Strategies for an Efficient Implementation of the Gauss–Bessel Quadrature for the Evaluation of Multicenter Integral Over STFs

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Abstract: In a previous work, a new Gauss quadrature was introduced with a view to evaluate multicenter integrals over Slater-type functions efficiently. The complexity analysis of the new approach, carried out using the three-center nuclear integral as a case study, has shown that for low-order polynomials its efficiency is comparable to the $S\bar{D}$. The latter was developed in connection with multi-center integrals evaluated by means of the Fourier transform of B functions. In this work we investigate the numerical properties of the Gauss–Bessel quadrature and devise strategies for an efficient implementation of the numerical algorithms for the evaluation of multi-center integrals in the framework of the Gaussian transform/Gauss–Bessel approach. The success of these strategies are essential to elaborate a fast and reliable algorithm for the evaluation of multi-center integrals over STFs.

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Introduction

Multi-center integrals over Slater-type functions (STFs) is one of the long-standing problems in the field of quantum chemistry. Aside from the overlap integrals, these quantities represent electron–nuclei or electron–electron interactions and constitute the basic building blocks needed to populate the Hamiltonian of a molecular system. From a mathematical perspective, multicenter integrals fall within one of two categories,

1. One-electron integrals, for which the most difficult is probably the so-called three-center nuclear attraction integral that is defined as,

$$\mathcal{J} = \int_{\mathbf{r}} \chi_{n_1,l_1}^{m_1}(\alpha \mathbf{r}_a) \frac{1}{\|\mathbf{r}_c\|} \chi_{n_2,l_2}^{m_2}(\beta \mathbf{r}_b) d\mathbf{r} \tag{1}$$

   where $\mathbf{r}_u = \mathbf{r} - \mathbf{u}$ represents the coordinate of the electron with respect to a point defined by its location vector $\mathbf{u}$ in some fixed frame of reference. The term $\chi_{n,l}^{m}(\alpha \mathbf{r}_a)$ denotes any *acceptable* atomic orbital. In practice this can be either Gaussian or exponentially decaying (also referred to as STFs).
2. Two-electron integrals represents interactions between two–electron distributions. A useful pictorial representation of these quantities can easily be constructed using graphs, (Fig. 1) In these graphs, A, B, C, and D represent the atoms on which the orbitals are centered while (1) and (2) are the interacting electrons. From these graphs, one can easily write the corresponding definition of the integral. For instance from the graph (e), we can write,

$$\mathcal{J} = \int_{\mathbf{r}_1} \int_{\mathbf{r}_2} \chi_{n_1,l_1}^{m_1}(\alpha_1 \mathbf{r}_{1,a}) \chi_{n_2,l_2}^{m_2}(\alpha_2 \mathbf{r}_{1,b}) \frac{1}{\|\mathbf{r}_1 - \mathbf{r}_2\|} \chi_{n_3,l_3}^{m_3}(\alpha_3 \mathbf{r}_{2,b}) \chi_{n_4,l_4}^{m_4}(\alpha_4 \mathbf{r}_{2,c})\, d\mathbf{r}_1\, d\mathbf{r}_2 \tag{2}$$

   where $\mathbf{r}_{k,u} = \mathbf{r}_k - \mathbf{u}$ represent the coordinate of electron (k) with respect to the center defined by the vector $\mathbf{u}$ in some fixed frame of reference.

When the atomic orbitals are STFs, the evaluation of multicenter integrals becomes a challenging problem. In fact, over the past 50 years numerous scientists, who paved the road to modern computational chemistry, have tried to solve this difficult issue by proposing a diverse set of mathematical tools and numerical procedures. The efforts invested in this problem were motivated by the

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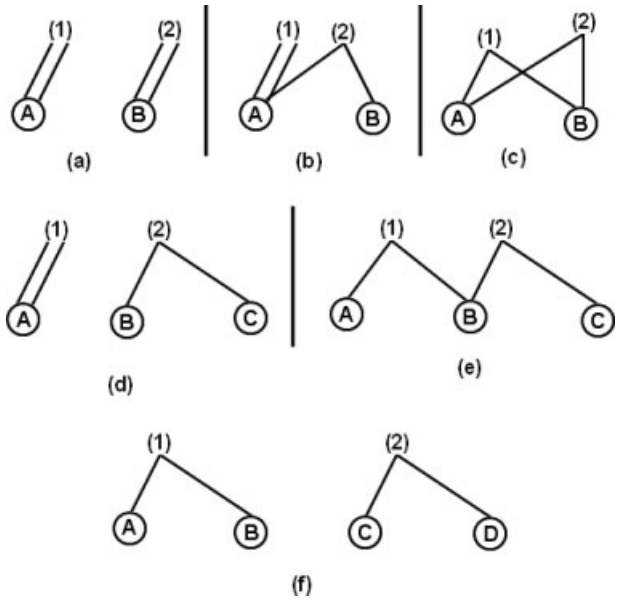

Figure 1. Graph representation of two-electron integrals. (a) two-center Coulomb, (b) two-center hybrid, (c) two-center exchange, (d) three-center hybrid, (e) three-center exchange, and (f) four-center integrals.

fact that STFs are considered the most suitable orbitals to be used for the construction of molecular wave functions. In fact, theoretical investigations of the behavior of the solutions of the Schrödinger equation have shown that such solutions must have a cusp[1] at the origin and an exponential decay at infinity.[2] Handy et al.[3] went even farther by showing that Hartree–Fock orbitals decrease asymptotically as $\exp[-2(-2\epsilon_j)^{1/2}r]$ in which ϵ_j is the energy of the jth spin orbital. This clearly is an additional theoretical proof supporting the adequacy of STFs.

In the past decades three major routes, geared toward elaborating an efficient algorithm for the evaluation of multicenter integrals over STFs, have been investigated.

