

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.

Results and conclusion. Numerical results are obtained for HCN, C₂H₂, Zn₃, BH₃, CH₄ and SF₆ 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

STO, Slater-type orbitals

GTO, Gaussian-type orbitals

ETO, exponential-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 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 \overline{SD} 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,

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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]:

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

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

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

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

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

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

and

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

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

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

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:

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

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:

$$\frac{1}{\nu^{\lambda+1}} \int_0^{\infty} \left(\frac{d}{x dx} \right)^{\lambda} \left[x^{n_x + \lambda - 1} g(x) \right] \sin(\nu x) dx \quad (7)$$

Where:

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

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):

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

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

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

and

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

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

4 RESULTS AND DISCUSSION

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

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

For the numerical evaluation of each term of the finite sum in the right hand side of equation (12), we used the procedure described in [14].

For the computation of the function $G(x)$ (11), we used Leibnitz formulae combined with equations (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 $Y_l^m(\theta, \varphi)$ 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.

In the numerical tables, Values 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 (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 that we performed for the present work. 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.

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 \overline{SD} 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. 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 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.

6 Numerical tables

TAB1 : 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						

TAB2 : Geometry used for molecular calculations.

Molecules	Geometry	Cartesian coordinates
HCN	Linear H-C = a = 2.000 a.u. 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 ₂ H ₂	Linear H-C = a = 2.002 a.u. 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 Zn-Zn = a = 5.03593 a.u. 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 B-H = a = 2.250 a.u. 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 C-H = a = 2.0665 a.u. 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 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)

TAB3 : Two-center exchange integrals over STOs.

Molecules	Integrals	Values	Values STOnG
HCN	$\langle 1s^N 1s^C 1s^C 1s^N \rangle$	0.243 975 171(-7)	0.243 952 818(-7)
	$\langle 2s^N 1s^C 1s^C 2s^N \rangle$	0.963 853 612(-2)	0.963 852 715(-2)
	$\langle 2p_z^N 1s^C 1s^C 2p_z^N \rangle$	0.179 652 035(-1)	0.179 652 008(-1)
	$\langle 2p_z^N 2p_z^C 2p_z^C 2p_z^N \rangle$	0.133 191 021(0)	0.133 191 021(0)
	$\langle 2p_{+1}^N 2p_{+1}^C 2p_z^C 2p_z^N \rangle$	-0.679 931 457(-1)	-0.679 931 457(-1)
C ₂ H ₂	$\langle 1s^{C1} 1s^{C2} 1s^{C2} 1s^{C1} \rangle$	0.442 480 198(-7)	0.442 431 402(-7)
	$\langle 2s^{C1} 1s^{C2} 1s^{C2} 2s^{C1} \rangle$	0.103 215 026(-1)	0.103 214 727(-1)
	$\langle 2p_z^{C1} 1s^{C2} 1s^{C2} 2p_z^{C1} \rangle$	0.235 015 751(-1)	0.235 015 641(-1)
	$\langle 2p_z^{C1} 2p_z^{C2} 2p_z^{C2} 2p_z^{C1} \rangle$	0.122 612 112(0)	0.122 612 112(0)
	$\langle 2p_{+1}^{C1} 2p_{+1}^{C2} 2p_z^{C2} 2p_z^{C1} \rangle$	-0.695 485 685(-1)	-0.695 485 685(-1)
BH ₃	$\langle 1s^B 1s^{H1} 1s^{H1} 1s^B \rangle$	0.105 851 555(-1)	0.105 851 420(-1)
	$\langle 2s^B 1s^{H1} 1s^{H1} 2s^B \rangle$	0.173 063 383(0)	0.173 063 383(0)
	$\langle 2p_z^B 1s^{H1} 1s^{H1} 2p_z^B \rangle$	0.202 801 420(0)	0.202 801 420(0)
	$\langle 1s^{H1} 1s^{H2} 1s^{H2} 1s^{H1} \rangle$	0.180 097 063(-1)	0.180 097 063(-1)
CH ₄	$\langle 1s^C 1s^{H1} 1s^{H1} 1s^C \rangle$	0.102 388 056(-1)	0.102 387 602(-1)
	$\langle 2s^C 1s^{H1} 1s^{H1} 2s^C \rangle$	0.196 677 543(0)	0.196 677 543(0)
	$\langle 2p_z^C 1s^{H1} 1s^{H1} 2p_z^C \rangle$	0.784 621 598(-1)	0.784 621 598(-1)
	$\langle 1s^{H1} 1s^{H2} 1s^{H2} 1s^{H1} \rangle$	0.362 760 883(-1)	0.362 760 883(-1)

TAB4: Three-center exchange integrals over STOs.

