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Use of Lanczos Tau Method to Derive Polynomial Approximate from the Addition Theorem of Slater Type Orbitals

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Abstract

Motivation. Multi-center integrals are certainly the building blocks of quantum chemistry packages ranging from semi-empirical to the so-called *ab-initio*. The efficiency (accuracy and speed) of the numerical methods used for the computation of such integrals is therefore of extreme importance since millions of these need to be computed for molecules of practical interest. In this work, the Lanczos τ method is applied to derive a polynomial approximate to the so-called one-center expansion of Slater Type Orbitals (STOs). The procedure is applied to the three-center nuclear attraction integrals, which are essential not only in quantum chemistry but also to model electron-molecule scattering.

Method. Starting with a spherical Slater Type Orbital a differential equation governing such functions is elaborated. The application of the Lanczos τ to the differential equation enables us to obtain a polynomial approximate, and more importantly the corresponding absolute error. Such an approximate is afterwards used in the master formula allowing the computation of multi-center integrals over STOs.

Results. Numerical values for three-center nuclear attraction integrals are reported. Comparison with previous work is performed.

Conclusions. Multi-center integrals over STOs are still a challenging problem. The case of nuclear attraction integral is among the problems that can be tackled with various approaches including the one presented in this work. However for fully functional quantum chemistry software using STOs to be efficient it is necessary to combine the best of all methods by selecting the most appropriate tool for each case.

Keywords. Slater Type Orbital, multi-center integrals, Lanczos τ method, Three-center nuclear attraction integrals, Static potential.

Abbreviations and notations

STO, Slater Type Orbital	ODE, ordinary differential equation
GTO, Gaussian Type Orbital	LCAO, Linear Combination of Atomic Orbitals

1 INTRODUCTION

From the early days of quantum chemistry, it has been recognized that STOs are suitable functions to be used in the elaboration of the LCAO *ansatz* [1]. However, because of the difficulties inherent to the evaluation of multi-center integrals, such functions have never been used as part of an efficient package that could be used in an operational and routine framework. It is to be mentioned that over the past decades, attempts have continuously been made to solve the bottleneck of multi-center integrals ([2]-[26] and references therein). GTOs were proposed because they provided a “miraculous” solution to the problem of multi-center integrals [27]. As a consequence, GTOs became the very foundation of the most widely used ab-initio packages since they offered a cost efficient way to perform quantum chemistry investigation of large systems with few hundreds

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atoms.

Among the arsenal of methods proposed to tackle the problem of multi-center integrals over STOs is the so-called one-center expansion which dates as back as 1951 with the pioneering work of Barnett and Coulson [11]. Such an approach is essentially an addition theorem allowing a displaced STO to be expressed as an infinite series in which the electron variables and the geometrical parameters of the molecule are separated.

In previous work [18], it has been established that the addition theorem of STO poses serious challenges since its convergence deteriorates when being close to the cusp. As a consequence, non-linear sequence transformations emerge as a necessary tool to be applied in connection with the approach based on such an addition theorem [18]. Although convergence accelerators dramatically improve the efficiency of the summation procedure, starting with a well behaving expansion will definitely be beneficial since this will increase even more the overall efficiency of the numerical algorithms. Based on this remark, we address the possibility of deriving a polynomial approximate for a displaced STO.

2 Mathematical Preliminaries

A STO centered on the origin is usually defined as,

$$\chi_{n,l}^{m}(\varsigma,\vec{r}) = N r^{n-l-1} \exp(-\varsigma r)\,\hat{Y}_l^m(\vec{r}) \tag{1}$$

