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A complexity analysis of the Gauss–Bessel quadrature as applied to the evaluation of multi-centre integrals over STFs*

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Abstract

In a previous work (Bouferguene 2005 *J. Phys. A: Math. Gen.* **38** 3923), we have shown that in the framework of the Gaussian integral transform, multi-centre integrals over Slater type functions can be evaluated to an acceptable accuracy using a tailored Gauss quadrature in which the weight function has the form $W(\sigma, \tau; z) = z^{\nu} \exp(-\sigma z - \tau/z)$. To be considered a solution worth implementing within a software for routine use in *ab initio* molecular simulations, the method must also prove to be at least as efficient as those methods previously published in the literature. Two major results are provided in this paper. Firstly, an improvement of the procedure used to generate the roots and weights of the Gauss–Bessel quadrature is proposed. Secondly, a computational cost analysis of the present method and the $S\bar{D}$ (Safouhi 2001 *J. Phys. A: Math. Gen.* **34** 2801) based approach are compared, hence proving the equivalence of the two from a complexity point of view.

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1. Introduction

From the earliest days of quantum theory, it was established that except for a very few systems, the Schrödinger equation cannot be fully and exactly solved. Consequently, it became obvious that for practical modelling, one has to turn to approximate solutions of the fundamental equation from which molecular properties could be extracted. On the road map to modern quantum chemistry one finds Roothaan's LCAO [1] method which enables approximate wavefunctions to be written in terms of linear combinations of atomic orbitals. Since it is practically impossible to construct exact analytical solutions of the Schrödinger

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equation, it proved very useful to know some of their properties since they could be used as a guidance when constructing the approximate trial functions. In fact, it was theoretically shown that such solutions must have a cusp at the origin [2] and an exponential decrease at infinity [3]. Based on these properties, an appropriate family of functions that could be used to represent atomic orbitals are the so-called Slater type functions (STFs) [4].

Unfortunately, although the choice of STFs as a basis set stands on a strong theoretical ground, their use was limited in practice. In fact over the past decades, only few softwares using STFs (allowing a full *ab initio* calculation at least at the SCF level) were made available to the scientific community [5–8]. The reasons for this state of affairs are the difficulties occurring during the computation of multi-centre integrals which are known to be the bottleneck in any quantum chemistry software. Indeed, at the *ab initio* level, any molecule of practical interest requires the evaluation of millions of such integrals in order to populate the Hamiltonian matrix. As a consequence, the development of robust and cost-efficient algorithms handling multi-centre integrals would constitute a tremendous progress in the direction of using STFs in the field of quantum chemistry.

Despite the difficulties, several authors devoted some of their efforts to explore ways that could be used to solve the problem of multi-centre integrals over STFs. These efforts have led to the publication of a wide variety of mathematical results and numerical procedures handling to some degree of efficiency the hard task of evaluating multi-centre integrals. Such procedures were developed following one of the three major axes.

(i) *Addition theorem*. When the mathematical structure of the radial part of STFs is examined, one finds that handling multi-centre integrals is difficult because the electronic and the molecular geometry parameters cannot be easily separated. Such parameters appear as the argument of a square root function, i.e. $\sqrt{\|\mathbf{r}-\mathbf{a}\|}$. Consequently, addition theorem-based methods usually operate by expanding the STFs as infinite series hence enabling the electronic and the geometric parameters to be uncoupled [9]. The end result of the methods in this category yields series representations of multi-centre integrals, the summation of which usually requires specialized algorithm to enhance their convergence.

(ii) *Integral transforms*. Two such methods were proposed in the literature: the Gaussian integral transform (GIT) [10, 11] and the Fourier integral transform (FIT) [12]. In the framework of each of these methods, multi-centre integrals are transformed into equivalent mathematical objects and are finally expressed as a multiple integral of the form,

$$\mathcal{I} = \int_0^1 \mathrm{d}u\, f_1(u) \int_0^1 \mathrm{d}v\, f_2(v) \cdots \underbrace{\int_0^{+\infty} \mathrm{d}z\, \mathcal{F}(u, v, \ldots, z)}_{\mathcal{S}(u,v,\ldots)} . \tag{1}$$

In the case of the FIT, the integrand of the semi-infinite integral is oscillatory due to a Bessel function of the first kind. As a consequence, an accurate evaluation of such an entity can only be carried out using highly specialized algorithms. One such algorithm is the so-called $S\bar{D}$ which was originally proposed by Safouhi [13, 14] and was extensively applied to the case of multi-centre integrals by Safouhi and co-workers [13–19]. As for the integrand occurring in the semi-infinite integral in the GIT method, it does not oscillate but exhibits a sharp peak making it a poorly behaving function, hence requiring tailored procedures to ensure a reliable evaluation. In addition to the series representation originally proposed by Shavitt and Karplus [10], we have proposed in a previous work [20] a special Gauss quadrature, referred to as Gauss–Bessel, to carry out the evaluation of $\mathcal{S}(u, v, \ldots)$. The preliminary results showed that Gauss–Bessel is able to achieve an accuracy comparable to that of other methods.

