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2005 J. Phys. A: Math. Gen. 38 3923

(http://iopscience.iop.org/0305-4470/38/18/004)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS A: MATHEMATICAL AND GENERAL

J. Phys. A: Math. Gen. **38** (2005) 3923–3935 doi:10.1088/0305-4470/38/18/004

A new Gauss quadrature for multicentre integrals over STOs in the Gaussian integral transform approach

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Received 27 December 2004, in final form 23 February 2005
Published 18 April 2005
Online at stacks.iop.org/JPhysA/38/3923

Abstract

When computing multicentre integrals over Slater-type orbitals (STOs) by means of the Shavitt and Karplus Gaussian integral transforms (Shavitt and Karplus 1962 *J. Chem. Phys.* **36** 550), one usually ends up with a multiple integral of the form $\int_0^1 \mathrm{d}u \int_0^1 \mathrm{d}v \cdots \int_0^\infty \mathrm{d}z\, \mathcal{F}(u, v, \ldots, z)$ (Shavitt and Karplus 1965 *J. Chem. Phys.* **43** 398) in which all the integrals are inter-related. The most widely used approach for computing such an integral is to apply a product of Gauss–Legendre quadratures for the integrals over $[0, 1]$ while the semi-infinite term is evaluated by a special procedure. Although numerous approaches have been developed to accurately perform the integration over $[0, \infty)$ efficiently, it is the aim of this work to add a new tool that could be of some benefit in carrying out the hard task of multicentre integrals over STOs. The new approach relies on a special Gauss quadrature referred to as Gauss–Bessel to accurately evaluate the semi-infinite integral of interest. In this work, emphasis is put on accuracy rather than efficiency since its aim is essentially to bring a proof of concept showing that Gauss–Bessel quadrature can successfully be applied in the context of multicentre integrals over STOs. The obtained accuracy is comparable to that obtained with other methods available in the literature.

PACS number: 02.30.Uu

1. Introduction

Practical quantum chemistry uses approximation methods with different degrees of sophistication in order to generate the data that are of interest to experimentalists and theoreticians. In practice, use of approximate methods is necessary mainly because the Schrödinger equation can only be solved exactly for very few atomic and molecular systems with limited interest, e.g., H, H_2^+ and suchlike.

Perhaps the most widely used technique to construct approximate molecular wavefunctions is the so-called Roothaan's linear combination of atomic orbitals (LCAO) [1]. As a result of using such an ansatz, the core component of most, if not all, quantum chemistry software is a module dedicated to the computation of multicentre integrals. Based on the results obtained from several investigations of the properties of the Schrödinger eigenfunctions, it can be argued that exponential-type functions (ETFs) constitute the most suitable class of functions to be used as part of the LCAO procedure. Among the legion of possible ETFs candidates, Slater-type orbitals (STOs) are probably those which attracted most of the attention owing to their analytical form in the coordinate space. However, although STOs (or more generally ETFs) are theoretically the most appropriate for quantum chemistry calculations, such functions have never been used extensively in practice because multicentre integrals always led to inefficient numerical algorithms. Gaussian-type orbitals (GTOs) were proposed since they allowed cost efficient procedures to be developed for multicentre integrals. GTOs owe their success to one very important feature: their multiplication theorem [2, 3 (p 154)] allowing a product of two such orbitals centred on two arbitrary points defined by **a** and **b** to be written as

$$\exp(-\alpha_1\|\mathbf{r}-\mathbf{a}\|^2)\exp(-\alpha_2\|\mathbf{r}-\mathbf{b}\|^2) = \exp\left(-\frac{\alpha_1\alpha_2}{\alpha_1+\alpha_2}\|\mathbf{a}-\mathbf{b}\|^2\right) \times \exp\left[-(\alpha_1+\alpha_2)\left\|\mathbf{r}-\frac{\alpha_1\mathbf{a}+\alpha_2\mathbf{b}}{\alpha_1+\alpha_2}\right\|^2\right]. \quad (1)$$

To within a constant, the result is obviously a new Gaussian centred on the centre of 'mass' (barycentre) of the two initial centres.

Evaluation of multicentre integrals over STOs, and especially the four centre which are the true bottleneck of any quantum chemistry package, was recognized to be a challenging mathematical and numerical problem from the early days of quantum chemistry. Various methods were proposed as possible routes to obtain efficient numerical procedures. These can be clustered into two major categories:

- Addition-theorem-based methods which can be referred to as one range [4] and two range [5].
- Integral transforms. Two of these methods have received particular attention in the literature: the Gaussian integral transform (GIT) [6, 7] and the Fourier integral transform (FIT) [8].

This work falls into the second category as it is based on the GIT originally introduced and investigated by Shavitt and Karplus in several milestone papers [6, 7]. When such an approach is used, STOs are first represented by a product of semi-infinite integrals in which the integrand involves a product of GTOs. This fact allows the Gaussian multiplication theorem to be applied, hence simplifying to some extent the computation. As a result, multicentre integrals end up being represented by a multiple integral which can be written in the form $\int_0^1 \mathrm{d}u \int_0^1 \mathrm{d}v \cdots \int_0^\infty \mathrm{d}z\, \mathcal{F}(u, v, \ldots, z)$. In their original work, Shavitt and Karplus have evaluated the innermost semi-infinite integral using suitable series expansions, i.e., one for small values of z and an asymptotic form for large values of z. More recently, Rico *et al* [9] have expanded the semi-infinite integral as an infinite series involving modified Bessel functions of the second kind $\mathbf{k}_v(z)$. Using this approach the authors were able to expand Slater-type two-centre charge distributions as an infinite series of ETFs located on the line joining the two centres. The aim of this work is to present an alternative to both approaches since it proposes to develop a special Gauss quadrature, referred to as Gauss–Bessel, specifically tailored to

the integrand involved in the semi-infinite integral. As an application of the new method, three-centre nuclear attraction integrals over s STOs are evaluated.