In which the normalization constant is given by $N = (2\varsigma)^{n+1/2}/\sqrt{(2n)!}$ and $\hat{Y}_l^m(\vec{r})$ represents the solid spherical harmonic of degree l and order m which using the Condon and Shortley phase convention [28] can be expressed as,

$$\hat{Y}_l^m(\vec{r}) = r^l\ Y_l^m(\theta,\varphi) = r^l\ i^{m+|m|}\sqrt{\frac{2l+1}{4\pi}\frac{(l-|m|)!}{(l+|m|)!}}\ P_l^{|m|}(\cos\theta)\,e^{im\varphi} \tag{2}$$

where the $P_l^{|m|}(\cos\theta)$ is the associated Legendre function and is defined as [29] (p. 174),

$$P_l^{|m|}(z) = (-1)^m\left(1-z^2\right)^{|m|/2}\left(\frac{d}{d\,z}\right)^{|m|} P_l(z) = (-1)^l\left(1-z^2\right)^{|m|/2}\left(\frac{d}{d\,z}\right)^{l+|m|}\left(\frac{\left(1-z^2\right)^l}{2^l\ l!}\right) \tag{3}$$

Of course in the case of a molecular system using the LCAO approximation, the spherical symmetry can no longer be sufficient and STOs are generally centered on the nuclei defined by the some location vector $\vec{a}$ with respect to some reference framework. In such a case, the definition in equation (1) is re-written as,

$$\chi_{n,l}^{m}(\varsigma,\vec{r}-\vec{a}) = N\,|\,\vec{r}-\vec{a}\,|^{n-l-1}\ \exp(-\varsigma\,|\,\vec{r}-\vec{a}\,|)\,\hat{Y}(\vec{r}-\vec{a}) \tag{4}$$

As can be seen from equation (4), the electron variable $\vec{r}$ and the molecular geometrical parameter $\vec{a}$ are inter-connected. The aim of an addition theorem is therefore to express the STO in such a way as the terms $\vec{r}$ and $\vec{a}$ end up separated. One such theorem, which can easily be obtained by differentiating the Gegenbauer addition theorem, can be written as [29] (p. 107),

$$|\,\vec{r}-\vec{a}\,|^{n-l-1}\ \exp(-\varsigma\,|\,\vec{r}-\vec{a}\,|) = \frac{1}{\sqrt{a\,r}}\sum(2\lambda+1)\ A_{l+1/2}^{n-l}(\varsigma,a,r)\ P_l\left(\frac{\vec{a}\bullet\vec{r}}{a\,r}\right) \tag{5}$$

where $P_l(z)$ represents the Lengdre polynomial of degree l and the terms $A^{n-l}_{l+1/2}(\varsigma, a, r)$ are defined recursively as,

$$\begin{cases} A^{0}_{l+1/2}(\varsigma, a, r) = & I_{l+1/2}(\varsigma\, \rho_<)\, K_{l+1/2}(\varsigma\, \rho_>) \\ A^{n}_{l+1/2}(\varsigma, a, r) = & -\partial/\partial\varsigma\, A^{n-1}_{l+1/2}(\varsigma, a, r) \end{cases} \qquad (6)$$

in which the terms $I_{l+1/2}(z)$ and $K_{l+1/2}(z)$ stand for the modified Bessel functions [30] (p. 80) and $\rho_<$ and $\rho_>$ for $\min(a,r)$ and $\max(a,r)$ respectively. Here it should be mentioned that variations of the above formulation were used as a starting point for numerical procedures geared towards an efficient evaluation of multi-center integrals. In the work of Jones and co-workers [15] many analytical forms, based on the so-called **C** matrix method, were derived for selected integrals. In such formulas the expansion coefficients were rational numbers, which made them suitable for benchmarking using symbolic algebra systems. In the following, for sake of simplicity but without loss of generality, emphasis will be put on the radial part of a STO as given by the left hand side of equation (5).