(iii) *Hybrid methods*. In this category, we find those methods which for some integrals propose new mathematical developments while for others, particularly the four-centre integrals, use series expansions in terms of Gaussian type functions [7, 21]. This strategy, which in a sense amounts to using a huge Gaussian basis set to represent a STF, offers the possibility of taking advantage of existing GTF-based algorithms which over the past 40 years have been extremely optimized.

Perhaps the major difficulty in setting up the Gauss–Bessel quadrature for the evaluation of multi-centre integrals over STFs is the computation of the corresponding roots and weights. Because such quantities are essential to the method under investigation, it is of paramount importance to use an efficient procedure for their computation. Let us point out that such a problem is, in a sense, common to all numerical techniques based on special Gauss quadratures. For instance, in the context of *ab initio* calculations over GTFs, one of the methods that is widely used to evaluate Boys functions is the so-called Gauss–Rys quadrature [22] whose success depends on its efficient implementation as described by Lindh *et al* [23]. The present work aims at investigating the advantage of determining the roots and weights required by the Gauss–Bessel quadrature by means of an algorithm based on matrix diagonalization. The complexity of the new procedure is compared to that of $S\bar{D}$ which shows, based on theoretical considerations, that the Gauss–Bessel approach is comparable to the $S\bar{D}$ from a computational cost perspective.

2. Definitions, properties and notation

A Slater type function centred on some arbitrary point, defined by its location vector $\mathbf{a}$, is generally defined as

$$\chi_{n,l}^{m}(\alpha, \mathbf{r}-\mathbf{a}) = \mathcal{N}_n(\alpha)\underbrace{\|\mathbf{r}-\mathbf{a}\|^{n-l-1}\exp(-\alpha\|\mathbf{r}-\mathbf{a}\|)}_{\text{Radial term}}\mathcal{Y}_l^m(\mathbf{r}-\mathbf{a}), \tag{2}$$

where $\mathcal{N}_n(\alpha) = (2\alpha)^{n+1/2}/\sqrt{(2n)!}$ is the normalization constants and $\mathcal{Y}_l^m(\mathbf{k})$ represents the solid spherical harmonic of degree l and order m which is defined as

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

where $P_l^m(z)$ stands for the associated Legendre function for which the Rodrigues representation is given in [24, p 94]. To carry out multi-centre integrals, it is of importance to note that solid spherical harmonics possess a very interesting addition theorem allowing the electronic variable $\mathbf{r}$ and the geometry parameter $\mathbf{a}$ to be separated. According to Steinborn and Ruedenberg [25], the solid spherical harmonic in equation (2) can be expanded as

$$\mathcal{Y}_l^m(\mathbf{r}-\mathbf{a}) = 4\pi(2l+1)!!\sum_{l'=0}^{l}\sum_{m'=-l'}^{l'}\frac{\langle lm|l'm'|l-l'm-m'\rangle}{(2l'+1)!![2(l-l')+1]!!}\mathcal{Y}_{l'}^{m'}(\mathbf{r})\mathcal{Y}_{l-l'}^{m-m'}(\mathbf{a}), \tag{4}$$

where $(2l+1)!! = (2l+1)!/(2^l l!)$ and $\langle l_1m_1|l_2m_2|l_3m_3\rangle$ denotes the so-called Gaunt coefficients [26]. The above equation clearly shows that solid spherical harmonics do not introduce any special difficulty when involved as part of multi-centre integrals. As a consequence, the efficiency of any algorithm geared towards the evaluation of multi-centre integrals over STFs depends on how fast it can handle the radial term as labelled in equation (2). In fact, for analytical work, it is customary to derive the appropriate formulae for the simple

case corresponding to 1s Slater orbital. Expressions for higher order orbitals are afterwards obtained by simply differentiating the 1s result with respect to the screening constant using the following property of STFs:

$$\|\mathbf{r}-\mathbf{a}\|^{n-l-1}\exp(-\alpha\|\mathbf{r}-\mathbf{a}\|) = \left(-\frac{\partial}{\partial\alpha}\right)^{n-l-1}\exp(-\alpha\|\mathbf{r}-\mathbf{a}\|). \tag{5}$$

In the framework of the GIT method, the starting point as proposed in [10] is to express the 1s Slater orbital as the Laplace transform of a suitably chosen function, which happens to involve a GTF

$$\chi^0_{1,0}(\alpha,\mathbf{r}-\mathbf{a}) = \mathcal{N}_1(\alpha)\int_0^{+\infty} s^{-3/2}\exp\left(-\frac{\alpha^2}{4s}\right)\underbrace{\exp(-s\|\mathbf{r}-\mathbf{a}\|^2)}_{\text{GTF}}\,\mathrm{d}s. \tag{6}$$

