21] was used for the numerical evaluation of Gaunt coefficients which occur in the complete expression of the molecular integrals under consideration. The spherical harmonics $Y_l^m(\theta_r,\varphi_r)$ are computed using the recurrence formulae presented in [21]. For the following the abbreviations $2p_z$, $2p_{+1}$, $3p_z$ and $3d_z$ refer to the 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. Numerical values in tables refer to the approximations obtained using the $\overline{SD}$ approach. Values STOnG are obtained using the ADGGSTNGINT code developed by Rico *et al.* [15].

**Table 2.** Geometry used for molecular calculations

| Molecules | Geometry | Cartesian coordinates |
|---|---|---|
| HCN | Linear<br>H–C = a = 2.000 a.u.<br>C–N = b = 2.187 a.u. | H(0.0, 0.0, –a) |
| | | C(0.0, 0.0, 0.0) |
| | | N(0.0, 0.0, b) |
| $C_2H_2$ | Linear<br>H–C = a = 2.002 a.u.<br>C–C = b = 2.281 a.u. | $H^1$(0.0, 0.0, –a–b/2) |
| | | $C^1$(0.0, 0.0, –b/2) |
| | | $C^2$(0.0, 0.0, b/2) |
| | | $H^2$(0.0, 0.0, a+b/2) |
| $Zn_3$ | Equilateral Triangle, Planar<br>Zn–Zn = a = 5.03593 a.u.<br>b = 2.90749 a.u. | $Zn^1$(b, 0.0, 0.0) |
| | | $Zn^2$(–b/2, a/2, 0.0) |
| | | $Zn^3$(–b/2, –a/2, 0.0) |
| $BH_3$ | Equilateral Triangle, Planar<br>B–H = a = 2.250 a.u.<br>b = 3.897 a.u. | B ( 0.0, 0.0, 0.0) |
| | | $H^1$( 0.0, 0.0, a) |
| | | $H^2$( b/2, 0.0, –a/2) |
| | | $H^3$(–b/2, 0.0, –a/2) |
| $CH_4$ | Regular Tetrahedron<br>C–H = a = 2.0665 a.u.<br>b = 1.1931 a.u. | C ( 0.0, 0.0, 0.0) |
| | | $H^1$( b, b, b) |
| | | $H^2$(b,–b, –b) |
| | | $H^3$(–b,b, –b) |
| | | $H^4$(–b,–b, b) |
| $SF_6$ | Regular Octahedron<br>S–F = a = 2.88769 a.u. | S ( 0.0, 0.0, 0.0) |
| | | $F^1$( a, 0.0, 0.0) |
| | | $F^2$( 0.0, a, 0.0) |
| | | $F^3$( –a, 0.0, 0.0) |
| | | $F^4$( 0.0, –a, 0.0) |
| | | $F^5$( 0.0, 0.0, a) |
| | | $F^6$( 0.0, 0.0, –a) |