2.1 Polynomial Approximation of STO Addition Theorem

The addition theorem as given by equation (5) is analytically attractive since it is expressed as a series in terms of Legendre polynomials. The coefficients $A^{n}_{l+1/2}(\varsigma, a, r)$ can be computed using some special routines usually based on the 3-term recurrence relations satisfied by Bessel functions [30] (p. 80) or some other form including their integral representations [31]. For numerical work it was shown [18] that the convergence of the series (5) poses challenging problems since it deteriorates when r gets closer to a. Indeed for $r = a$ the convergence of the series in (5) becomes logarithmic hence leaving no choice but to turn to convergence acceleration techniques based on non-linear sequence transformations. The polynomial approximation aims at deriving a finite approximate to the left hand side of equation (5) along with the corresponding error due to the truncation of the series representation. In doing so, the error is known hence allowing to assess the accuracy of the results. In the rest of this section we describe the procedure to be used in order to derive a polynomial approximate to the addition theorem in (5) using the Lanczos τ method [32]. Historically Lanczos approximation method was applied from the earliest days of automatic computing to derive polynomial approximates to transcendental functions [33] and Clenshaw's procedure ([33], [35]), referred to as economization of infinite series, is certainly its widely used form. To apply the τ method we first need to derive the ODE satisfied by the radial part of STO. Writing such a radial term as,

$$(\varsigma\,|\vec{r}-\vec{a}|)^n \exp(-\varsigma\,|\vec{r}-\vec{a}|) = \left(z\sqrt{1-b\,x}\right)^n \exp\left(-z\sqrt{1-b\,x}\right) \qquad (7)$$

where $z = \varsigma\sqrt{a^2+r^2}$, $b = 2\,a\,r/\left(a^2+r^2\right)$ and $x = \cos(\theta) = \left(\vec{r}\bullet\vec{a}\right)/\left(a\,r\right)$, we finally obtain after some algebra the ODE satisfied by the right hand side of equation (7),

$$4(1-b\,x)\frac{d^2}{d\,x^2}S(x) + 2b(2n-1)(1-b\,x)\frac{d}{d\,x}S(x) - \left[(z\,b)^2(1-b\,x) - n(n+1)b^2\right]S(x) = 0 \qquad (8)$$

Before going any further, it is of importance to notice that because the parameter z involved in equation (7) appears in the ODE (8) with an even power, the same ODE should be satisfied by,

$$\left(z\sqrt{1-b\,x}\right)^n \exp\left(-z\sqrt{1-b\,x}\right) \text{ and } \left(-z\sqrt{1-b\,x}\right)^n \exp\left(z\sqrt{1-b\,x}\right) \tag{9}$$

or any linear combination of the above. To apply the Lanczos τ method, we first assume a polynomial expansion for $S(x)$. However, because $S(x)$ is now approximated, equation (8) is no longer valid. Instead, its right hand side must be replaced by an error term, which in a way is a measure of the accuracy of the assumed approximation. This yields a linear system the solution of which yields the polynomial coefficients $\{a_0(a,r), a_1(a,r), \cdots, a_N(a,r)\}$ that are functions of a and r

$$\begin{cases} -(b\,z)^2\,a_0 & -2b\,a_1 & -8\,a_2 & = \tau\, C_0^N \\ -(b\,z)^2\,a_p & -2b(p+1)(2p+1)\,a_{p+1} & -4(p+1)(p+2)\,a_{p+2} & = \tau\, C_p^N \\ -(b\,z)^2\,a_{N-1} & -2b(N(2N-1)\,a_N & & = \tau\, C_{N-1}^N \\ -(b\,z)^2\,a_N & & & = \tau\, C_N^N \end{cases} \tag{10}$$

where $1 \le p \le N-1$ and $\{C_0^N, C_1^N, \cdots, C_N^N\}$ are the coefficients of the Chebyshev polynomial of the first kind $T_n(z)$ [30]. As for the τ parameter, which represents the accuracy of the approximate, it is determined by some initial condition. Because, the solution of the ODE in (8) is a linear combination of the terms in (9), the regular solution at infinity is determined by the following,

$$\left(z\sqrt{1-b\,x}\right)^n \exp\left(-z\sqrt{1-b\,x}\right) = \frac{1}{2}\left[1 + \frac{n}{z}\frac{1}{\sqrt{1-b\,x}}\right] S(x) + \frac{\sqrt{1-b\,x}}{b\,z}\left(\frac{d}{d\,x} S(x)\right) \tag{11}$$