1. The one-center expansion originated with the pioneering work of Coolidge,[4] Löwdin,[5] and Barnett and Coulson.[6] This method aimed at constructing an addition theorem which allowed an arbitrary STF centered on some point defined by a location vector **a** to be expanded in terms of spherical harmonics. In this context, STFs end up being represented by a two-range infinite series,[7–9] similar in a way to the multipole expansion of the Coulomb operator. Perhaps the major drawback of this method, as far as complicated multicenter integrals are concerned, is the slow convergence of the leading infinite series which require special numerical devices in order to keep computation times from being prohibitively long. In addition to the afore mentioned multipole expansion, some work has been devoted to investigate the theoretical aspects of the one-center one-range expansion.[10] However, and to the best of our knowledge, this method has not been used extensively in practice.
2. The Gaussian integral transform (GIT), which was introduced by Shavitt and Karplus back in the early 60s[11] appeared as a promising route, since instead of infinite series,[12–15] multicenter integrals end up being represented by multiple integrals whose structure is as follows,

$$\mathcal{J} \propto \int_0^1 du\, u^a (1-u)^b \int_0^1 dv\, v^{a'} (1-v)^{b'} \ldots \int_0^\infty dz\, \mathcal{F}_{\mathrm{GIT}}(u, v, \ldots, z) \exp\left[-\frac{\sigma}{z} - \tau z\right] \quad (3)$$

At this point the precise definition of $\mathcal{F}(u, v, \ldots, z)$ is not crucial for the argument we intend to make regarding the evaluation of the earlier integral; it will certainly be given in due time. To evaluate the afore mentioned multiple integral, the term $x^\alpha (1-x)^\beta$ in the integrals over the range [0, 1] suggest the use of a Gauss–Jacobi quadrature (at least when α and $\beta > -1$). As for the innermost integral, this requires greater care since the integrands exhibit a moving sharp peak due to the function $\exp(-\sigma/z - \tau z)$. To solve this problem, various strategies can be used. The first and perhaps the most straightforward is to use an infinite series representation which can then be accelerated in order to improve its convergence.[11] An alternative to this method is to rely on a tailored Gauss quadrature specifically designed to use the term $\exp(-\sigma/z - \tau z)$ as part of its weight function. This quadrature is referred to as Gauss–Bessel (GB) allows the *singular* term to be removed from the integrand leaving a well behaving function that can be accurately interpolated by a polynomial.
3. The Fourier integral transform (FIT) was first used in connection to multicenter integrals over STFs by Bonham and Coworkers.[16] This method was later thoroughly studied by Steinborn and coworkers and led to a new set of exponentially decreasing orbitals known as the B functions. These functions were selected as the basis of choice in the framework of the FIT approach, since their Fourier transform is the simplest in comparison to other STFs. In this context multicenter integrals are represented by a multiple integral whose mathematical structure is of the form,

$$\mathcal{J} = \int_0^1 du\, u^r (1-u)^s \int_0^1 dv\, v^{r'} (1-v)^{s'} \ldots \int_0^\infty dz\, \mathcal{F}_{\mathrm{FIT}}(u, v, \ldots, z)\, j_\nu(\alpha z) \quad (4)$$

in which $j_\nu(\alpha z)$ is a spherical Bessel function. As for the term $\mathcal{F}_{\mathrm{FIT}}(u, v, \ldots, z)$, it is an exponentially decreasing function which ensures the convergence of the innermost integral. The best numerical strategy for evaluating the semi-infinite integral occurring in eq. (4) is to rely on the $S\bar{D}$ nonlinear transformation that was introduced by Safouhi[18] and which was shown to be a very powerful tool for semi-infinite integrals containing strongly oscillating Bessel functions. As a last remark, it is important to notice that eq. (4) and (3) show a certain similarity in the mathematical structure of multicenter integrals, as expressed in both the FIT and GIT approaches. However in some instances, as is the case for four-center integrals, GIT-based multi-integrals may have an additional integral over the range [0,1].

Previously,[19] it was shown that, in the case of three-center nuclear attraction integrals, the numerical algorithm using the GB quadrature has a complexity comparable to that of the $S\bar{D}$ for low-order polynomials. In fact, when the roots and weights of the GB quadrature are computed on the fly, the complexity of the procedure used to evaluate the three-center nuclear attraction integrals increases as n^3, where n is the order of the GB quadrature. This complexity can clearly be penalizing if high-order quadratures are required. As a consequence, this work is devoted to exploring strategies that can be used for an efficient implementation of the GB quadrature. The end result of this investigation is an algorithm with linear complexity.

For the sake of completeness, we intend to address two approaches both used to evaluate the semi-infinite integral occurring in eq. (3): the Shavitt and Karplus infinite series[11] which we refer to as the SK-series and the GB quadrature.

1. First (cf. Convergence Analysis of the SK-Series section), we address the convergence properties of the SK-series which is shown to converge linearly, except for specific values of some parameters for which such a convergence becomes logarithmic. This poses severe numerical issues when accelerating techniques are applied to speed up the summation procedure.
2. Second (cf. Implementation Strategy of the GB Quadrature for the Evaluation of $T_{l,m}(\sigma,\tau)$ section), we focus on the GB quadrature for which the integrand is transformed allowing a minimal number of roots and weights to be stored. This strategy is shown to yield an algorithm with linear complexity.
3. Third, it is also shown (cf. Complexity Analysis section) that when the GB quadrature is implemented using the procedure described in Implementation Strategy of the GB Quadrature for the Evaluation of $T_{l,m}(\sigma,\tau)$ section, the leading algorithm has a linear complexity similar to that of the $S\bar{D}$ method (as applied in the context of the FIT).