**Table 3.** Two–center exchange integrals over STOs

| Molecules | Integrals | Values | Values STOnG |
|---|---|---|---|
| HCN | | | |
| | $<1s^{N}\,1s^{C}\vert\,1s^{C}\,1s^{N}>$ | 0.243 975 171(–7) | 0.243 952 818(–7) |
| | $<2s^{N}\,1s^{C}\vert\,1s^{C}\,2s^{N}>$ | 0.963 853 612(–2) | 0.963 852 715(–2) |
| | $<2p_z^{N}\,1s^{C}\vert\,1s^{C}\,2p_z^{N}>$ | 0.179 652 035(–1) | 0.179 652 008(–1) |
| | $<2p_z^{N}\,2p_z^{C}\vert\,2p_z^{C}\,2p_z^{N}>$ | 0.133 191 021( 0) | 0.133 191 021( 0) |
| | $<2p_{+1}^{N}\,2p_{+1}^{C}\vert\,2p_z^{C}\,2p_z^{N}>$ | –0.679 931 457(–1) | –0.679 931 457(–1) |
| $C_2H_2$ | | | |
| | $<1s^{C1}\,1s^{C2}\vert\,1s^{C2}\,1s^{C1}>$ | 0.442 480 198(–7) | 0.442 431 402(–7) |
| | $<2s^{C1}\,1s^{C2}\vert\,1s^{C2}\,2s^{C1}>$ | 0.103 215 026(–1) | 0.103 214 727(–1) |
| | $<2p_z^{C1}\,1s^{C2}\vert\,1s^{C2}\,2p_z^{C1}>$ | 0.235 015 751(–1) | 0.235 015 641(–1) |
| | $<2p_z^{C1}\,2p_z^{C2}\vert\,2p_z^{C2}\,2p_z^{C1}>$ | 0.122 612 112( 0) | 0.122 612 112( 0) |
| | $<2p_{+1}^{C1}\,2p_{+1}^{C2}\vert\,2p_z^{C2}\,2p_z^{C1}>$ | –0.695 485 685(–1) | –0.695 485 685(–1) |
| $BH_3$ | | | |
| | $<1s^{B}\,1s^{H1}\vert\,1s^{H1}\,1s^{B}>$ | 0.105 851 555(–1) | 0.105 851 420(–1) |
| | $<2s^{B}\,1s^{H1}\vert\,1s^{H1}\,2s^{B}>$ | 0.173 063 383( 0) | 0.173 063 383( 0) |
| | $<2p_z^{B}\,1s^{H1}\vert\,1s^{H1}\,2p_z^{B}>$ | 0.202 801 420( 0) | 0.202 801 420( 0) |
| | $<1s^{H1}\,1s^{H2}\vert\,1s^{H2}\,1s^{H1}>$ | 0.180 097 063(–1) | 0.180 097 063(–1) |
| $CH_4$ | | | |
| | $<1s^{C}\,1s^{H1}\vert\,1s^{H1}\,1s^{C}>$ | 0.102 388 056(–1) | 0.102 387 602(–1) |
| | $<2s^{C}\,1s^{H1}\vert\,1s^{H1}\,2s^{C}>$ | 0.196 677 543( 0) | 0.196 677 543( 0) |
| | $<2p_z^{C}\,1s^{H1}\vert\,1s^{H1}\,2p_z^{C}>$ | 0.784 621 598(–1) | 0.784 621 598(–1) |
| | $<1s^{H1}\,1s^{H2}\vert\,1s^{H2}\,1s^{H1}>$ | 0.362 760 883(–1) | 0.362 760 883(–1) |

Table 1 contains the values of the screening parameters, which occur in the analytic expression of STOs. Table 2 contains the geometry used for the calculations performed for the present work.

**Table 4.** Three–center exchange integrals over STOs

| Molecules | Integrals | Values | Values STOnG |
|---|---|---|---|
| HCN | | | |
| | $\langle 1s^{N}\,1s^{H} \vert 1s^{C}\,1s^{N}\rangle$ | 0.127 620 475(–5) | 0.127 619 737(–5) |
| | $\langle 2s^{N}\,1s^{H} \vert 1s^{C}\,2s^{N}\rangle$ | 0.675 018 598(–2) | 0.675 018 594(–2) |
| | $\langle 2p_z^{N}\,1s^{H} \vert 1s^{C}\,2p_z^{N}\rangle$ | 0.860 798 342(–2) | 0.860 798 343(–2) |
| | $\langle 2p_{+1}^{N}\,1s^{H} \vert 1s^{C}\,2p_{+1}^{N}\rangle$ | 0.898 860 131(–4) | 0.898 860 102(–4) |
| | $\langle 2p_z^{N}\,1s^{H} \vert 2p_z^{C}\,2p_z^{N}\rangle$ | 0.249 011 534(–1) | 0.249 011 534(–1) |
| | $\langle 2p_z^{N}\,1s^{H} \vert 2p_{+1}^{C}\,2p_{+1}^{N}\rangle$ | –0.170 766 308(–1) | –0.170 766 308(–1) |
| | $\langle 2p_{+1}^{N}\,1s^{H} \vert 2p_z^{C}\,2p_{+1}^{N}\rangle$ | 0.467 638 749(–2) | 0.467 638 750(–2) |
| $C_2H_2$ | | | |
| | $\langle 1s^{C1}\,1s^{C2} \vert 1s^{H}\,1s^{C1}\rangle$ | 0.130 739 389(–4) | 0.467 638 750(–2) |
| | $\langle 2s^{C1}\,2s^{C2} \vert 1s^{H}\,2s^{C1}\rangle$ | 0.274 923 735(–1) | 0.274 923 741(–1) |
| | $\langle 2p_z^{C1}\,2p_z^{C2} \vert 1s^{H}\,1s^{C1}\rangle$ | –0.168 852 102(–1) | –0.168 852 102(–1) |
| | $\langle 2p_z^{C1}\,2p_z^{C2} \vert 1s^{H}\,2p_z^{C1}\rangle$ | 0.248 702 455(–1) | 0.248 702 455(–1) |
| | $\langle 2p_{+1}^{C1}\,2p_{+1}^{C2} \vert 1s^{H}\,2p_z^{C1}\rangle$ | –0.494 475 624(–1) | –0.494 475 624(–1) |
| | $\langle 2p_{+1}^{C1}\,2p_z^{C2} \vert 1s^{H}\,2p_{+1}^{C1}\rangle$ | –0.217 852 119(–1) | –0.217 852 119(–1) |
| $BH_3$ | | | |
| | $\langle 1s^{B}\,1s^{H1} \vert 1s^{H2}\,1s^{B}\rangle$ | 0.102 603 529(–1) | 0.102 603 394(–1) |
| | $\langle 2s^{B}\,1s^{H1} \vert 1s^{H2}\,2s^{B}\rangle$ | 0.125 812 602( 0) | 0.125 812 602( 0) |
| | $\langle 2p_z^{B}\,1s^{H1} \vert 1s^{H2}\,2p_z^{B}\rangle$ | –0.157 273 465(–1) | –0.157 273 464(–1) |
| | $\langle 1s^{H1}\,1s^{H2} \vert 1s^{H3}\,1s^{H2}\rangle$ | 0.148 704 520(–1) | 0.148 704 520(–1) |
| $CH_4$ | | | |
| | $\langle 1s^{C}\,1s^{H1} \vert 1s^{H2}\,1s^{C}\rangle$ | 0.100 453 277(–1) | 0.100 452 821(–1) |
| | $\langle 2s^{C}\,1s^{H1} \vert 1s^{H2}\,2s^{C}\rangle$ | 0.155 295 223( 0) | 0.155 295 223( 0) |
| | $\langle 2p_z^{C}\,1s^{H1} \vert 1s^{H2}\,2p_z^{C}\rangle$ | 0.185 191 461(–3) | 0.185 191 465(–3) |
| | $\langle 1s^{H1}\,1s^{H2} \vert 1s^{H3}\,1s^{H2}\rangle$ | 0.308 175 489(–1) | 0.308 175 489(–1) |