2.2 Nuclear Attraction Integrals

Nuclear attraction integrals are quantities defined as,

$$I_{n,l,m}^{n',l',m'}(\varsigma,\varsigma',\vec{b},\vec{c}) = \left\langle \chi_{n,l}^{m}(\varsigma,\vec{r}) \middle| \frac{1}{|\vec{r}-\vec{c}\,|} \middle| \chi_{n',l'}^{m'}(\varsigma',|\,\vec{r}-\vec{a}\,|) \right\rangle \tag{12}$$

Using the Laplace representation of the Coulombic interaction potential,

$$\frac{1}{|\vec{r}-\vec{c}\,|} = \sum_{l=0}^{+\infty} \frac{4\pi}{2l+1} \frac{r_<^l}{r_>^{l+1}} P_l\left(\frac{\vec{r}\bullet\vec{c}}{r\,c}\right) \text{ where } r_< = \min(r,c) \text{ and } r_> = \max(r,c) \tag{13}$$

In combination with the polynomial approximate as derived using the Lanczos τ method (*c.f.* equation 10), one ends up with an infinite series of the form,

$$I_{n,l,m}^{n',l',m'}(\varsigma,\varsigma',\vec{b},\vec{c}) = \sum_{l=0}^{+\infty} \frac{4\pi}{2l+1} \sum_{p=0}^{N} \left\langle r^{n-1}\exp(-\varsigma\, r) \middle| \frac{r_<}{r_>} \middle| a_p(b,r) \right\rangle \left\langle Y(\theta,\varphi) \middle| P_l\left(\frac{\vec{r}\bullet\vec{c}}{r\,c}\right) \middle| \left(\frac{\vec{r}\bullet\vec{a}}{r\,a}\right)^p \right\rangle \tag{14}$$

As for the computation of the above series, the radial terms are evaluated using a combination of Gauss-Legendre and Gauss-Laguerre quadratures. In proceeding this way we ensure that the partial sums of the above series are computed accurately [18]. Regarding the angular terms, these are first expressed as combinations of the well-known Gaunt coefficients for which computer code is already available in the literature [34]. To increase the efficiency of the procedure handling the summation of the series (14) Wynn's [36] ε algorithm is applied. The choice of such an accelerator is based on our previous investigation [18] of the nuclear attraction integral in which a theoretical argument was presented to explain why the ε algorithm performs better than the Levin u transformation [37].

3 RESULTS AND DISCUSSION

Two major results are provided in this work. First, applying the Lanczos τ method allows one to obtain a polynomial approximate of the addition theorem of STOs. To illustrate the advantage of using Lanczos τ method, we have listed in table (1) the coefficients of the polynomial approximate obtained for a 1s STO, $\chi_{1,0}^{0}(1.5,|\vec{r}-3.0\vec{k}\,|)$, located on the z-axis. On the cusp, *i.e.* $r = a$, the series expansion (5) is known to be logarithmically convergent [18], hence requiring thousands of terms to be summed in order to achieve convergence. On the contrary a polynomial approximate of degree 20 computed by means of Lanczos τ method allows one to evaluate the same series (5) with a high degree of accuracy (error in the order of 10^{-20}) and extremely fast.

Table 1 Lanczos τ method coefficients corresponding to a 1s STO with the parameters, $\varsigma = 1.5$, $a = 3$ and $r = a$ (on the cusp). Numbers in brackets denote powers of 10.

n	a_n	a_n	a_n
0	2.90270214243746[2]	2.90271536375708[2]	2.90271536375693[2]
1	-9.23628692089880[2]	-9.23632891847663[2]	-9.23632891847618[2]
2	1.23858592263836[3]	1.23859142994010[3]	1.23859142994004[3]
3	-9.39330456582493[2]	-9.39334790022894[2]	-9.39334790022834[2]
4	4.57974203096526[2]	4.57977275247655[2]	4.57977275247641[2]
5	-1.54954101477319[2]	-1.54954144775564[2]	-1.54954144775711[2]
6	3.83543454867823[1]	3.83517218144107[1]	3.83517218142957[1]
7	-7.21944943795341[0]	-7.22152133365157[0]	-7.22152133291221[0]
8	1.06335790093702[0]	1.06664219088861[0]	1.06664219146854[0]
9	-1.29103493098012[-1]	-1.26657942734321[-1]	-1.26657944550326[-1]
10	1.37597143959723[-2]	1.23379951507955[-2]	1.23379936724341[-2]
11		-1.00275048939097[-3]	-1.00274808809830[-3]
12		6.89736316450617[-5]	6.89756193791877[-5]
13		-4.06367837942569[-6]	-4.06531357479104[-6]
14		2.08847712909750[-7]	2.07498298267557[-7]
15		-9.72222111821248[-9]	-9.25772177233801[-9]
16			3.64024254574633[-10]
17			-1.27074184206376[-11]
18			3.96351573618861[-13]
19			-1.11458064883464[-14]
20			2.89362283832071[-16]
τ	-1.08841490827515[-3]	2.40325900444095[-11]	-2.23525476364114[-20]