The motivation for introducing the above integral representation is the presence of a GTF as part of its integrand. Indeed, when dealing with products of STFs as they occur in the definition of multi-centre integrals, the GIT allows one to apply the well-known multiplication theorem of GTFs hence simplifying the final expressions. In the original work of Shavitt and Karplus [10], considered as the pillar of the GIT method, the authors have provided a detailed roadmap of equations allowing to simplify the algebra hence easing the development of numerical procedures. In the following section, some aspects of multi-centre integrals treated within the FIT approach will be considered. It hence seems appropriate to define the most relevant mathematical objects that will be needed later. Perhaps the most important of such objects is the so-called B functions which in spite of their complicated analytical form, were shown to have the simplest Fourier transform [27]. This very property makes the B functions the ideal basis set to be used in the context of the FIT method. According to Filter and Steinborn the B functions are defined as [28]

$$B^m_{n,l}(\alpha,\|\mathbf{r}-\mathbf{a}\|) = \frac{1}{2^{n+l}(n+l)!}\hat{k}_{n-1/2}(\alpha\|\mathbf{r}-\mathbf{a}\|)\mathcal{Y}^m_l[\alpha(\mathbf{r}-\mathbf{a})], \tag{7}$$

where the reduced Bessel function $\hat{k}_{n-1/2}(z)$ are defined as

$$\hat{k}_{n-1/2}(z) = \sum_{p=1}^{n}\frac{(2n-p-1)!}{(p-1)!(n-p)!}2^{p-n}\underbrace{z^{p-1}\exp(-z)}_{\text{Un-normalized STF}}. \tag{8}$$

Despite their complicated form in the coordinate space, B functions were selected because of the simplicity of their Fourier integral transform as compared to any other exponentially decreasing function

$$\begin{aligned}\bar{B}^m_{n,l}(\alpha,\mathbf{p}) &= \frac{1}{(2\pi)^{3/2}}\int_{\mathbf{r}}\mathrm{e}^{-\mathrm{i}\mathbf{p}\cdot\mathbf{r}}B^m_{n,l}(\alpha,\mathbf{r})\,\mathrm{d}\mathbf{r}\\ &= \sqrt{\frac{2}{\pi}}\alpha^{2n+l-1}\frac{(-\mathrm{i}\|\mathbf{p}\|)^l}{(\alpha^2+\|\mathbf{p}\|^2)^{n+l+1}}Y^m_l(\theta_{\mathbf{p}},\phi_{\mathbf{p}}).\end{aligned} \tag{9}$$

As a last remark, it is of interest to mention that, as can be seen from equation (8), B functions can easily be expressed in terms of STFs. The inverse is also true as was shown by Weniger and Steinborn in [27 (equation (3.22))].

3. Evaluation of multi-centre integrals using the Gauss–Bessel quadrature

In the following, we describe an approach that can be used for setting up a procedure for the evaluation of multi-centre integrals in the framework of the GIT method (based on the Gauss–Bessel quadrature). It will be shown later that from a computational cost point of view, the new procedure is comparable to the algorithms developed for the FIT approach. To do

so, we start by pointing out the structural similarities between the expressions of multi-centre integrals as obtained within the FIT and the GIT approaches.

3.1. Structure of multi-centre integrals in the FIT and GIT methods

Previously we have hinted that the expressions of multi-centre integrals obtained within the FIT and the GIT frameworks were structurally similar. Indeed, in both methods multi-centre integrals always end up being represented by a multiple integral the innermost of which is semi-infinite. To be more specific, let us explore the case of the three-centre nuclear attraction integral which for the sake of simplicity will only involve s type STFs

$$\mathcal{T}_{n_1,0,0}^{n_2,0,0} = \left\langle \chi_{n_1,0}^{0}(\alpha_1, \mathbf{r}-\mathbf{a}) \middle| \frac{1}{\|\mathbf{r}-\mathbf{c}\|} \middle| \chi_{n_2,0}^{0}(\alpha_2, \mathbf{r}-\mathbf{b}) \right\rangle. \tag{10}$$