Definitions

A STF centered on some arbitrary point $A(x_A, y_A, z_A)$ defined by a location vector $\mathbf{a}$ can generally be written in spherical coordinates as,

$$f^m_{n,l}(\zeta \mathbf{r}_a) = \mathcal{P}_{n,l}(\zeta \|\mathbf{r}_a\|) \exp(-\zeta \|\mathbf{r}_a\|) Y^m_l(\theta_{\mathbf{r}_a}, \phi_{\mathbf{r}_a}) \tag{5}$$

where $\mathbf{r}_a = \mathbf{r} - \mathbf{a}$ and $Y^m_l(\theta_{\mathbf{r}_a}, \phi_{\mathbf{r}_a})$ stands for the spherical harmonic of degree l and order m. As for the term $\mathcal{P}_{n,l}(\zeta \|\mathbf{r}_a\|)$, it is a polynomial in the variable $\|\mathbf{r}_a\|$ also referred to as the radial part of the orbital. Of course, based on the specific definition of this polynomial one can build a variety of useful exponentially decaying orbitals. For instance,

$$\begin{cases} \mathcal{P}_{n,l}(\zeta r)\exp(-\zeta r) = L^{2l+1}_{n-l-1}(2\zeta r)\exp(-\zeta r) & \text{yields hydrogen-like orbitals} \\ \mathcal{P}_{n,l}(\zeta r)\exp(-\zeta r) = (\zeta r)^l \mathbf{K}_{n-1/2}(\zeta r) & \text{yields B functions} \\ \mathcal{P}_{n,l}(\zeta r)\exp(-\zeta r) = r^{n-1}\exp(-\zeta r) & \text{yields Slater orbitals} \end{cases} \tag{6}$$

in which $\mathbf{K}_\nu(z)$ stands for the modified Bessel function of the second kind. Although the spherical representation of atomic orbitals is the most widely used in quantum chemistry textbooks, Cartesian coordinates can also be very useful in practice. In fact, certain numerical procedures used to evaluate multicenter integrals are tailored for cartesian coordinates since high-order orbitals are easily obtained as a result of applying a shift operator to the simplest instance, e.g. 1s orbital. In this respect, the work of Fernandez and Coworkers[20] is an excellent reference to clearly understand the elegance of shift operators in the context of multicenter integrals.

Strategies for the Evaluation of $T_{l,m}(\sigma,\tau)$

As mentioned earlier, when the GIT approach is used, multicenter integrals over Slater orbitals can be expressed as a sum of multiple integrals, the innermost of which is semi-infinite. According to Shavitt and Karplus,[11] such an integral can generally be written as,

$$\Gamma(m+1/2)T_{l,m}(\sigma,\tau) = \int_0^\infty z^{l-m} F_m\left(\frac{1}{z}\right)\left[\sqrt{z}\exp\left(-\frac{\sigma}{z} - \tau z\right)\right] dz \tag{7}$$

where σ and τ are the two parameters which depend on the screening constants of the orbitals, the coordinates of the centers and the integration variables of the outer integrals. Referring to the general mathematical definition given in eq. (3), we can write,

$$\begin{aligned} \sigma &= \sigma(\zeta_1, \zeta_2, \ldots, \text{geometry}, u, v, \ldots), \\ \tau &= \tau(\zeta_1, \zeta_2, \ldots, \text{geometry}, u, v, \ldots) \end{aligned} \tag{8}$$

At this point one may be tempted to use a combination of Gauss quadratures, eg. Gauss–Legendre and Gauss–Laguerre, to evaluate the function $T_{l,m}(\sigma,\tau)$. In fact analysis of the integrand in (7) shows that the term $\exp(-\sigma/z - \tau z)$ introduces a moving peak which can be very sharp. In such a case, Gauss interpolation polynomials will fail to capture this special behavior, hence leading to inaccurate results. Consequently, three strategies may be adopted to solve this difficulty,

1. Increase the number of points in the classical Gauss quadratures. This however is not the best solution, since not only it yields costly algorithms but more importantly it still can fail for specific values of σ and τ.

2. Turn to a series representation of $T_{l,m}(\sigma,\tau)$. One of such representations is what we previously called the SK-series.[11] Perhaps, the major drawback of this type of expansions is the possibility of obtaining a slowly convergent series that would require a special procedure for its evaluation. This adds another level of complexity to the algorithms which, of course, comes with a computational penalty.
3. Use a tailored Gauss quadrature built using the term $\exp(-\sigma/z-\tau\, z)$ as part of the weight function.[15,19] The authors would like to draw attention to the work of Gautschi, who has previously considered a quadrature for which the weight function is of the form $\exp(-1/x-x)$,[21] which obviously is a special case of the GB quadrature. This specific work by Gautcshi came to the attention of the authors after publishing our previous work. A complexity analysis of the algorithm based on this method has shown that the number of operations, in the case of the three-center nuclear attraction integrals, grows as n^3 where n is the order of the interpolating polynomial.[19] Although for low-order polynomials, such a complexity is comparable to that based on the $S\bar{D}$ technique, improvements must be introduced in order to make the GB approach efficient enough for a routine use.
4. Application of an extrapolation technique. In this respect, it appears that Gray's G[22,23] transformation might be the most appropriate for the integrand occurring earlier.

Let us mention, here, that the earlier listed methods can be viewed as the basic building blocks for the algorithms used to evaluate multicenter integrals in the GIT approach. In practice, however, we believe that a suitable combination of two (or more) of these methods will perform better than any single method implemented to handle all cases. With this view in mind, the rest of this section is dedicated to explore the possibility the strengths of the SK-series and the GB-quadrature.

Convergence Analysis of the SK-Series

When infinite series expansions are used for numerical computations, two major drawbacks can render the corresponding algorithm inefficient. On the one hand, the numerical stability of the summation procedure and on the other hand the convergence of the series. In the following these two aspects will be investigated in the SK-series representation of the semi-infinite integral $T_{l,m}(\sigma,\tau)$. The series in question is defined as,

$$T_{l,m}(\sigma,\tau)=\sum_{p=m-l}^{\infty}\frac{1}{\Gamma(l+p+3/2)}\left(\sqrt{\frac{\tau}{1+\sigma}}\right)^{p+1/2}\mathbf{K}_{p+1/2}(2\sqrt{(1+\sigma)\tau}) \quad (9)$$

To study the convergence of this series, let us start by recalling some important results that will be used later in the section.