2. Mathematical preliminaries

Among the legion of functions that may be used as the building block for the trial LCAO wavefunction, Slater-type orbitals (STOs) [10] are probably the functions with the simplest analytical form in the coordinate space. In the framework of the LCAO methodology, atomic orbitals (which in the case of interest are STOs) are centred on the atoms constituting the molecule. As a consequence, STOs involved as part of the trial wavefunction are expressed as

$$\chi_{n,l}^{m}(\alpha\|\mathbf{r}-\mathbf{a}\|) = \mathcal{N}_n(\alpha)\|\mathbf{r}-\mathbf{a}\|^{n-l-1}\exp(-\alpha\|\mathbf{r}-\mathbf{a}\|)\mathcal{Y}_l^m\left(\frac{\mathbf{r}-\mathbf{a}}{\|\mathbf{r}-\mathbf{a}\|}\right)$$
$$\text{with}\quad \mathcal{N}_n(\alpha) = \frac{(2\alpha)^{n+1/2}}{\sqrt{(2n)!}} \tag{2}$$

in which the vector $\mathbf{a}$ gives the location of the centre (atom) with respect to some chosen reference framework. $\mathcal{Y}_l^m(\mathbf{k})$ stands for the solid spherical harmonic of degree n and order m and is related to the corresponding surface harmonic. Using the Condon and Shortley convention, solid spherical harmonics can be expressed as

$$\begin{aligned}\mathcal{Y}_l^m(\mathbf{k}) &= \|\mathbf{k}\|^l Y_l^m(\theta_{\mathbf{k}},\phi_{\mathbf{k}})\\ &= \mathrm{i}^{m+|m|}\sqrt{\frac{2l+1}{4\pi}\frac{(l-|m|)!}{(l+|m|)!}}P_l^{|m|}(\cos\theta)\,\mathrm{e}^{\mathrm{i}m\phi}\end{aligned} \tag{3}$$

where $P_l^m(z)$ represents the associated Legendre function [11 (pp 174, 232)].

Among the methods that were proposed in the early days of quantum chemistry to solve the problem of multi-centre integrals over STOs is the so-called Gaussian integral transform approach (GIT). Perhaps the strongest incentive behind the work of Shavitt and Karplus when they proposed the GIT method was the unprecedented success of GTOs in leading to very efficient algorithms for computing multi-centre integrals over GTOs. Thus, to take advantage of such efficient algorithms, Shavitt and Karplus start by representing a 1s Slater orbital by a semi-infinite integral in which a Gaussian-like function occurs

$$\chi_{1,0}^{0}(\alpha\|\mathbf{r}-\mathbf{a}\|) = \mathcal{N}_1(\alpha)\frac{\alpha}{2\sqrt{\pi}}\int_0^{+\infty} s^{-3/2}\exp\left(-\frac{\alpha^2}{4s}\right)\underbrace{\exp(-s\|\mathbf{r}-\mathbf{a}\|^2)}_{\text{Gaussian-type orbital}}\,\mathrm{d}s. \tag{4}$$

According to [7], the above formulation can be viewed as the equivalent of a series representation in which a STO would be expressed as a sum of an infinite number of GTO-like orbitals. The major consequence of using the above integral transform is the possibility for multi-centre integrals over STOs to be represented by multiple integrals in which the integrand involves GTO-like terms. The next step of course is to simply perform the integration over electronic coordinates using Boys formulae [2] routinely used in the context of multi-centre integrals over GTOs basis sets. In the case of multi-centre integrals over STOs, proceeding in the way outlined above yields a multiple integral in which the innermost integral is semi-infinite. The contribution of this work is related to this particular aspect of the computation. In the following, three points are addressed:

1. Formulae for three-centre nuclear attraction integrals used in this work are presented.
2. Details on the derivation of the numerical algorithms, namely derivation of a new class of orthogonal polynomials, to be used for numerical experiments are shown.

3. Comparative numerical experiments are presented showing the potential of the current method as compared to others.

3. Three-centre nuclear integrals

Three centre nuclear attraction integrals over STOs are by far the most difficult one-electron integrals which need to be computed for *ab initio* quantum chemical calculations. As a consequence, an efficient computational procedure would not only help the standard SCF procedure but would also be beneficial for techniques such as density functional theory (DFT). Indeed in the latter three-centre nuclear attraction integrals are probably among the most difficult quantities needed for a full quantum mechanical calculation on molecular systems. For the sake of completeness, we start with an outline of the route originated by Shavitt and Karplus which leads to the master formula describing three-centre nuclear attraction integrals involving 1s STOs. Three-centre integrals (using 1s STOs) are defined as

$$\mathcal{I}^{1,0,0}_{1,0,0}(\alpha_1, \alpha_2, \mathbf{a}, \mathbf{b}, \mathbf{c}) = \left\langle \chi^0_{1,0}(\alpha_1, \|\mathbf{r}-\mathbf{a}\|) \left| \frac{1}{\|\mathbf{r}-\mathbf{c}\|} \right| \chi^0_{1,0}(\alpha_2, \|\mathbf{r}-\mathbf{b}\|) \right\rangle. \quad (5)$$