Note, that within the FIT approach, one should use s type B functions since these are the ones leading to the simplest analytical forms. Thus, the expression of the three-centre nuclear attraction integral of interest as derived in the context of the GIT formulation can be written as [20]

$$\begin{aligned}\mathcal{G}_{n_1,0,0}^{n_2,0,0}(\alpha_1, \alpha_2, \mathbf{a}, \mathbf{b}, \mathbf{c}) &= \mathcal{N}_{n_1}(\alpha_1)\mathcal{N}_{n_2}(\alpha_2) 2^{-(n_1+n_2-1)} \int_{u=0}^{1} \mathrm{d}u\, u^{-(n_1+1)/2}(1-u)^{-(n_2+1)/2} \\ &\quad \times \int_0^{+\infty} z^{(n_1+n_2-2)/2} \mathbf{H}_{n_1}\left[\frac{\alpha_1 p}{2}\frac{\sqrt{z}}{\sqrt{u}}\right] \mathbf{H}_{n_2}\left[\frac{\alpha_2 p}{2}\frac{\sqrt{z}}{\sqrt{1-u}}\right] \\ &\quad \times F_0\left(\frac{1}{z}\right) \exp\left(-\frac{\sigma}{z} - \tau z\right) \mathrm{d}z,\end{aligned} \tag{11}$$

where

$$p = \|u\mathbf{a} + (1-u)\mathbf{b} - \mathbf{c}\|, \qquad \sigma = u(1-u)\frac{\|\mathbf{a}\|^2}{p^2} \qquad \text{and} \qquad \tau = \frac{p^2}{4}\left(\frac{\alpha_1^2}{u} + \frac{\alpha_2^2}{1-u}\right). \tag{12}$$

$\mathbf{H}_n(z)$ represents the Hermite polynomial of degree n [29, p 250] while $F_0(z)$ is the Boys function defined as

$$F_m(z) = \int_0^1 t^{2m} \exp(-zt^2)\, \mathrm{d}t. \tag{13}$$

In the FIT approach, the expression of the three-centre nuclear attraction integrals obtained with s type B functions [30] is defined as

$$\begin{aligned}\mathcal{F}_{n_1,0,0}^{n_2,0,0}(\alpha_1, \alpha_2, \mathbf{a}, \mathbf{b}, \mathbf{c}) &= \sqrt{\frac{2}{\pi}} \frac{\alpha_1^{2n_1-1}\alpha_2^{2n_2-1}}{\pi n_1! n_2! 2^{n_1+n_2}} \mathbf{b}^{n_1+n_2+1/2} \\ &\quad \times \int_0^1 \mathrm{d}u\, u^{n_2}(1-u)_1^n \int_0^{+\infty} \frac{K_{n_1+n_2+1/2}[\mathbf{b}\beta(u,k)]}{[\beta(u,k)]^{n_1+n_2+1/2}} j_0(\|\mathbf{v}\|k)\, \mathrm{d}k,\end{aligned} \tag{14}$$

where

$$\mathbf{v} = u(\mathbf{a}-\mathbf{b}) + (\mathbf{b}-\mathbf{c}) \qquad \text{and} \qquad [\beta(u,k)]^2 = (1-u)\alpha_1^2 + u\alpha_2^2 + u(1-u)k^2. \tag{15}$$

The term $j_0(z)$ stands for the spherical Bessel function which can be written in a simpler form as $\sin(z)/z$.

From equations (11) and (14) one can clearly note the structural similarity in the expressions of the three-centre nuclear attraction integrals as obtained within the GIT and the FIT methods. Indeed, in both cases the definition of the three-centre nuclear attraction integral of interest is expressed in term of a double integral with the same boundaries. In addition, the outermost integral involves the same terms, u and $(1-u)$ albeit the exponents are totally different. However, in both cases it is possible to use a similar numerical integration

technique, namely shifted Gauss–Jacobi, because of the presence of a weight function of the form $u^a(1-u)^b$. Previous work due to Homeier and Steinborn [31] showed that a Gauss–Möbius quadrature leads to better results for the integration over [0, 1]. Regarding the semi-infinite integral, perhaps the major difference is due to the oscillating term, $j_0(z)$, in the FIT. It is the above-mentioned similarity that sets the ground for the present study, since it seemed reasonable to believe that Gauss–Bessel quadrature can possibly be improved to be as efficient as those methods elaborated in the context of FIT, in particular, the $S\bar{D}$ method which uses the nonlinear transformations $\bar{D}$ originally proposed by Sidi [32, 33].

3.2. The Gauss–Bessel quadrature

Generally, when the structure of multi-centre integrals over STFs in the GIT approach is examined, one finds that the semi-infinite integral (innermost integral) involves a function of the form $W(\sigma,\tau;z)=z^{\nu}\exp(-\sigma/z-\tau z)$ in which σ and τ are defined in terms of $u, v, \ldots$, the geometrical parameters and the screening constants. In a previous work [20], our investigation of the three-centre nuclear attraction integral, which for s Slater orbitals is given by (11), led us to identify $W(\sigma,\tau;z)=\sqrt{z}\exp(-\sigma/z-\tau z)$ as an admissible weight function to be used for the so-called Gauss–Bessel quadrature. The numerical setup of the new technique was carried out as a two-step process. First, a set of polynomials, $p_r(x)_{r=0,1,2,\ldots}$, orthogonal with respect to $W(\sigma,\tau;z)$, was constructed by means of the Gram–Schmidt orthogonalization scheme which uses the following property of the moments:

$$\int_0^{+\infty} z^n\left[z^{1/2}\exp\left(-\frac{\sigma}{z}-\tau z\right)\right]\mathrm{d}z = 2\sqrt{\left(\frac{\sigma}{\tau}\right)^{n+3/2}}\mathbf{K}_{n+3/2}(2\sqrt{\sigma\tau}). \tag{16}$$