Let $\mathbf{s}=\sum_n^{\infty}a_n$ *be a infinite series and such that the term* a_n *has a Poincaré type asymptotic expansion of the form,*

$$a_n\sim\lambda^n n^{\Theta}\left[\alpha_0+\frac{\alpha_1}{n}+\frac{\alpha_2}{n^2}+\ldots\right] \quad \textit{where} \quad \begin{cases}\alpha_0\neq 0\\ n\longrightarrow+\infty\end{cases} \quad (10)$$

According to theorem 1 in ref. 24 (p. 6), the series $\mathbf{s}$ *converges linearly for* $|\lambda|<1$ *and logarithmically for* $|\lambda|=1$ *and* $\Re(\Theta)<-1$. *Obviously when* $|\lambda|>1$ *the series diverges.*

In terms of computational effort, a linearly convergent series can be evaluated by a brute force algorithm using direct summation. Although this is not the most efficient approach to carry out such an evaluation, computer time may still end up within reasonable bounds. On the contrary, a logarithmically convergent series cannot be evaluated, in practice, by a direct summation. A famous example falling in this category is the so-called Riemann's $\zeta(1)$ function, which after summing a million terms yields a value of 14.3927 giving a false impression of convergence. Of course, a theoretical investigation of this series clearly shows that it diverges. In the light of the earlier remarks, let us start by deriving the Poincaré-type asymptotic representation of its general term for large values of the index p. According to ref. 25 (Eq. 3.10), the asymptotic expansion of the modified Bessel function can be written as,

$$\mathbf{K}_{\nu}(z)\sim\frac{1}{2}\left(\frac{2}{z}\right)^{\nu}\Gamma(\nu)\sum_{p=0}^{P}(-1)^p\frac{\Gamma(\nu-p)}{\Gamma(\nu)}\frac{1}{p!}\left(\frac{z}{2}\right)^p+O(\nu^{-P-1}) \quad \nu\longrightarrow+\infty \quad (11)$$

Inserting the above asymptotic representation into the definition of the general term of the series expansion (9), referred to as U_n, yields the following approximate,

$$U_n\sim\frac{1}{2}\frac{\Gamma(n+1/2)}{\Gamma(n+l+3/2)}\left[\frac{1}{1+\sigma}\right]^{n+1/2}\times\sum_{p=0}^{P}(-1)^p\frac{\Gamma(n+1/2-p)}{\Gamma(n+1/2)}\left[\sqrt{\tau(1+\sigma)}\right]^p \quad \text{with } n\longrightarrow+\infty \quad (12)$$

At this point, further simplifications can be carried out by noticing that, for large values of n, $\Gamma(n+\alpha)\sim n^{\alpha}$. Thus, after some simple algebra the asymptotic representation of the terms U_n can be brought into a form similar to that of eq. (10),

$$U_n\sim\left[\frac{1}{1+\sigma}\right]^n n^{-l-1}\left[\frac{1}{2\sqrt{1+\sigma}}-\frac{\sqrt{\tau(1+\sigma)}}{2\sqrt{1+\sigma}}\frac{1}{n}+\frac{\sqrt{\tau(1+\sigma)}^2}{2\sqrt{1+\sigma}}\frac{1}{n^2}-\frac{\sqrt{\tau(1+\sigma)}^3}{2\sqrt{1+\sigma}}\frac{1}{n^3}+\ldots\right] \quad (13)$$

In the light of the results presented in connection with eq. (10), we may easily conclude that for $\sigma>0$, i.e. $1/(1+\sigma)<1$, the SK-series representation of $T_{l,m}(\sigma,\tau)$ converges linearly. Of course, from a practical point of view, though the SK-series is still linearly convergent for small values of σ, its convergence deteriorates making the summation procedure computationally expensive. The result of the earlier analysis can be summarized pictorially using a color-coded map similar to those used for digital elevation models

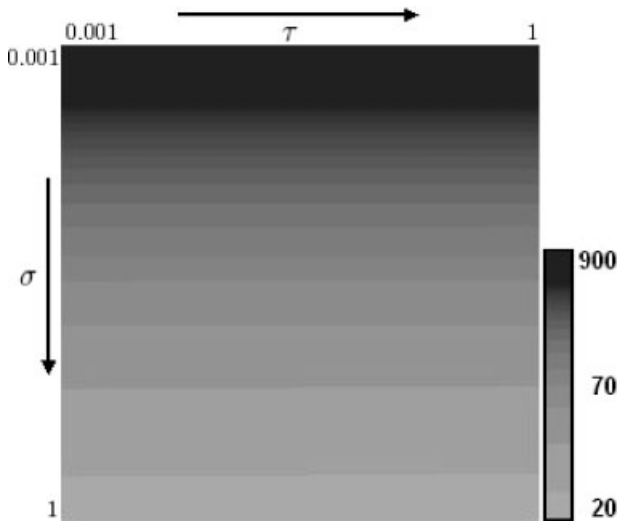

Figure 2. Number of terms ensuring the convergence of the SK-series $T_{5,0}(\sigma,\tau)$ as a function of σ and τ. These parameters were such that $0.001 \leq \sigma \leq 1$ and $0.001 \leq \tau \leq 1$.

in geospatial data analysis. This approach allows the 3-D function $N = f(\sigma,\tau)$, where N is the number of terms required to achieve convergence, to be easily analysed. Accordingly, it can easily be seen on Figure 2 that as σ gets closer to zero (top left corner) the number of terms needed to ensure convergence increases rapidly. On the other hand and as predicted by the theory, τ has little influence on the convergence of the SK-series (constant gray intensity horizontally from left to right, Fig. 2).

Fortunately, this difficulty can be solved by means of a suitable convergence accelerating technique that has been developed in the past few decades. In fact, in the original paper on the GIT method, Shavitt and Karplus have noticed that the convergence of the SK-series varies widely and the earlier paragraph provides a proof as to which parameters controls its convergence, i.e. σ. In their original paper, the authors have used the Aitken's Δ^2 nonlinear transformation to accelerate the convergence of their series. In the following, we would like to investigate the advantages of using the Levin u transformation.[26] In the review paper of Weniger,[27] the generalized u transformation is defined as,

$$\mathcal{L}_{k,l}^{(n)}(\beta, s_n, \omega_n) = \frac{\displaystyle\sum_{j=0}^{k}(-1)^j \binom{k}{j} \frac{(\beta+n+j)^{k-l-1}}{(\beta+n+k)^{k-1}} \frac{s_{n+j}}{\omega_{n+j}}}{\displaystyle\sum_{j=0}^{k}(-1)^j \binom{k}{j} \frac{(\beta+n+j)^{k-l-1}}{(\beta+n+k)^{k-1}} \frac{1}{\omega_{n+j}}} \tag{14}$$