In the above definition each of the 1s STO is replaced by its GIT as given by equation (4) which yields

$$\mathcal{I}^{1,0,0}_{1,0,0}(\alpha_1, \alpha_2, \mathbf{a}, \mathbf{b}, \mathbf{c}) = \mathcal{N}_1(\alpha_1)\mathcal{N}_2(\alpha_2)\frac{\alpha_1\alpha_2}{4\pi}\int_{x=0}^{+\infty}\int_{y=0}^{+\infty}(xy)^{-3/2}\exp\left(-\frac{\alpha_1^2}{4x}-\frac{\alpha_2^2}{4y}\right) \times \left\langle \exp(-x\|\mathbf{r}-\mathbf{a}\|^2)\left|\frac{1}{\|\mathbf{r}-\mathbf{c}\|}\right|\exp(-y\|\mathbf{r}-\mathbf{b}\|^2)\right\rangle_{\mathbf{r}} \mathrm{d}x\,\mathrm{d}y. \quad (6)$$

The last term in the above integrand, i.e., the integral over the electron coordinates $\mathbf{r}$, can be replaced following Boys approach [2 (equation (17))] which yields

$$\mathcal{I}^{1,0,0}_{1,0,0}(\alpha_1, \alpha_2, \mathbf{a}, \mathbf{b}, \mathbf{c}) = \mathcal{N}_1(\alpha_1)\mathcal{N}_2(\alpha_2)\frac{\alpha_1\alpha_2}{4\pi}\int_{x=0}^{+\infty}\int_{y=0}^{+\infty}(xy)^{-3/2}\exp\left(-\frac{\alpha_1^2}{4x}-\frac{\alpha_2^2}{4y}\right) \times \frac{2\pi}{x+y}\exp\left(-\frac{xy}{x+y}\|\mathbf{a}-\mathbf{b}\|^2\right)F_0[(x+y)\|\mathbf{p}-\mathbf{c}\|^2]\,\mathrm{d}x\,\mathrm{d}y \quad (7)$$

in which the vector $\mathbf{p}$ is related to $\mathbf{a}$ and $\mathbf{b}$ by the following relationship [3 (p 154)]:

$$\mathbf{p} = \frac{x\mathbf{a}+y\mathbf{b}}{x+y}. \quad (8)$$

The function $F_0(z)$ appearing in equation (7) is usually referred to as the Boys function and is generally defined as

$$F_m(z) = \int_0^1 t^{2m}\exp(-zt^2)\,\mathrm{d}t. \quad (9)$$

Here, it is worth reminding the reader that the evaluation of the function $F_m(z)$ has received particular attention in the context of multi-centre integrals over GTOs. In addition to the obvious approach in which series representations and classical Gauss quadratures are used, there has also been a procedure that used a special class of orthogonal polynomials (Rys polynomials). The implementation of this approach was widely used in Hondo [12].

Now, by introducing two new variables, $u = x/(x + y)$ and $z = x + y$, one can re-write equation (7) according to [7] as

$$\mathcal{I}^{1,0,0}_{1,0,0}(\alpha_1, \alpha_2, \mathbf{a}, \mathbf{b}, \mathbf{c}) = \mathcal{N}_1(\alpha_1)\mathcal{N}_2(\alpha_2)\frac{\alpha_1\alpha_2}{2}\int_{u=0}^{1}[u(1-u)]^{-3/2}\int_{z=0}^{+\infty} z^{-3} \times \exp\left[-u(1-u)\|\mathbf{a}-\mathbf{b}\|^2 z - \frac{1}{4}\left(\frac{\alpha_1^2}{u} + \frac{\alpha_2^2}{1-u}\right)\frac{1}{z}\right] F_0[z\|\mathbf{p}-\mathbf{c}\|^2]\,\mathrm{d}z\,\mathrm{d}u \tag{10}$$

At this point it is worth noting that the $\mathbf{p} - \mathbf{c}$ depends only on u since we have, $\mathbf{p} - \mathbf{c} = u\mathbf{a} + (1-u)\mathbf{b} - \mathbf{c}$. Following the notation of [7] and define two parameters

$$a = \|\mathbf{a} - \mathbf{b}\| \qquad \text{and} \qquad p = \|\mathbf{p} - \mathbf{c}\|. \tag{11}$$

Furthermore, to bring equation (10) into the Shavitt and Karplus [7] form we perform a change of variable $w = p^2 z$ which yields after some simplifications

$$\mathcal{I}^{1,0,0}_{1,0,0}(\alpha_1, \alpha_2, \mathbf{a}, \mathbf{b}, \mathbf{c}) = \mathcal{N}_1(\alpha_1)\mathcal{N}_2(\alpha_2)\frac{\alpha_1\alpha_2}{2}\int_{u=0}^{1}\frac{1}{[u(1-u)]^{3/2}}p^4 T_{5/2,0}(\sigma, \tau)\,\mathrm{d}u \tag{12}$$

in which the semi-infinite integral is generalized to have the following form:

$$T_{l,m}(\sigma, \tau) = \int_0^{+\infty} w^{m-l-1/2}F_0(w)\exp\left(-\sigma w - \frac{\tau}{w}\right)\mathrm{d}z \tag{13}$$

where the parameters σ and τ are such that

$$\sigma = u(1-u)\frac{a^2}{p^2} \qquad \text{and} \qquad \tau = \frac{p^2}{4}\left(\frac{\alpha_1^2}{u} + \frac{\alpha_2^2}{1-u}\right). \tag{14}$$