Once the orthogonal polynomials are generated, their roots are computed by means of an appropriate numerical method, e.g. Newton–Raphson [34]. The second step consists in computing the weights of the quadrature using the relationship,

$$w_j = \frac{\langle p_{n-1}|p_{n-1}\rangle}{p_{n-1}(x_j)p_n'(x_j)}, \tag{17}$$

where x_j denotes the jth root of the orthogonal polynomial $p_n(x)$. From an efficiency perspective the above-described procedure is not optimal for a routine evaluation of multi-centre integrals. Luckily, it turns out that the computation of the roots and weights of the Gauss–Bessel quadrature can substantially be improved by using a more efficient approach due to Boley and Golub [35] and Gautschi [36]. Indeed, given a weight function $w(z)$, the orthogonal polynomials (with respect to $w(z)$) are connected by a three-term recurrence relation of the form,

$$\begin{aligned} &p_{k+1}(z)=(z-\alpha_k)p_k(z)-\beta_k p_{k-1}(z), \qquad k=0,1,2,\ldots \\ &p_0(z)=1, \qquad \text{and} \qquad p_{-1}(z)=0, \end{aligned} \tag{18}$$

where β_0 is customarily defined as $\beta_0=\int_a^b w(z)\,\mathrm{d}z$. For the purpose of this work, we provide the definition of the coefficients α_k and β_k for $k\geqslant 1$ in the next section. The nth order Jacobi matrix for the weight function $w(z)$ is a tridiagonal symmetric matrix defined by

$$J_n(W)=\begin{bmatrix} \alpha_0 & \sqrt{\beta_1} & & & 0 \\ \sqrt{\beta_1} & \alpha_2 & \sqrt{\beta_2} & & \\ & \sqrt{\beta_2} & & \ddots & \\ & & \ddots & \ddots & \sqrt{\beta_{n-1}} \\ 0 & & & \sqrt{\beta_{n-1}} & \alpha_{n-1} \end{bmatrix}. \tag{19}$$

The nodes of the polynomials $\{p_k\}_{1\leqslant k\leqslant n}$ (orthogonal with respect to the weight $w(z)$) are the eigenvalues of $J_n(W)$ while the weights w_k are expressible in terms of the first component $v_{k,1}$ of the corresponding normalized eigenvectors,

$$w_k = \beta_0 v_{k,1}^2, \qquad k = 1, 2, \ldots, n. \tag{20}$$

As can be seen, the construction of a Gauss quadrature in practice amounts to solving an eigenvalue problem involving a symmetric tridiagonal matrix. Fortunately, the diagonalization of such matrices is a routine problem in numerical analysis for which very efficient algorithms are already available in the literature. The implementation of such algorithms can be found in a wide variety of highly optimized commercial numerical libraries. For the purpose of this work, a version of the QR algorithm found in [34] was used. Note that Gautschi has already published a set of general purpose routines that could be used for generating the roots and weights of an arbitrary Gauss quadrature, given the appropriate input [37, 38]. However, it was found that using the specifics of the problem in hand, namely the appropriate recurrence relations and storing frequently used values, leads to a much more efficient procedure.

3.3. Numerical analysis

Now, that we have an efficient procedure that could be used for the computation of the roots and weights of the Gauss–Bessel quadrature, it is of interest to address its complexity so as to have a feel of its computational cost. Perhaps the most obvious shortcoming in the present form of the Gauss–Bessel approach is the necessity to generate the coefficients α_k and β_k occurring in the three-term relationship (18), since these are used to populate the Jacobi matrix (19). Assuming that the kth orthogonal polynomial can generally be written as $p_k(z) = \sum_{p=0}^{k} a_{k,p} z^k$, we can easily derive the working formula for α_k,

$$\alpha_k = \sqrt{\sigma/\tau}\left[\sum_{p=0}^{2k} S_{k,p}\mathbf{K}_{p+5/2}[2\sqrt{\sigma\tau}]\right] \Bigg/ \left[\sum_{p=0}^{2k} S_{k,p}\mathbf{K}_{p+3/2}[2\sqrt{\sigma\tau}]\right] \tag{21}$$

and β_k,

$$\beta_k = \left[\sum_{p=0}^{2k} S_{k,p}\mathbf{K}_{p+3/2}[2\sqrt{\sigma\tau}]\right] \Bigg/ \left[\sum_{p=0}^{2(k-1)} S_{k-1,p}\mathbf{K}_{p+3/2}[2\sqrt{\sigma\tau}]\right], \tag{22}$$

where the term $S_{k,p}$ occurring above is defined as

$$S_{k,p} = \left[\sum_{q=\max(0,p-k)}^{\min(k,p)} a_{k,p}a_{k,p-q}\right]\sqrt{\left(\frac{\sigma}{\tau}\right)^p}. \tag{23}$$