Second, nuclear attraction integrals appearing as part of the potential energy matrix in molecular structure calculations were calculated using the scheme described above. It was found that the present values are in good agreement with those previously published in the literature. Indeed, using HCN and H2O as case studies, *cf.* table (3) and (4), it can be seen that a good agreement is obtained when comparing the values generated with the method described above with those of other approaches.

Table 2 Atomic orbital parameter describing the ground state of the HCN molecule

Atom	Atomic orbital and screening constant	
H	*1s*	1.24
C	*1s*	5.67
	2s	1.61
	2p(z)	1.56
	2p(x, y)	1.54
N	*1s*	6.66
	2s	1.94
	2p(z)	1.92
	2p(x, y)	1.80

Table 3 Selected three-center nuclear attraction integrals and comparisons with previous work. Numbers in parenthesis denote powers of 10.

Integral	This work	Reference[18]	Alchemy[39]	DTest*
$\left\langle 1s(H) \mid 1s(C) \right\rangle$	2.945496054(-1)	2.945496054(-1)	2.945496054(-2)	2.945494454(-2)
$\left\langle 1(H) \mid 2s(C) \right\rangle$	1.606646078(-1)	1.606646078(-1)	1.606646041(-1)	1.606645937(-1)
$\left\langle 1(H) \mid 2pz(C) \right\rangle$	-1.163866018(-1)	-1.163866018(-1)	-1.163866018(-1)	-1.163865846(-1)
$\left\langle 1s(C) \mid 1s(N) \right\rangle$	3.710041454(-5)	3.710041454(-5)	3.710041454(-5)	3.710152495(-5)
$\left\langle 1s(C) \mid 2s(N) \right\rangle$	2.695528880(-2)	2.695528880(-2)	2.695528880(-2)	2.695532230(-2)
$\left\langle 1s(C) \mid 2pz(N) \right\rangle$	-4.621491513(-2)	-4.621491513(-2)	-4.621491513(-2)	-4.621497451(-2)
$\left\langle 2s(C) \mid 1s(N) \right\rangle$	1.408177370(-2)	1.408177370(-2)	1.408177370(-2)	1.408441969(-2)
$\left\langle 2s(C) \mid 2s(N) \right\rangle$	1.467233406(-1)	1.467233406(-1)	1.467233406(-1)	1.467232649(-1)
$\left\langle 2s(C) \mid 2pz(N) \right\rangle$	-1.530415963(-1)	-1.530415963(-1)	-1.530415963(-1)	-1.530415938(-1)
$\left\langle 2px(C) \mid 2px(N) \right\rangle$	1.009914329(-1)	1.009914329(-1)	1.00914329(-1)	1.009914330(-1)

* Values computed with the code based on the Legendre-Mobius quadrature [38] for which the controlling parameter are LRM 90| 30, 20; 1(-6) | 20, 16; 1(-7) | 10, 10; 1(-8)

Table 4 Three-center nuclear integrals over STOs. The values were generated for H_2O defined in spherical coordinates as, O(0,0,0), H_1(1.81, 52.5°, 0.0), H_2(1.81, 52.5°, 180°)