For the purpose of this work, the numerical algorithms and experiments will be illustrated using arbitrary s-type orbitals because of their intrinsic simplicity and the ease of the corresponding working formulae. Indeed a general formula for three-centre nuclear attraction integrals involving high-order s-type orbitals can readily be derived by differentiating the un-normalized form of equation (10) with respect to the screening parameters α_1 and α_2. However, in order to make subsequent analytical work straightforward, it is highly desirable to start by representing the un-normalized version of equation (10) as the first partial derivative with respect to α_1 and α_2. Thus noticing that such a differentiation operation yields

$$\begin{aligned}\mathcal{U}^{1,0,0}_{1,0,0}(\alpha_1, \alpha_2, \mathbf{a}, \mathbf{b}, \mathbf{c}) &= \mathcal{I}^{1,0,0}_{1,0,0}(\alpha_1, \alpha_2, \mathbf{a}, \mathbf{b}, \mathbf{c})/[\mathcal{N}_1(\alpha_1)\mathcal{N}_2(\alpha_2)] \\ &= 2\int_{u=0}^{1}[u(1-u)]^{-1/2}\int_{z=0}^{+\infty} z^{-1}F_0(z)\left(-\frac{\partial}{\partial\alpha_1}\right) \\ &\quad \times \left(-\frac{\partial}{\partial\alpha_2}\right)\exp\left(-\sigma z - \frac{\tau}{z}\right)\mathrm{d}z\,\mathrm{d}u\end{aligned} \tag{15}$$

it is clear that three-centre nuclear attraction integrals involving arbitrary s orbitals can easily by obtained by means of the following:

$$\mathcal{I}^{n_2,0,0}_{n_1,0,0}(\alpha_1, \alpha_2, \mathbf{a}, \mathbf{b}, \mathbf{c}) = \mathcal{N}_{n_1}(\alpha_1)\mathcal{N}_{n_2}(\alpha_2)\left(-\frac{\partial}{\partial\alpha_1}\right)^{n_1}\left(-\frac{\partial}{\partial\alpha_2}\right)^{n_2}\mathcal{U}^{1,0,0}_{1,0,0}(\alpha_1, \alpha_2, \mathbf{a}, \mathbf{b}, \mathbf{c}). \tag{16}$$

From equations (15) and (14) it is clear that the differentiation operator will only act on the term involving τ which is $\exp(-\tau/z)$. For instance, the n_1th derivative with respect to α_1 is obtained from

$$\left(-\frac{\partial}{\partial\alpha_1}\right)^{n_1}\exp\left(-\frac{p^2}{4uz}\alpha_1^2\right). \tag{17}$$

As pointed out in [7], the above differentiation should lead to a Hermite polynomial of order n_1 since the derivatives given above are closely related to Rodrigues representation [13 (p 768)] of such polynomials,

$$\mathrm{H}_n(z) = \exp(z^2)\left(-\frac{\mathrm{d}}{\mathrm{d}z}\right)^n \exp(-z^2). \tag{18}$$

As a consequence, three-centre nuclear attraction integrals involving arbitrary s STOs can finally be obtained by combining equations (16), (15) and the Rodrigues representation of Hermite polynomials (18). This yields

$$\begin{aligned}\mathcal{I}_{n_1,0,0}^{n_2,0,0}(\alpha_1,\alpha_2,\mathbf{a},\mathbf{b},\mathbf{c}) = \mathcal{N}_{n_1}(\alpha_1)\mathcal{N}_{n_2}(\alpha_2)2^{-(n_1+n_2-1)}\int_{u=0}^{1} u^{-(n_1+1)/2}(1-u)^{-(n_2+1)/2}\\ \times\int_{z=0}^{+\infty} z^{-(n_1+n_2+2)/2}\mathrm{H}_{n_1}\left[\frac{\alpha_1 p}{2\sqrt{u}}\frac{1}{\sqrt{z}}\right]\mathrm{H}_{n_2}\\ \times\left[\frac{\alpha_1 p}{2\sqrt{1-u}}\frac{1}{\sqrt{z}}\right]F_0(z)\exp\left(-\sigma z-\frac{\tau}{z}\right)\mathrm{d}z\,\mathrm{d}u.\end{aligned} \tag{19}$$

For the computation that will take place in the next section, it is advisable to introduce a change of variable $x = 1/z$ allowing the semi-infinite integral occurring above to be transformed into the following:

$$\begin{aligned}\mathcal{T}(n_1,n_2,u,a,p) = \int_0^{+\infty} \underbrace{x^{(n_1+n_2-2)/2}\mathrm{H}_{n_1}\left[\frac{\alpha_1 p}{2}\frac{\sqrt{x}}{\sqrt{u}}\right]\mathrm{H}_{n_2}\left[\frac{\alpha_2 p}{2}\frac{\sqrt{x}}{\sqrt{1-u}}\right]}_{\mathcal{P}_{n_1+n_2-1}(x)} F_0\left(\frac{1}{x}\right)\\ \times\exp\left(-\frac{\sigma}{x}-\tau x\right)\mathrm{d}x.\end{aligned} \tag{20}$$