in which s is the limit of the sequence, s_n its n-th partial sum and ω_n the n-th remainder, that is $\omega_n = s - s_n$. The earlier formula provides the exact limit for any sequence that can be written as,

$$s_n = s + (\beta+n)^l \omega_n \sum_{j=0}^{k-1} \frac{c_j}{(\beta+n)^j}, \quad k,l,n \in \mathbb{N}^* \tag{15}$$

where $\mathbb{N}^* = \mathbb{N} - \{0\}$. As can be seen, the extrapolation formula (14) depends on the remainder ω_n. Although for general series the analytical expression of ω_n is unknown, few suggestions were made and were found to work very well in practice. For instance for logarithmic,[26] alternating[26] and convergent strictly alternating[28] series, the following remainders were suggested,

$$\begin{cases} \omega_n = (\beta+n)a_n & \text{for logarithmicaly convergent series} \\ \omega_n = a_n & \text{for alternating series} \\ \omega_n = a_{n+1} & \text{for convergent strictly alternating series} \end{cases} \tag{16}$$

The derivation of the aforementioned formulas as well as many of their theoretical aspects were thoroughly discussed by Weniger in ref. 27. In addition a useable FORTRAN routine, referred to as GLEVIN (ref. 27, p. 52), was also provided. This routine is used to illustrate the benefits of the Levin u transformation in improving the convergence of the SK-series. The outcome of this experiment is summarized in Table (1) in which the values of the SK-series were generated for selected values of σ purposely chosen to be close to zero, since it is in this region that convergence difficulties occur.

Based on the values listed in Table 1, it can clearly be seen that accelerating the original SK-series improves its convergence, since extra exact digits are gained in the process. However, even though the calculations required by Levin's u transformation were carried out using appropriate recurrence relations to ensure numerical stability, the acceleration process is not fully stable. Indeed, according to the values of Table 1, it may be noticed that after $n = 17$ or 18, the estimated limit starts fluctuating, which ultimately leads to a loss of accuracy. This observation is obviously in conflict with the theory which predicts that the estimated limit should be more accurate as the number of partial sums increases. Obviously, enlarging the internal representation of floating numbers, that is using quadruple precision (as provided in many Fortran compilers), yields a more stable procedure. This workaround is, however, not very suitable for an intensive routine that is at the heart of any GIT-based multicenter integral, since it will lead to a dramatic computational penalty.

Implementation Strategy of the GB Quadrature for the Evaluation of $T_{l,m}(\sigma,\tau)$

In previous work,[29] preliminary results have shown that a numerical procedure using a tailored Gauss quadrature, known as GB, can be a good candidate for the evaluation of the semi-infinite integral $T_{l,m}(\sigma,\tau)$. The selection of this method was motivated by two facts. On the one hand, series expansions can be very costly owing to their poor convergence. On the other hand, applying a classical quadrature is not recommended because of the *singular* behavior of the integrand. GB quadrature was elaborated with a view to compensate for these shortcomings, since the singular term is included as part of the weight function $W(z) = \sqrt{z}\exp(-\sigma/z - \tau z)$. Note that the term $\sqrt{z}$ is merely a convenience, since this allows the moments to be expressed in terms modified Bessel functions of the second kind $\mathbf{K}_{n+1/2}(2\sqrt{\sigma\tau})$ that have closed analytical expressions.

Table 1. Acceleration of the SK-Series Using Levin's u Transformation.

n	$10^4\mathcal{L}_n^n(\beta, s_n, (\beta+n)a_n)$[a]	$10^4\mathcal{L}_n^n(\beta, s_n, (\beta+n)a_n)$[b]	$10^4\mathcal{L}_n^n(\beta, s_n, (\beta+n)a_n)$[c]	$10^4\mathcal{L}_n^n(\beta, s_n, (\beta+n)a_n)$[d]
15	5.56979540388427(−4)	5.56979540416457(−4)	5.53018006840289(−4)	5.53018006846880(−4)
16	5.56979540318605(−4)	5.56979540244135(−4)	5.53018006219076(−4)	5.53018006202258(−4)
17	5.56979539905240(−4)	5.56979540133946(−4)	5.53018005806925(−4)	5.53018005802322(−4)
18	5.56979540784951(−4)	5.56979540062138(−4)	5.53018005254347(−4)	5.53018005549722(−4)
19	5.56979537825869(−4)	5.56979540014497(−4)	5.53018007065773(−4)	5.53018005387549(−4)
20	5.56979546193032(−4)	5.56979539982370(−4)	5.53017999091708(−4)	5.53018005281870(−4)
21	5.56979522978574(−4)	5.56979539960380(−4)	5.53018023148069(−4)	5.53018005212064(−4)
22	5.56979589202469(−4)	5.56979539945119(−4)	5.53017959850841(−4)	5.53018005165375(−4)
23	5.56979379859304(−4)	5.56979539934391(−4)	5.53018119654682(−4)	5.53018005133788(−4)
24	5.56980140547945(−4)	5.56979539926761(−4)	5.53017692867075(−4)	5.53018005112191(−4)
25	5.56977779658011(−4)	5.56979539921272(−4)	5.53019099520965(−4)	5.53018005097280(−4)
26	5.56992914489160(−4)	5.56979539917284(−4)	5.53015596051774(−4)	5.53018005086892(−4)
27	5.56972046491779(−4)	5.56979539914358(−4)	5.52958206952717(−4)	5.53018005079595(−4)
28	5.56963549818559(−4)	5.56979539912192(−4)	5.53011953601722(−4)	5.53018005074428(−4)
29	5.56968184364744(−4)	5.56979539910575(−4)	5.53008554588115(−4)	5.53018005070744(−4)
30	5.56964410712436(−4)	5.56979539909358(−4)	5.52989656312023(−4)	5.53018005068099(−4)
31	5.56956914942583(−4)	5.56979539908435(−4)	5.53017094564084(−4)	5.53018005066189(−4)
32	5.56993537853547(−4)	5.56979539907731(−4)	5.53015792453635(−4)	5.53018005064800(−4)
33	5.56978780721298(−4)	5.56979539907190(−4)	5.53015518944974(−4)	5.53018005063786(−4)
34	5.56976340230520(−4)	5.56979539906771(−4)	5.53015354080221(−4)	5.53018005063041(−4)
35	5.56975279473866(−4)	5.56979539906445(−4)	5.53015002685314(−4)	5.53018005062491(−4)
36	5.56974758728678(−4)	5.56979539906190(−4)	5.53012606356496(−4)	5.53018005062084(−4)
37	5.56974948999922(−4)	5.56979539905990(−4)	5.53018159599067(−4)	5.53018005061781(−4)
38	5.56975808602963(−4)	5.56979539905832(−4)	5.53016894836986(−4)	5.53018005061554(−4)
39	5.56976698622764(−4)	5.56979539905706(−4)	5.53016636833971(−4)	5.53018005061384(−4)
40	5.56977252570164(−4)	5.56979539905605(−4)	5.53016561659583(−4)	5.53018005061256(−4)
41	5.56977482887447(−4)	5.56979539905525(−4)	5.53016562041707(−4)	5.53018005061159(−4)
42	5.56977402001894(−4)	5.56979539905460(−4)	5.53016599029677(−4)	5.53018005061086(−4)
43	5.56976461640496(−4)	5.56979539905407(−4)	5.53016640223254(−4)	5.53018005061030(−4)
44	5.56983876441984(−4)	5.56979539905369(−4)	5.53016642240955(−4)	5.53018005060989(−4)
45	5.56979581692137(−4)	5.56979539905317(−4)	5.53016482131995(−4)	5.53018005060950(−4)