Integral	ς_1	ς_2	This work*	$S\overline{D}$ †
$\left\langle 1s(O) \mid 1s(H_1) \right\rangle$	7.67	1.21	0.3067870371(-1)	0.3067870402(-1)
$\left\langle 2s(O) \mid 1s(H_1) \right\rangle$	2.09	1.21	0.2313538733	0.2313538730
$\left\langle 2pz(O) \mid 1s(H_1) \right\rangle$	1.50	1.21	0.1710199941	0.1710199961

$\langle 2pz(O) \mid 1s(H_1)\rangle$	3.50	1.21	0.7740274814	0.7740274802(-1)
$\langle 2p_1(O) \mid 1s(H_1)\rangle$	1.50	1.21	0.7699878531(-1)	0.7699898494(-1)
$\langle 2p_1(O) \mid 1s(H_1)\rangle$	3.50	1.21	0.2997862984(-1)	0.2997862979(-1)
$\langle 2p_{-1}(O) \mid 1s(H_1)\rangle$	1.50	1.21	-0.7699878531(-1)	-0.7699898494(-1)
$\langle 2p_{-1}(O) \mid 1s(H_1)\rangle$	3.50	1.21	-0.2997862984(-1)	-0.2997862979(-1)
$\langle 1s(O) \mid 1s(H_1)\rangle$	7.67	1.25	0.3000060089(-1)	0.3000060106(-1)
$\langle 2s(O) \mid 1s(H_1)\rangle$	2.09	1.25	0.2269676906	0.2269676902
$\langle 2pz(O) \mid 1s(H_1)\rangle$	1.50	1.25	0.1700603512	0.1700603538
$\langle 2pz(O) \mid 1s(H_1)\rangle$	3.50	1.25	0.7739215284(-1)	0.7739215272(-1)
$\langle 2p_1(O) \mid 1s(H_1)\rangle$	1.50	1.25	0.7936141395(-1)	0.7936139417(-1)
$\langle 2p_1(O) \mid 1s(H_1)\rangle$	3.50	1.25	0.3124157383(-1)	0.3124157378(-1)
$\langle 2p_{-1}(O) \mid 1s(H_1)\rangle$	1.50	1.25	-0.7936141395(-1)	-0.7936139417(-1)
$\langle 2p_{-1}(O) \mid 1s(H_1)\rangle$	3.50	1.25	-0.3124157383(-1)	-0.3124157378(-1)

[*] The abbreviations $2p_1$ and $2p_{-1}$ refer to STOs defined by the quantum numbers, *(n=2, l=1, m=1)* and *(n=2, l=1, m=-1)*.

[†] Values computed using the method based on the $S\overline{D}$ approach, *cf.* refs [23] and [24]

Beyond the numerical values of isolated integrals, it is to mentioned that nuclear attraction integrals are of prime importance in the field of electron/positron – molecule scattering. Indeed, in the framework of perturbation theory the first order correction of the energy is given by,

$$V_s(\vec{s}) = \left\langle \Psi^0(\vec{x}) \left| \sum_i \frac{q}{|\vec{x}_i - \vec{s}|} \right| \Psi^0(\vec{x}) \right\rangle \tag{5}$$

where $\Psi^0(\vec{x})$ stands for the wave function of the isolated target in which $\vec{x}$ represents the coordinates of bound electrons (collectively) while $\vec{s}$ is the location of the incoming projectile whose charge is q. This clearly illustrates the importance of having an accurate scheme for the evaluation of nuclear attraction integrals.

4 Conclusion

Perhaps the major difficulty in using the one-center expansion method (5) is the elaboration of an efficient summation procedure enabling a fast computation of multi-center integrals occurring in quantum chemistry. This work constitutes a first step towards eliminating/reducing the convergence difficulties inherent to the addition theorem (5). However, it has to be mentioned that an efficient procedure is yet to be elaborated since the computation of the coefficients of Lanczos polynomial approximate, as described by equation (10), requires solving a linear system which for each value of the integration variable r. This clearly introduces undesirable overhead, which slows the numerical procedure. On the bright side of things, this work provides a proof of concept that molecular integrals over STOs can benefit from such a technique as the Lanczos τ method.

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Second 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 multicenter integrals over Slater-type orbitals and related functions.