According to the definition of the Jacobi matrix (19), it can easily be seen that an nth order quadrature requires the computation of the coefficients $\{(\alpha_k, \beta_k)\}_{0\leqslant k\leqslant n-1}$ which, in turn, need the values of the modified Bessel functions $\{\mathbf{K}_{p+1/2}[2\sqrt{\sigma\tau}]\}_{1\leqslant p\leqslant 2n+2}$. Figure 1 shows the organigram underlying the current implementation of the Gauss–Bessel quadrature. When equations (21), (22) and the organigram (1) are put together, it is clear that the major overhead in using the Gauss–Bessel approach lies in the generation of the orthogonal polynomials. In this respect, it is advisable to generate beforehand the numerical values $\mathbf{K}_{p+1/2}[2\sqrt{\sigma\tau}]$ and $\sqrt{(\sigma/\tau)^p}$ for $0 \leqslant p \leqslant 2n+2$.

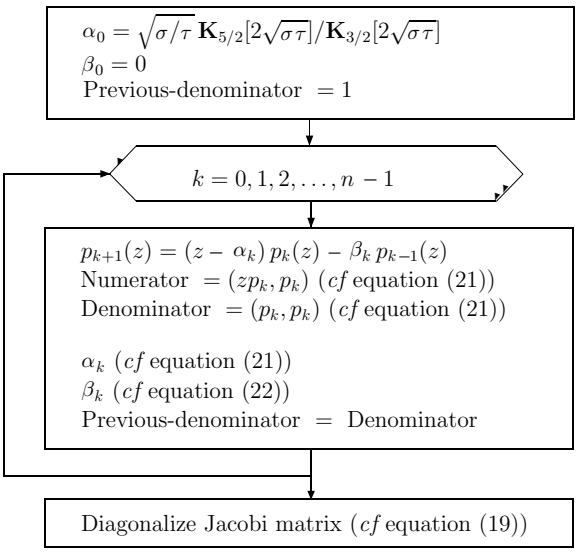

Figure 1. Organigram showing the current implementation of the Gauss–Bessel nodes and weights generation.

3.4. Complexity analysis

In the previous work, it was shown that when the FIT approach is used to evaluate multi-centre integrals, the most appropriate method to handle the semi-infinite integral as it occurs for instance in (14) is to use the so-called $S\bar{D}$ nonlinear transformation,

$$S\bar{D}_n^{(2,j)} = \frac{\sum_{i=0}^{n+1}\binom{n+1}{i}(1+i+j)^n F(x_{i+j})\big/\big[x_{i+j}^2 G(x_{i+j})\big]}{\sum_{i=0}^{n+1}\binom{n+1}{i}(1+i+j)^n\big/\big[x_{i+j}^2 G(x_{i+j})\big]}, \tag{24}$$

where $\{x_l = (l+1)\pi\}_{l=0,1,2,\ldots}$, $j = 0, 1, 2, \ldots$ and $F(x) = \int_0^t G(t)\sin(t)\,\mathrm{d}t$. In the special case of the three-centre nuclear attraction integral given by (14), the function $G(x)$ is defined as

$$G(x) = \frac{1}{\|\mathbf{v}\|x}\frac{\mathbf{K}_{n_1+n_2+1/2}[b\beta(u,x)]}{[\beta(u,x)]^{n_1+n_2+1/2}}. \tag{25}$$

According to [16], the finite integral $F(x_{i+j})$ is evaluated as

$$F(x_{i+j}) = F[(i+j+1)\pi] = \int_0^{(i+j+1)\pi} G(x)\sin(x)\,\mathrm{d}x = \sum_{k=0}^{i+j}\int_{k\pi}^{(k+1)\pi} G(x)\sin(x)\,\mathrm{d}x. \tag{26}$$

For each integral occurring within the above summation sign, a Gauss–Legendre quadrature is used.

In order to fairly compare the computational cost associated with the $S\bar{D}$ and the Gauss–Bessel approaches, we use the absolute metric which amounts to counting the number of operations required for the evaluation of the semi-infinite integral. Although more tedious to carry out, the complexity analysis of the algorithms provides a true indication of the cost for both methods as opposed to simply relying on the timings which obviously depend on the hardware, software (compilers and operating systems), and the programmer's skills.