[a]Estimated limit of the SK-series $T_{5,0}(0.001, 1)$ using double precision.
[b]Estimated limit of the SK-series $T_{5,0}(0.001, 1)$ using quadruple precision. $s_{45} = 5.56979307996937(-4)$ and $s = 5.56979539905165(-4)$.
[c]Estimated limit of the SK-series $T_{5,0}(0.005, 1)$ using double precision.
[d]Estimated limit of the SK-series $T_{5,0}(0.005, 1)$ using quadruple precision. $s_{45} = 5.53017824256391(-4)$ and $s = 5.53018005060845(-4)$.

In the following we describe the implementation of a numerical procedure geared toward the calculation of $T_{l,m}(\sigma, \tau)$ in which strong emphasis is put on efficiency. Two cases are to be studied separately.

1. For large values of σ, the SK-series is expected to converge fast and hence the motivation to rely on this representation for $\sigma \geq 2$. In fact, the larger the σ the faster is the convergence of the SK-series; this feature should be used in order to optimize the number of terms that need to be computed. To refine the observation of Shavitt and Karplus, a simple regression analysis was applied in order to build a functional relationship between the number of terms (ensuring a satisfactory convergence) and the parameter σ,

$$n = \left\lfloor -0.0200\sigma^3 + 0.4959\sigma - 4.346\sigma + 23.567 + \frac{1}{2} \right\rfloor \quad (17)$$

2. For small values of σ, the use of a tailored Gauss quadrature provides a possible solution allowing the algorithmic complexity to be maintained within reasonable bounds. In this case, the computation can be optimized by transforming slightly the integral $T_{l,m}(\sigma, \tau)$,

$$\begin{aligned}\Gamma(m+1/2)T_{l,m}(\sigma,\tau) &= \int_0^{+\infty} z^{l-m-2} F_m\left(\frac{1}{z}\right) \\ &\quad \times \left[\sqrt{z}\exp\left(-\frac{\sigma}{z} - \tau z\right)\right] dz \\ &= \sigma^{l-m-1/2} \int_0^{\infty} z^{l-m-2} F_m\left(\frac{1}{\sigma u}\right) \\ &\quad \times \left[\sqrt{u}\exp\left(-\frac{1}{u} - \beta u\right)\right] du \quad (18)\end{aligned}$$

where $\beta = \sigma\tau$. With respect to algorithmic efficiency, the evaluation of multicenter integrals by means of the GB quadrature is likely to be slow if the corresponding roots and weights are to be evaluated on the fly for each value of σ and τ. The change of variable introduced in the integral given by (18) allows a special GB weight $W(1,\beta;z)$ to occur within the integrand. This is advantageous since the number of roots and weights to be computed is likely to be smaller than when the general weight $W(\sigma,\tau;z)$ is used. Indeed, for a general GB weight function, a set of roots and weights needs to be computed for each couple (σ,τ) while for $W(1,\beta;z)$ the computation needs to be done for each value of β. To further increase the efficiency of the algorithms, the roots and weights of the GB quadrature corresponding to $W(1,\beta;z)$ are computed for values of β ranging from near zero to some large value. A small increment is used. During a typical computation of a given multicenter integral, one of the following scenarios may occur,

(a) The product $\sigma\tau$ coincides *exactly* with one of the values of β for which the roots and weights have been stored. In this very unlikely case, the computation is straightforwardly done.
(b) The product $\sigma\tau \leq \beta_{\max}$. In this case, the integration will be carried out using the GB roots and weights that have been computed for β closest possible to $\sigma\tau$. Clearly, an additional term of the form $\exp[-(\sigma\tau-\beta)u]$ needs to be included as part of the integrand.
(c) The product $\sigma\tau > \beta_{\max}$. In this case, a set of new roots and weights are computed on the fly.

It must emphasized that introducing the term β into the calculation makes it easy to calculate the weights and roots of the GB quadrature. Of course, the parameter σ is now part of the Boys function for which a variety of very efficient algorithms have been developed. For real case studies, i.e., computation of molecular structures, some intelligence needs to be implemented within the software so as to gather statistics that will be used to select the value of $\beta_{\max}$ in such a way as to minimize the number of orthogonal polynomials to be computed on the fly.