**Table 5.** Four–center two–electron integrals over STOs

| Molecules | Integrals | Values | Values STOnG |
|---|---|---|---|
| $C_2H_2$ | | | |
| | $\langle 1s^{H1}\,1s^{C1} \vert 1s^{C2}\,1s^{H2}\rangle$ | 0.258 403 185 (–2) | 0.258 403 144 (–2) |
| | $\langle 1s^{H1}\,2s^{C1} \vert 2s^{C2}\,1s^{H2}\rangle$ | 0.913 277 985 (–1) | 0.913 277 985 (–1) |
| | $\langle 1s^{H1}\,2p_z^{C1} \vert 2s^{C2}\,1s^{H2}\rangle$ | –0.538 260 731 (–1) | –0.538 260 731 (–1) |
| | $\langle 1s^{H1}\,2p_z^{C1} \vert 2p_z^{C2}\,1s^{H2}\rangle$ | –0.327 338 167 (–1) | –0.327 338 167 (–1) |
| | $\langle 1s^{H1}\,2p_{+1}^{C1} \vert 2p_{+1}^{C2}\,1s^{H2}\rangle$ | 0.473 085 665 (–2) | 0.473 085 665 (–2) |
| | $\langle 1s^{C1}\,1s^{C2} \vert 1s^{H1}\,1s^{H2}\rangle$ | 0.332 120 355 (–5) | 0.332 120 421 (–5) |
| | $\langle 1s^{C1}\,2s^{C2} \vert 1s^{H1}\,1s^{H2}\rangle$ | 0.136 080 233 (–2) | 0.136 080 232 (–2) |
| | $\langle 2s^{C1}\,2s^{C2} \vert 1s^{H1}\,1s^{H2}\rangle$ | 0.948 583 025 (–2) | 0.948 583 024 (–2) |
| | $\langle 2p_z^{C1}\,2s^{C2} \vert 1s^{H1}\,1s^{H2}\rangle$ | 0.724 269 212 (–2) | 0.724 269 213 (–2) |
| | $\langle 2p_z^{C1}\,2p_z^{C2} \vert 1s^{H1}\,1s^{H2}\rangle$ | –0.526 504 948 (–2) | –0.526 504 940 (–2) |
| | $\langle 2p_{+1}^{C1}\,2p_{+1}^{C2} \vert 1s^{H1}\,1s^{H2}\rangle$ | 0.534 650 086 (–2) | 0.534 650 082 (–2) |
| $BH_3$ | | | |
| | $\langle 1s^{B}\,1s^{H1} \vert 1s^{H2}\,1s^{H3}\rangle$ | 0.856 095 760 (–2) | 0.856 095 756 (–2) |
| | $\langle 2s^{B}\,1s^{H1} \vert 1s^{H2}\,1s^{H3}\rangle$ | 0.400 583 908 (–1) | 0.400 583 908 (–1) |
| | $\langle 2p_z^{B}\,1s^{H1} \vert 1s^{H2}\,1s^{H3}\rangle$ | 0.306 774 048 (–1) | 0.306 774 048 (–1) |
| $CH_4$ | | | |
| | $\langle 1s^{C}\,1s^{H1} \vert 1s^{H2}\,1s^{H3}\rangle$ | 0.111 715 585 (–1) | 0.111 713 904 (–1) |
| | $\langle 2s^{C}\,1s^{H1} \vert 1s^{H2}\,1s^{H3}\rangle$ | 0.646 387 830 (–1) | 0.646 387 830 (–1) |
| | $\langle 2p_z^{C}\,1s^{H1} \vert 1s^{H2}\,1s^{H3}\rangle$ | 0.198 498 772 (–1) | 0.198 498 772 (–1) |
| $SF_6$ | | | |
| | $\langle 2s^{F1}\,2s^{F2} \vert 2s^{F3}\,2s^{F4}\rangle$ | 0.347 853 730 (–3) | 0.347 853 730 (–3) |
| | $\langle 2p_z^{F1}\,2p_z^{F2} \vert 2p_z^{F3}\,2p_z^{F4}\rangle$ | 0.320 176 089 (–5) | 0.320 175 851 (–5) |
| | $\langle 2p_z^{F1}\,2p_z^{F3} \vert 2p_z^{F5}\,2p_z^{S}\rangle$ | –0.124 943 479 (–5) | –0.124 943 392 (–5) |
| | $\langle 2p_z^{F1}\,2p_z^{F3} \vert 2p_z^{F5}\,3p_z^{S}\rangle$ | –0.150 917 109 (–4) | –0.150 917 115 (–4) |
| | $\langle 2p_z^{F1}\,2p_z^{F3} \vert 2p_z^{F5}\,3d_z^{S}\rangle$ | –0.127 096 896 (–4) | –0.127 096 900 (–4) |