Using the fact that Hermite polynomials are defined as [11 (p 250)]

$$\mathrm{H}_n(z) = n!\sum_{m=0}^{[n/2]}\frac{(-1)^m(2z)^{n-2m}}{m!(n-2m)!} \tag{21}$$

it is clear that the product referred to as $\mathcal{P}_{n_1+n_2-1}(z)$ in equation (20) is indeed a polynomial of degree n_1+n_2-1 as can easily be seen from the following:

$$\begin{aligned}\mathcal{P}_{n_1+n_2-1}(z) &= z^{(n_1+n_2-2)/2}\mathrm{H}_{n_1}(r\sqrt{z})\mathrm{H}_{n_2}(s\sqrt{z})\\ &= n_1!n_2!\sum_{m_1=0}^{[n_1/2]}\sum_{m_2=0}^{[n_2/2]}\frac{(-1)^{m_1}}{m_1!(n_1-2m_1)!}\frac{(-1)^{m_2}}{m_2!(n_2-2m_2)!}\\ &\quad\times(2r)^{n_1-2m_1}(2s)^{n_2-2m_2}z^{n_1+n_2-m_1-m_2-1}\end{aligned} \tag{22}$$

in which $r = (\alpha_1 p)/(2\sqrt{u})$ and $s = (\alpha_2 p)/(2\sqrt{1-u})$. This fact is very important since the following section relies on it to justify the usefulness of a special quadrature for the computation of the semi-infinite integral (20). As a last note, it is worth mentioning that equation (20) can be written as a finite sum involving integrals similar to that of given by (13)

$$\begin{aligned}\mathcal{T}(n_1,n_2,u,a,p) = n_1!n_2!\sum_{m_1}^{[n_1/2]}\sum_{m_2}^{[n_2/2]}\frac{(-1)^{m_1}}{m_1!(n_1-2m_1)!}\frac{(-1)^{m_2}}{m_2!(n_2-2m_2)!}\\ \times(2r)^{n_1-2m_1}(2s)^{n_2-2m_2}T_{n_1+n_2+1/2,m_1+m_2}(z).\end{aligned} \tag{23}$$

4. Evaluation of the semi-infinite integral

As can be seen from equations (10) and (19), three-centre nuclear attraction integrals are represented by a double integral the innermost of which is semi-infinite. For numerical work Shavitt and Karplus computed the semi-infinite integrals $T_{l,m}(\sigma, \tau)$ of (13) by means of its series representation. Furthermore, to improve the computational efficiency, the authors had recourse to the so-called Aitken Δ^2 convergence accelerator [14]. This indeed was a brilliant idea and nowadays much more sophisticated techniques, such as Wynn's epsilon algorithm [15] or Levin u [16] transformation and its generalizations [17], can be applied to the same infinite series to potentially get an even better convergence. More recently, Rico *et al* [9] implemented a numerical procedure in which the semi-infinite integral $T_{l,m}(\sigma, \tau)$ was evaluated as a series involving modified Bessel functions of the second kind $\mathbf{k}_\nu(z)$ (also known as McDonald functions). According to the authors, when proceeding in this way, the leading numerical procedure is accurate and reasonably cost efficient. This work adds to the arsenal of methods that could possibly be applied to evaluate $T_{l,m}(\sigma, \tau)$. Indeed, because of the severe efficiency constraints that are to be imposed on the numerical algorithms used to compute multi-centre integrals over STOs, we would like to investigate the potential benefits of a new approach which could possibly be considered as an alternative to the work of Shavitt and Karplus and Rico *et al*. Of course, the objective of this work is mostly focused on the accuracy of the results as opposed to the efficiency of the procedure which will be addressed as more insight is gained through more experimentations. When considering the semi-infinite integral $\mathcal{T}(n_1, n_2, u, a, p)$ of equation (20) it can be noted that its integrand is represented by a product of three terms: a polynomial $\mathcal{P}_{n_1+n_2-1}(z)$ (by virtue of equation 22), a Boys function $F_0(z)$ and an exponential term with a special argument. Luckily, in the case of three-centre nuclear attraction integrals the term $F_0(z)$ reduces to $\sqrt{\pi}/2)\,\mathrm{erf}(\sqrt{z})/\sqrt{z}$. As a consequence, the integrand of equation (19) can be represented as

$$\text{Integrand} = \frac{\sqrt{\pi}}{2}\mathcal{P}_{n_1+n_2-1}(z)\,\mathrm{erf}\left(\frac{1}{\sqrt{z}}\right)\underbrace{\sqrt{z}\exp\left(-\frac{\sigma}{z}-\tau z\right)}_{W(\sigma,\tau;z)} \tag{24}$$

in which $\mathrm{erf}(z)$ stands for the error function. In the above equation, the term referred to as $W(\sigma, \tau; z)$ is obviously a non-negative function $\forall z \in \mathbb{R}_+$. As a consequence, the core idea of this work is to set up a special Gauss quadrature for which $W(\sigma, \tau; z)$ would be considered as the weight function. In fact, the present investigation was motivated by two major facts. (1) If the weight function $W(\sigma, \tau; z)$ is omitted from the integrand (24), the rest of the integrand is a smooth function that can be approximated by a low-order polynomial. (2) For certain values of the parameters σ and τ, $W(\sigma, \tau; z)$ presents a rather sharp peak around its unique moving extremum located at $z = [1/2 + \sqrt{1/4 + 4\sigma\tau}]/(2\tau)$. This particular feature of $W(\sigma, \tau; z)$ makes it hard for classical Gauss quadratures to be reliable without having recourse to splitting the integration range so to concentrate the quadrature nodes where the integrand is most significant (figure 1).