Table 1. Number of operations for the Gauss–Bessel approach.

Term	Number of operations	Total
Numerator (α_k)	$\sum_{p=0}^{k}\left(\left[\sum_{q=0}^{p} 1\right]+2\right)+\sum_{p=k+1}^{2k}\left(\left[\sum_{q=p-k}^{k} 1\right]+2\right)$	k^2+6k+3
Denominator (α_k)[a]	$\sum_{p=0}^{2k} 1$	$2k+1$
α_k		$(k^2+6k+3)+(2k+1)+1$
β_k[b]		1
Total for an nth order quadrature	$\sum_{k=1}^{n}[(k^2+6k+3)+(2k+1)+2]$	$(1/3)n(n^2+9n+26)$

[a] The evaluation of the denominator requires only one operation since the product $S_{k,p}=\left[\sum_q a_q a_{p-q}\right]\sqrt{(\sigma/\tau)}^p$ was computed for the numerator.
[b] The value of β_k needs only one division since the numerator was counted for in the computation of α_k and the denominator is saved from the previous iteration.

Before going into the details of complexity analysis, we assume that in both $S\bar{D}$ and Gauss–Bessel-based algorithms, the most costly operations are the multiplications, divisions and the evaluation of transcendental functions. Thus, starting with the Gauss–Bessel quadrature, we assume the following.

(i) Inspection of equations (21) and (22) shows that for each $k > 1$, computing the numerator and denominator occurring in the definition of α_k suffice since it can also be used to generate β_k , cf figure 1 and table 1.
(ii) The modified Bessel functions $\mathbf{K}_{p+1/2}(2\sqrt{\sigma\tau})$ and the terms $\sqrt{(\sigma/\tau)^p}$ are tabulated beforehand which makes the corresponding computational time negligible.
(iii) The diagonalization of the Jacobi matrix is a one time operation, carried out at the end of the process, cf organigram (1). This provides a justification for neglecting the corresponding time especially since the order n of the matrix $J_n(W)$ is rather small. This proved to be a fair assumption by comparing a large number of numerical experiments.
(iv) The time associated with an addition is negligible.

Using the above-enumerated hypotheses, we can calculate the number of elementary operations required to calculate the semi-infinite integral in (11). Table 1 provides a summary of the number of operations required to generate the coefficients α_k and β_k for an nth order quadrature,

$$N_{\mathrm{GB}}=\frac{n(n^2+9n+26)}{3}. \tag{27}$$

Regarding the $S\bar{D}$ approach, inspection of equation (24) clearly shows that since the upper bound of the summation over i does not exceed 10 (in general), the inventory of the elementary operations for $S\bar{D}$ was restricted to those involved in computation of $F(x_{i+j})$. In addition, to minimize the number of operations, the value of $F(x_{i+j})$ is obtained from $F(x_{i+j-1})$ (calculated at the previous iteration) by adding a term of the form $\int_{(i+j)\pi}^{(i+j+1)\pi} G(t)\sin(t)\,\mathrm{d}t$. Starting at $i=0$, one needs to evaluate $F(x_j)$ which according to [16] is computed as

$$F(x_j)=\sum_{m=0}^{j}\int_{m\pi}^{(m+1)\pi} G(t)\sin(t)\,\mathrm{d}t. \tag{28}$$

As a consequence, in the framework of the $S\bar{D}$ approach, one needs to use the Gauss–Legendre quadrature $(j+1)+(n+1)$ times. In this case, the calculation of the number of elementary operations is carried out under the following assumptions.

(i) The values of $1/(\|\mathbf{v}\|t_i)$ and $\sin(t_i)$, in which t_i stands for the ith node of the chosen Gauss–Legendre, are computed beforehand and stored for later use in appropriate arrays.

Table 2. Number of elementary operations, i.e. multiplications, divisions and transcendental functions evaluation, in the $S\bar{D}$ approach.

Term	Number of operations
$1/\|\mathbf{v}\|t_i$ and $\sin(t_i)$	Computed beforehand
$\beta(u,t_i)=\sqrt{a+bt_i^2}$	3
$b\beta(u,t_i)$	$3+1=4$
$\mathbf{K}_{n_1+n_2+1/2}[b\beta(u,t_i)]$	$4+3(n_1+n_2)+3$
$\beta(u,t_i)^{n_1+n_2+1/2}$	1
$G(t_i)=1/(\|\mathbf{v}\|t_i)\mathbf{K}_{n_1+n_2+1/2}[b\beta(u,t_i)]/[\beta(u,t_i)]^{n_1+n_2+1/2}\sin(t_i)$	$1+4+3(n_1+n_2)+3+1+1=10+3(n_1+n_2)$