Complexity Analysis

Based on the mathematical structure of multicenter integrals in the FIT approach (4), it may be argued that FIT is more advantageous than GIT, particularly in the case of four-center integrals, since these quantities end up defined as a triple integral as opposed to a quadruple integral in the case of the GIT. Although, this may seem to be an interesting argument from a theoretical point of view, this is not necessarily true when addressing the computability of such quantities. The following intends to show that by suitably implementing the GB-based algorithm for the GIT approach, its complexity ends up to be similar to what was done for the FIT. Indeed, it is well known that, in the FIT approach, the innermost semi-infinite integral involves a strongly oscillating integrand that requires a specialized technique to ensure its accurate evaluation. This aspect of the computation has been thoroughly studied by one of us and led to the $S\bar{D}$ method.[18] The benefits of this method have been reported in many papers supported by a large number of numerical experiments. In the following we compare the complexity of the GIT- and FIT-based methods in the case of a four-center integral involving s orbitals.

Starting from the expression of the four-center integral derived by Shavitt and Karplus using 1s orbitals [see eq. (16) in ref. 11], we obtain after some algebra the following formula in the case of arbitrary s orbitals,

$$\begin{aligned}\mathcal{J}_{\mathrm{GIT}}(n_1,n_2,n_3,n_4) = {} & \frac{\mathcal{N}(n_1,\alpha_1)\mathcal{N}(n_2,\alpha_2)\mathcal{N}(n_3,\alpha_3)\mathcal{N}(n_4,\alpha_4)}{2^{n_1+n_2+n_3+n_4+4}\pi}\int_{u=0}^{1}\frac{du}{u^{(n_1+1)/2}(1-u)^{(n_2+1)/2}}\int_{v=0}^{1}dv\frac{p^{n_1+n_2+n_3+n_4+1}}{v^{(n_3+1)/2}(1-v)^{(n_4+1)/2}}\\ & \times\int_{w=0}^{1}dw(1-w)^{(n_1+n_2-1)/2}w^{(n_3+n_4-1)/2}\sigma^{3/2}\int_{z=0}^{+\infty}dz(\sigma z)^{(n_1+n_2+n_3+n_4)/2}H_{n_1}\left[\frac{\alpha_1 p}{2}\sqrt{\frac{1-w}{u}}\sqrt{\sigma z}\right]\\ & \times H_{n_2}\left[\frac{\alpha_2 p}{2}\sqrt{\frac{1-w}{1-u}}\sqrt{\sigma z}\right]H_{n_3}\left[\frac{\alpha_3 p}{2}\sqrt{\frac{w}{v}}\sqrt{\sigma z}\right]H_{n_4}\left[\frac{\alpha_4 p}{2}\sqrt{\frac{w}{1-v}}\sqrt{\sigma z}\right]\mathrm{erf}\left(\frac{1}{\sqrt{\sigma z}}\right)\mathcal{W}(1,\sigma\tau;z)\end{aligned} \tag{19}$$

in which the normalization term is such that $\mathcal{N}(n,\alpha) = (2\alpha)^{n+1/2}/\sqrt{(2n)!}$ and $\mathcal{W}(\mu,\nu;z)$ is the GB weight function defined as,[15]

$$\mathcal{W}(\mu,\nu;z) = \sqrt{z}\exp\left[-\frac{\mu}{z}-\nu z\right], \quad \text{with} \quad \begin{cases}\Re(\mu) & > & 0\\ \Re(\nu) & > & 0\end{cases} \tag{20}$$

The parameters p, σ, and τ occurring in the earlier equations are such that,

$$\sigma = \frac{u(1-u)}{1-w}\frac{a^2}{p^2}+\frac{v(1-v)}{w}\frac{c^2}{p^2} \tag{21}$$

$$\tau = \frac{p^2}{4}\left[\frac{1-w}{u}\alpha_1^2+\frac{1-w}{1-u}\alpha_2^2+\frac{w}{v}\alpha_3^2+\frac{w}{1-v}\alpha_4^2\right] \tag{22}$$

$$p = \|u\overrightarrow{AB}-v\overrightarrow{CD}+\overrightarrow{BD}\| \tag{23}$$

where A, B, C, and D are the centers of the orbitals. In practice, the condition on μ and ν given in eq. (20) is satisfied, because the integration of the multiple integral defining the interaction integrals is usually carried out by means of a suitable Gauss product rule. As a result and based on the definitions of σ and τ [cf. eqs. (21) and (22)], these parameters cannot vanish, since classical Gauss quadratures (excluding Gauss–Lobatto) do not use the boundaries of the integration interval.

At this point, let us count the number of elementary operations needed to compute the integral (19). Since multiplications and the evaluation of transcendental functions are the most demanding in CPU time, these only will be included in our counting procedure.

On the basis of the values listed in Table 2, we are now in a position to give the number of elementary operations required by the multiple quadruple integral in eq. (19),

$$N_{\mathrm{GB}} = \sum_{i=1}^{N_u}\left\{7+\sum_{j=1}^{N_v}\left[19+\sum_{k=1}^{N_w}23 + \left(\sum_{l=1}^{N_z}3(n_1+n_2+n_3+n_4)+7\right)\right]\right\}$$
$$= [3(n_1+n_2+n_3+n_4)+7]N_zN_wN_vN_u + 23N_wN_vN_u + 19N_vN_u + 7N_u \quad (24)$$

Table 2. Counting Elementary Operations for the Computation of the Multiple Integral in Eq. (19).