According to [18 (section 1.10)], a given function $W(z)$ is an *admissible* weight if the following conditions are satisfied:

$$\begin{aligned}
&\mathrm{C}_1\text{:} \quad W(z) \geqslant 0 \qquad \forall z \in [0, \infty)\\
&\mathrm{C}_2\text{:} \quad \int_0^{+\infty} W(z)\,\mathrm{d}z > 0\\
&\mathrm{C}_3\text{:} \quad \forall n \in \mathbb{N} \quad \int_0^{+\infty} z^n W(z)\,\mathrm{d}z < \infty.
\end{aligned}$$

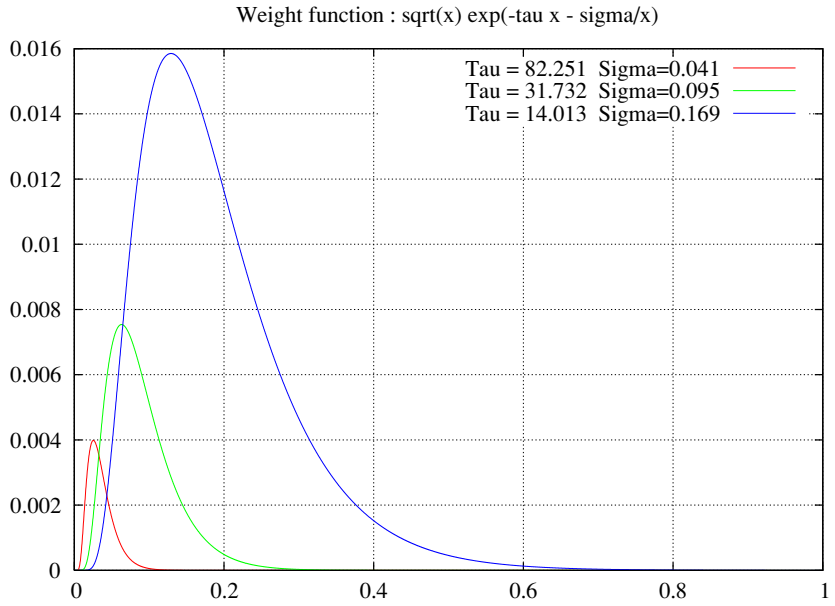

Figure 1. Plot of the weight function $W(\sigma, \tau; z)$ as defined by equation (24) for selected values of σ and τ.

In the context of this work, $W(\sigma, \tau; z)$ is an admissible weight function since it clearly satisfies the conditions enumerated above. The moments defined by condition C_3 and needed to set up the Gauss–Bessel quadrature in the next section, can be expressed analytically according to [11 (p 85)]

$$\int_0^{+\infty} z^n \underbrace{\left[z^{1/2} \exp\left(-\frac{\sigma}{z} - \tau z \right) \right]}_{W(\sigma,\tau;z)} \mathrm{d}z = 2\sqrt{\left(\frac{\sigma}{\tau}\right)^{n+3/2}} \mathbf{k}_{n+3/2}(2\sqrt{\sigma\tau}) \qquad \text{with} \quad \begin{cases} \Re(\sigma) > 0 \\ \Re(\tau) > 0 \end{cases} \tag{25}$$

where $\mathbf{k}_{n+1/2}(z)$ is the modified Bessel function of the second kind which because of its half integral order can be represented by a closed formula [19 (p 80)] as

$$\mathbf{k}_{n+1/2}(z) = \sqrt{\frac{\pi}{2z}} \exp(-z) \sum_{p=0}^{n} \frac{(n+p)!}{p!(n-p)!(2z)^p}. \tag{26}$$

In practice, the parameters τ and σ are both strictly positive since the outermost integral in (12) is generally computed using Gauss quadratures which do not necessarily use the boundary.

4.1. Setup of the Gauss–Bessel quadrature

Generally for a given admissible weight function satisfying the conditions enumerated above, the algorithm used to construct the corresponding Gauss quadrature proceeds in three steps. Although specialized books in numerical analysis define such a procedure based on rigorous mathematical foundations [20 (pp 105–12), [18] (pp 95–120)], in practice we found that [21 (pp 148–50)] provides a more computationally oriented description:

1. Build a family of polynomial orthogonal with respect to the inner product, $\langle f(z)|W(\sigma, \tau; z)|g(z)\rangle$. Clearly, the integration is to performed over the range of interest which in the present case would be $[0, +\infty)$.

2. Compute the roots of the newly created polynomials. To help speed up the process one may take advantage of the interlacing property of the roots of consecutive polynomials [21 (p 149)].
3. Compute the weights of the quadrature using the relationship

$$w_j = \frac{\langle p_{n-1}|p_{n-1}\rangle}{p_{n-1}(x_j)p'_n(x_j)} \tag{27}$$

in which $p'_n(x_j)$ is the derivative of the orthogonal polynomial at its zero x_j.