(ii) The Bessel function $\mathbf{K}_{n_1+n_2+1/2}$ are computed using the three-term relationship,

$$\mathbf{K}_{(n+1/2)+1}(z)=\frac{2n+1}{z}\mathbf{K}_{n+1/2}(z)+\mathbf{K}_{(n+1/2)-1}(z) \qquad \text{with}$$
$$\mathbf{K}_{-1/2}(z)=\mathbf{K}_{1/2}(z)=\sqrt{\frac{\pi}{2z}}\exp(-z). \tag{29}$$

Thus, $\mathbf{K}_{n_1+n_2+1/2}(z)$ requires $3(n_1+n_2)+3$ operations in which the second '3' comes from the evaluation of $\mathbf{K}_{1/2}(z)$.

The last row in table 2 summarizes the number of elementary operations required to evaluate the integrand in (14) for a given root t_i of the Gauss–Legendre quadrature selected for the evaluation of $F(x_{i+j})$. Keeping in mind that $S\bar{D}$ requires the application of the Gauss–Legendre quadrature $(j+1)+(n+1)$ times, we can finally write the number of operations associated with this task as

$$N_{S\bar{D}}=[(j+1)+(n+1)]N_{\mathrm{Leg}}[3(n_1+n_2)+10], \tag{30}$$

where N_{Leg} represents the order of the Gauss–Legendre quadrature used to evaluate the partial integral in equation (28). From the numerical discussion in [16], it can be seen that $S\bar{D}_n^{(2,0)}$ was used to evaluate the semi-infinite integral occurring in the case of three-centre integrals. From the values listed in tables 1 and 5 of [16], one can note that on average $n=5$ and since the authors have selected $N_{\mathrm{Leg}}=20$ we obtain

$$N_{S\bar{D}}=[(0+1)+(5+1)]20[3(n_1+n_2)+10]=1400+420(n_1+n_2). \tag{31}$$

Since the complexity of the $S\bar{D}$ approach depends on the quantum numbers n_1 and n_2, it seems fair to consider the average number of operations required for the computation of the integrals in which n_1 and n_2 vary from 1 to 3 (1s to 3s orbitals). In such a case, we have

$$\begin{aligned}\text{Average number of operations} &= 1400+420\left[\frac{1}{9}\sum_{n_1=1}^{3}\sum_{n_2=1}^{3}(n_1+n_2)\right]\\ &= 3080.\end{aligned} \tag{32}$$

Regarding the Gauss–Bessel approach, the complexity depends mainly on the order of the quadrature as given in (27). Previously [20] it was found that a quadrature of order 12 was able to produce sufficiently accurate values in the case of three-centre nuclear attraction integrals involving s type orbitals. In such a case the computation of the semi-infinite integral requires 1112 elementary operations. Of course, we expect that for a different type of integrals, higher order polynomials might be needed to properly approximate the integrand

Table 3. Comparison of the number of elementary operations required by the $S\bar{D}$ and the Gauss–Bessel methods.

$n_1 + n_2$	$S\bar{D}$	n	Gauss–Bessel
2	2240	12	1112
3	2660	14	1624
4	3080	16	2272
5	3500	18	3072
6	3920	20	4040

of the corresponding semi-infinite integral which in other words means a larger number of operations. Nevertheless, in the case of three-centre nuclear attraction integrals, we can clearly see that the computation of the semi-infinite integral as it occurs in the FIT and the GIT methods using the Gauss–Bessel quadrature and the $S\bar{D}$ transformations requires a similar number of operations. Indeed, comparing the values in table 3 shows that the $S\bar{D}$ requires on average 3080 elementary operations corresponding to $n_1 + n_2 = 4$. This, of course, is comparable to the number of operations required by a Gauss–Bessel quadrature of order 18 (3072 operations). As a last note, it should be emphasized that even though the number of operations in the Gauss–Bessel approach grows as $O(n^3)$, a low order quadrature will generally be sufficient to achieve acceptable accuracy and this will make the two methods, i.e. Gauss–Bessel and $S\bar{D}$, comparable from a computational cost perspective.

4. Conclusion

In the original paper devoted to the description of the Gauss–Bessel quadrature for the evaluation of multi-centre integrals in the context of GIT, emphasis was essentially put on how accurate the new method is. Of course, in order to be a viable technique in practice, the method must be at least as efficient as those already available in the literature. As a consequence, we have presented above the tools that can possibly allow one to develop an efficient algorithm based on the Gauss–Bessel quadrature for the evaluation of multi-centre integrals. In addition to the efficiency provided by the use of Jacobi tridiagonal matrix, one must not forget the possibility of speeding up the computations by appropriately storing typical quantities, such as the roots and weights for typical values of the parameters σ and τ.

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