Table 3 contains values obtained for two–center exchange integrals over STOs. Table 4 contains values obtained for three–center exchange integrals over STOs. Table 5 contains values obtained for two–electron four–center exchange integrals over STOs.

The numerical results listed in Tables 3–5 are obtained with HCN, $C_2H_2$, $Zn_3$, $BH_3$, $CH_4$ and $SF_6$ 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). 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, Levin's $u$ transform or the epsilon algorithm of Wynn.

For the computation of $S\overline{D}_n^{(2,j)}$, we used the recurrence relations developed in [12,13], which allowed a better control of the degree of accuracy. From the numerical tables, one can easily notice that the values obtained using the algorithm described in the present work are in a complete agreement with those obtained using the ADGGSTNGINT code, namely 9 similar digits in most cases for two–center exchange integrals over STOs (Table 3), 10 correct digits for the three–center exchange integrals over STOs (Table 4) and 10 correct digits for four–center exchange integrals over STOs (Table 5). From these arguments, it follows that the $S\overline{D}$ approach is the key to the development of a complete software for an accurate and fast numerical evaluation of molecular integrals over STOs. All the calculations were performed on a PC–Workstation Intel Xeon Processor 2.4GHz.

## 5 CONCLUSIONS

The basis set of STOs was used to represent atomic orbitals. These STOs constitute an important basis set for all calculations of physical properties of molecules and solids, which use the linear combination of atomic orbitals (LCAO) approach. Molecular integrals over STOs are expressed as finite linear combinations of integrals over B functions in order to apply the Fourier transform method to obtain analytic expressions of the integrals of interest. These analytic expressions turned to be difficult to evaluate rapidly and to a high pre–determined accuracy because of the presence of highly oscillatory semi–infinite integrals. With the help of the $S\overline{D}$ approach, these semi–infinite integrals are transformed into semi–infinite integrals involving the simple sine function suitable to apply the $\overline{D}$ transformation using Cramer's rule.

Recurrence relations were developed for the computation of the approxiamtions $S\overline{D}_n^{(2,j)}$. These relations further improved the accuracy and the rapidity of the algorithm.

The numerical results obtained for the molecular integrals for HCN, $C_2H_2$, $Zn_3$, $BH_3$, $CH_4$ and $SF_6$ molecules are very accurate and in a complete accordance with those obtained using existing codes. A complete optimized code using the algorithm described in the present contribution will be submitted in the near future.

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