Perhaps the most intuitive procedure to use for building the orthogonal polynomials required by the mechanical quadrature to be used in this work is to proceed using the Gram–Schmidt orthogonalization method. The algorithm to be used relies on two theorems which according to [18 (pp 30, 31)] state the following:

Theorem 4.1. *If $p_0(x)$, $p_1(x)$, ..., are polynomials with*

$$p_n(x) = k_n x^n + \cdots \qquad \text{with} \quad k_n > 0 \tag{28}$$

orthogonal with respect to the inner product (f, g) then we have the recurrence

$$p_{n+1}(x) = \gamma_n x p_n(x) - \sum_{s=0}^{n} a_{n,s} p_s(x) \qquad \text{with} \quad n = 0, 1, 2, \ldots \tag{29}$$

where

$$p_0(x) \equiv k_0, \qquad \gamma_n = \frac{k_{n+1}}{k_n} \qquad \text{and} \qquad a_{n,s} = \gamma_n \frac{(xp_n, p_s)}{(p_s, p_s)} \qquad s = 0, 1, \ldots, n. \tag{30}$$

Theorem 4.2. *If the inner product satisfies the further condition that $(xf, g) = (f, xg)$, then the recurrence relation (30) reduces to the three term recurrence*

$$p_{n+1}(x) = (\gamma_n x - \alpha_n)p_n(x) - \beta_n p_{n-1}(x) \qquad n = 0, 1, \ldots \tag{31}$$

where we write $p_{-1}(x) = 0$, and where

$$\alpha_n = \gamma_n \frac{(xp_n, p_n)}{(p_n, p_n)}, \qquad n = 0, 1, \ldots$$
$$\beta_n = \gamma_n \frac{(xp_n, p_{n-1})}{(p_{n-1}, p_{n-1})} = \frac{\gamma_n}{\gamma_{n-1}} \frac{(p_n, p_n)}{(p_{n-1}, p_{n-1})}, \qquad n = 1, 2, \ldots. \tag{32}$$

Using the above theorems we can derive using the Gram–Schmidt orthogonalization procedure a family of polynomials orthogonal with respect to the weight function given in (24). To initiate the algorithm $p_0(x)$ and $p_1(x)$ are computed as

$$p_0(x) = 1 \qquad \text{and} \qquad p_1(x) = \left[x - \frac{(xp_0, p_0)}{(p_0, p_0)}\right] p_0(x). \tag{33}$$

Although the leading coefficients in $p_0(x)$ and $p_1(x)$ can be chosen rather arbitrarily, a legitimate and sensible choice would be (using the notation of theorem 4.1) $k_0 = 1$ and $k_1 = 1$. As a consequence of this, using equations (30) and (32) we can compute recursively $p_2(x)$, $p_3(x)$, ... This yields high-order polynomials in which the leading coefficient is such that, $k_n = 1$,

$$p_{n+1}(x) = \left[x - \frac{(xp_n, p_n)}{(p_n, p_n)}\right] p_n(x) - \frac{(p_n, p_n)}{(p_{n-1}, p_{n-1})} p_{n-1}(x). \tag{34}$$

Table 1. First few polynomials orthoginal with respect to the inner product $\langle f|W(1,1;z)|g\rangle_{[0,+\infty)}$.

	$p_1(z)$	$p_2(z)$	$p_3(z)$	$p_4(z)$	$p_5(z)$
x^0	−3/2	38/8	−865/61	1423 437/21 236	−43 806 791 147/112 925 752
x^1	1	−19/4	5967/244	−6214 591/42 472	228 819 254 915/225 851 504
x^2		1	−603/61	1820 901/21 236	−10 850 130 815/14 115 719
x^3			1	−179 991/10 618	6305 606 105/28 231 438
x^4				1	−366 590 090/14 115 719
x^5					1

To illustrate the above procedure, a selection of polynomials orthogonal with the respect to the weight function $W(1,1;x)$ (cf equation (24)) is listed in table 1. Now that we have the orthogonal polynomials constructed, the next step would be to determine the roots of such polynomials. This can easily be done by means of a specialized routine available from many mathematical libraries. For this work the roots of the selected polynomial were determined using an adapted version of a routine from [21] which is based on the Newton–Raphson algorithm. As a final step, the weights were computed using equation (27).

5. Numerical experiments

In the following, results for three-centre nuclear attractions are reported and comparisons with the literature are made from an accuracy point of view. Of course, because of the limitation imposed in the beginning of this work the results presented below involve only s orbitals. Two different molecular systems were considered: the HCN molecule representing the linear case and H_2O as an example of nonlinear systems. In addition to these, we also generated some values for a C3 system, C3 for which particular convergence problems arouse in the framework of the one-centre expansion method [22]. For the numerical experiments listed below, the integral over u in equation (19) was calculated using a Gauss–Legendre quadrature of order 32. However, before presenting results for three-centre nuclear attraction integrals, it is of importance to assess the stability of the Gauss–Bessel quadrature as a function of the number nodes used in the computation of the semi-infinite integral occurring in (19). For such a purpose, we compared values of $T_{5/2,0}(\sigma,\tau)$ as obtained by Gauss–Bessel quadrature against those obtained with its series representation. One such series was given by Shavitt and Karplus [7]

$$T_{l,m}(\sigma,\tau) = \sum_{i=m-l} [\Gamma(l+i+3/2)]^{-1} \left(\frac{\tau}{\sigma+1}\right)^{i+1/2} \mathbf{k}_{i+1/2}(2\sqrt{(\sigma+1)\tau}). \tag{35}$$

After comparing numerous values, mainly as the integrals listed in table 2 were computed a rough estimate was made for the order of the Gauss–Bessel quadrature that achieves the required accuracy for practical purposes. It was indeed found that using a quadrature of order 12 usually yields values for the semi-infinite integral in good agreement with those obtained by the series representation. In light of these findings it seemed reasonable to use a Gauss–Bessel of order 12 as part of the algorithm used to compute the selection of three-centre nuclear attraction integrals listed below. In fact, as far as accuracy is concerned, the values reported in tables 2 and 3 show a good agreement with alternative approaches, e.g., FIT using Gauss-Mobius quadrature [23], FIT combined with $\bar{D}$-like transformations [24–27], single centre expansion approach combined with nonlinear sequence transformation [22].