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

CH ₄	$\langle 1s^C 1s^{H1} 1s^{H2} 1s^C \rangle$	0.100 453 277(-1)	0.100 452 821(-1)
	$\langle 2s^C 1s^{H1} 1s^{H2} 2s^C \rangle$	0.155 295 223(0)	0.155 295 223(0)
	$\langle 2p_z^C 1s^{H1} 1s^{H2} 2p_z^C \rangle$	0.185 191 461(-3)	0.185 191 465(-3)
	$\langle 1s^{H1} 1s^{H2} 1s^{H3} 1s^{H2} \rangle$	0.308 175 489(-1)	0.308 175 489(-1)

TAB5 : Four-center two-electron integrals over STOs.

Molecules	Integrals	Values	Values STOnG
C ₂ H ₂	$\langle 1s^{H1} 1s^{C1} 1s^{C2} 1s^{H2} \rangle$	0.258 403 185 (-2)	0.258 403 144 (-2)
	$\langle 1s^{H1} 2s^{C1} 2s^{C2} 1s^{H2} \rangle$	0.913 277 985 (-1)	0.913 277 985 (-1)
	$\langle 1s^{H1} 2p_z^{C1} 2s^{C2} 1s^{H2} \rangle$	-0.538 260 731 (-1)	-0.538 260 731 (-1)
	$\langle 1s^{H1} 2p_z^{C1} 2p_z^{C2} 1s^{H2} \rangle$	-0.327 338 167 (-1)	-0.327 338 167 (-1)
	$\langle 1s^{H1} 2p_{+1}^{C1} 2p_{+1}^{C2} 1s^{H2} \rangle$	0.473 085 665 (-2)	0.473 085 665 (-2)
	$\langle 1s^{C1} 1s^{C2} 1s^{H1} 1s^{H2} \rangle$	0.332 120 355 (-5)	0.332 120 421 (-5)
	$\langle 1s^{C1} 2s^{C2} 1s^{H1} 1s^{H2} \rangle$	0.136 080 233 (-2)	0.136 080 232 (-2)
	$\langle 2s^{C1} 2s^{C2} 1s^{H1} 1s^{H2} \rangle$	0.948 583 025 (-2)	0.948 583 024 (-2)
	$\langle 2p_z^{C1} 2s^{C2} 1s^{H1} 1s^{H2} \rangle$	0.724 269 212 (-2)	0.724 269 213 (-2)
	$\langle 2p_z^{C1} 2p_z^{C2} 1s^{H1} 1s^{H2} \rangle$	-0.526 504 948 (-2)	-0.526 504 940 (-2)
	$\langle 2p_{+1}^{C1} 2p_{+1}^{C2} 1s^{H1} 1s^{H2} \rangle$	0.534 650 086 (-2)	0.534 650 082 (-2)
	BH ₃	$\langle 1s^B 1s^{H1} 1s^{H2} 1s^{H3} \rangle$	0.856 095 760 (-2)
$\langle 2s^B 1s^{H1} 1s^{H2} 1s^{H3} \rangle$		0.400 583 908 (-1)	0.400 583 908 (-1)
$\langle 2p_z^B 1s^{H1} 1s^{H2} 1s^{H3} \rangle$		0.306 774 048 (-1)	0.306 774 048 (-1)
CH ₄	$\langle 1s^C 1s^{H1} 1s^{H2} 1s^{H3} \rangle$	0.111 715 585 (-1)	0.111 713 904 (-1)
	$\langle 2s^C 1s^{H1} 1s^{H2} 1s^{H3} \rangle$	0.646 387 830 (-1)	0.646 387 830 (-1)
	$\langle 2p_z^C 1s^{H1} 1s^{H2} 1s^{H3} \rangle$	0.198 498 772 (-1)	0.198 498 772 (-1)
SF ₆	$\langle 2s^{F1} 2s^{F2} 2s^{F3} 2s^{F4} \rangle$	0.347 853 730 (-3)	0.347 853 730 (-3)
	$\langle 2p_z^{F1} 2p_z^{F2} 2p_z^{F3} 2p_z^{F4} \rangle$	0.320 176 089 (-5)	0.320 175 851 (-5)
	$\langle 2p_z^{F1} 2p_z^{F3} 2p_z^{F5} 2p_z^S \rangle$	-0.124 943 479 (-5)	-0.124 943 392 (-5)
	$\langle 2p_z^{F1} 2p_z^{F3} 2p_z^{F5} 3p_z^S \rangle$	-0.150 917 109 (-4)	-0.150 917 115 (-4)
	$\langle 2p_z^{F1} 2p_z^{F3} 2p_z^{F5} 3d_z^S \rangle$	-0.127 096 896 (-4)	-0.127 096 900 (-4)

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Biographies

First Author 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 integrals over STOs.

Second Author Dr. Berlu just obtained his Ph.D. degree in theoretical physical chemistry from the University Blaise Pascal. 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.