Table 2. Selected three-centre nuclear attraction integrals occurring in HCN[a]. The semi-infinite integral of (19) is computed by means of a Gauss–Bessel of order 12.

Integral	This work	Reference [22]	ALCHEMY [28]	DTEST[b] [23]
$\langle 1s(1.25, H)\|1s(5.67, C)\rangle$	2.945 496 055(−2)	2.945 496 054(−2)	2.945 496 054(−2)	2.945 494 454(−2)
$\langle 1s(1.25, H)\|2s(1.61, C)\rangle$	1.606 646 064(−1)	1.606 646 078(−1)	1.606 646 041(−1)	1.606 645 937(−1)
$\langle 1s(5.67, H)\|1s(6.66, N)\rangle$	3.710 041 454(−5)	3.710 041 454(−5)	3.710 041 454(−5)	3.710 152 495(−5)
$\langle 1s(5.67, H)\|2s(1.94, N)\rangle$	2.695 528 880(−2)	2.695 528 880(−2)	2.695 528 880(−2)	2.695 532 230(−2)
$\langle 2s(1.61, H)\|1s(6.66, N)\rangle$	1.408 177 371(−2)	1.408 177 370(−2)	1.408 177 370(−2)	1.408 441 969(−2)
$\langle 2s(1.61, H)\|2s(1.94, N)\rangle$	1.467 233 410(−1)	1.467 233 406(−2)	1.467 233 406(−1)	1.467 232 649(−1)

[a] The HCN molecule is along the Z-axis and such that $d(H, C) = 2.0143$ and $d(C, N) = 4.1934$.
[b] Values obtained with DTEST program in which the control parameters were such that LRM 90|30, 20; 1(−6)|20, 16; 1(−7)|10, 10; 1(−8).

Table 3. Selected three-centre nuclear attraction integrals from nonlinear systems. The semi-infinite integral of (19) is computed by means of a Gauss–Bessel quadrature of order 12.

Integral	This work[a]	This work[b]	FIT with $S\bar{D}$[c]
$\langle 1s(7.67, O)\|1s(1.21, H_1)\rangle$[d]	3.067 873 120(−2)	3.067 870 402(−2)	3.067 870 402(−2)
$\langle 2s(2.09, O)\|1s(1.21, H_1)\rangle$[d]	2.313 538 707(−1)	2.313 538 707(−1)	2.313 538 730(−1)
$\langle 1s(7.67, O)\|1s(1.25, O_1)\rangle$[d]	3.000 060 106(−3)	3.000 060 106(−2)	3.000 060 106(−2)
$\langle 2s(2.09, O)\|1s(1.25, O_1)\rangle$[d]	2.269 676 910(−1)	2.269 676 910(−1)	2.269 676 902(−1)
Integral	This work[a]	Reference [22]	DTEST
$\langle 1s(5.67, C_1)\|1s(5.57, C_2)\rangle$[e]	2.320 323 542(−5)	2.320 346 760(−5)	2.320 320 390(−5)
$\langle 2s(1.61, C_1)\|1s(5.57, C_2)\rangle$[e]	2.036 354 376(−2)	2.036 349 670(−2)	2.036 346 710(−2)
$\langle 2s(1.61, C_1)\|2s(1.61, C_2)\rangle$[e]	1.949 350 808(−1)	1.949 350 000(−1)	1.949 349280(−1)

[a,b] Numerical evaluation were performed using a 32 and 96 Gauss–Legendre for the outermost integral in equation (19).
[b] Values obtained with DTEST program in which the control parameters were such that LRM 90|30, 20; 1(−6)|20, 16; 1(−7)|10, 10; 1(−8).
[c] Based on the method developed in [26, 27].
[d] Selected three-centre nuclear attraction integrals from H_2O defined in spherical coordinates (r, θ, ϕ) as O(0, 0, 0), $H_1(1.81, 52.5^\circ, 0.0^\circ)$, $H_2(1.81, 52.5^\circ, 180.0^\circ)$.
[e] Selected three-centre nuclear attraction integrals from C_3 defined in Cartesian coordinates as $C_1(0, 0, 0)$, $C_2(0, 0, 2.519)$ and $C_3(2.18152, 0, 1.25950)$, cf [22].

6. Conclusion

In this work, we presented a new approach to be used for the computation of the semi-infinite integrals occurring in the algorithms based on the Gaussian integral transform of Shavitt and Karplus. The main objective of the current investigation was mainly to bring a proof of concept showing that a special Gauss quadrature having $W(\sigma, \tau; z) = \sqrt{z}\exp(\sigma z - \tau/z)$ as a weight function can lead to an accurate numerical procedure with which multi-centre integrals over STOs can be evaluated. However, at present it must be pointed out that it is premature to claim that the present approach can be used within an operational setting for routine computation of multi-centre integrals over STOs. The present method has nonetheless shown some potential making it worth further investigation which should enable us gain more insight into its numerical advantages and limitations especially from an efficiency point of view.

Acknowledgment

A computer time grant from WestGrid Canada is gratefully acknowledged.

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