Integration over u	Operations
$u_1 = \sqrt{u}$	1
$u_2 = \sqrt{1-u}$	1
$u_1^{-(n_1+1)} \times u_2^{-(n_2+1)}$	$1+1+1$
Total	$5+(1+1)^a$
Integration over v	**Operations**
$v_1 = \sqrt{v}$	1
$v_2 = \sqrt{1-v}$	1
Denominator $= v_1^{-(n_3+1)} \times v_2^{-(n_4+1)}$	$1+1+1$
$p_{x,y,z} = u\overrightarrow{AB}_{x,y,z} - v\overrightarrow{CD}_{x,y,z} + \overrightarrow{BD}_{x,y,z}$	$3(1+1)$
$p^2 = p_x^2 + p_y^2 + p_z^2$	$1+1+1$
$p = \sqrt{p^2}$	1
$p^{n_1+n_2+n_3+n_4}$/denominator	$1+1$
Total	$17+(1+1)^a$
Integration over w	**Operations**
$w_1 = \sqrt{1-w}$	1
$w_2 = \sqrt{w}$	1
$\sigma = [u(1-u)/(1-w)](a^2/p^2) + \ldots$	$4+4$
$\tau = (p^2/4)[(1-w)/u\alpha_1^2 + \ldots]$	$2+2+2+2+2$
$\sigma^{3/2}$	1^b
Total	$21+(1+1)^a$
Integration over z	**Operations**
$z_1 = \sqrt{\sigma z}$	1
$z_1^{n_1+n_2+n_3+n_4}$	1
$x_1 = (\alpha_1 p)/2(w_2/u_1)z_1$	5
$H_{N+1}(x_1) =$ $2x_1H_N(x_1) - 2NH_{N-1}(x_1) =$ $H_1(x_1)H_N(x_1) - 2NH_{N-1}(x_1)$	$3(N-1)$
$\mathrm{erf}(1/z_1)$	$1+1$
$\exp[-(\sigma\tau - \beta^c)z]$	$1+1+1$
$z_1^{n_1+n_2+n_3+n_4} \times H_{n_1}(x_1) \times H_{n_2}(x_2) \times \ldots$	6
Total	$3(n_1+n_2+n_3+n_4)+6+1^a$

The roots and weights of the Gauss–Bessel quadrature are assumed to be computed beforehand.

[a]Extra operations due to a multiplication by the weighting factor and the innermost integral (when applicable).

[b]The term $w_1^{n_1+n_2-1} \times w_2^{n_3+n_4-1}$ does not occur in the computation, since it is accounted for as part of the Gauss-Jacobi weights.

[c]The parameter β corresponds to the value of $\sigma\tau$ for which the roots and weights are stored.

Based on this relationship, it can clearly be seen that when the roots and weights of the GB quadrature are stored, the cost of the computational procedure is proportional to the product of the orders of the interpolating polynomials used to evaluate each integral. At this point, it is of interest to count the number of elementary operations needed by the semi-infinite integral occurring in (19) if the evaluation is performed solely by means of the SK series. Expanding the Hermite polynomials and collecting the appropriate powers of the integration variable, yields after some algebra to the following result,

$$\mathcal{S} = \sum_{a}^{\lfloor n_1/2\rfloor}\frac{(-1)^a}{a!(n_1-2a)!}\left[\alpha_1 p\sqrt{\frac{1-w}{u}}\right]^{n_1-2a} \times \sum_{b}^{\lfloor n_2/2\rfloor}\frac{(-1)^b}{b!(n_2-2b)!}\left[\alpha_2 p\sqrt{\frac{1-w}{1-u}}\right]^{n_2-2b} \times \sum_{c}^{\lfloor n_3/2\rfloor}\frac{(-1)^c}{c!(n_3-2c)!}\left[\alpha_3 p\sqrt{\frac{w}{v}}\right]^{n_3-2c} \times \sum_{d}^{\lfloor n_4/2\rfloor}\frac{(-1)^d}{d!(n_4-2d)!}\left[\alpha_4 p\sqrt{\frac{w}{1-v}}\right]^{n_4-2d} T_{\alpha,0}(\sigma,\tau) \quad (25)$$

where $\alpha = n_1+n_2+n_3+n_4-(a+b+c+d)+1$. Interestingly, the number of operations required by $T_{\alpha,0}(\sigma,\tau)$ (7) when computed by means of the following three-term recurrence relation,

$$U_{p+1} = \frac{1}{(\alpha+p+3/2)(1+\sigma)}\left[\frac{\tau}{(\alpha+p+1/2)}U_{p-1} + (p+1/2)U_p \qquad p = m-l+1, m-l+2, \ldots p_{\max}\right] \quad (26)$$

is at least $6p_{\max}+\alpha$. This number is then compounded since the earlier operation is performed inside the innermost summation in eq. (25). In contrast, a brute force scheme in which the terms are computed independently requires only $p_{\max}+\alpha+1$ operations to be performed inside the innermost summation. As a result, it is this

implementation that is used to compare the complexity of the GB and SK-series based algorithms.

Now, inserting the number of operations needed as part of the innermost summation in eq. (25) and taking into account that each summation requires an additional multiplication, since the Hermite polynomial coefficients must multiply the next summation, yields the following,

$$\begin{aligned} N_{\mathrm{SK}} &= (\lfloor n_1/2\rfloor+1\rfloor)+(\lfloor n_1/2\rfloor+1\rfloor)(\lfloor n_2/2\rfloor+1\rfloor) \\ &+(\lfloor n_1/2\rfloor+1\rfloor)(\lfloor n_2/2\rfloor+1\rfloor)(\lfloor n_3/2\rfloor+1\rfloor) \\ &+(\lfloor n_1/2\rfloor+1\rfloor)(\lfloor n_2/2\rfloor+1\rfloor)(\lfloor n_3/2\rfloor+1\rfloor)(\lfloor n_4/2\rfloor+1\rfloor) \\ &+\left[p_{\max}+1-\frac{1}{2}(\lfloor n_1/2\rfloor+\lfloor n_2/2\rfloor+\lfloor n_3/2\rfloor+\lfloor n_4/2\rfloor)\right] \\ &\times(\lfloor n_1/2\rfloor+1)(\lfloor n_2/2\rfloor+1)(\lfloor n_3/2\rfloor+1)(\lfloor n_4/2\rfloor+1) \end{aligned} \tag{27}$$

In the earlier equation, we have omitted to add the overhead cost required for the computation of the Hermite coefficients and the terms T_p described in parts one and two of Table 3. Inspection of the earlier equation clearly shows that, since N_{SK} depends on the product of the quantum numbers n_1, n_2, n_3 and n_4, it is expected to grow rapidly as such quantum numbers increase. In contrast, according to eq. (24) a GB-based algorithm will require $[3(n_1+n_2+n_3+n_4)+7]N_z$ operations and it grows linearly with increasing values of the quantum numbers. This feature is very advantageous in practice, since it helps keeping the computational effort within reasonable bounds.

Let us turn, now, to count the number of operations required by the evaluation of the semi-infinite integral in the framework of the FIT method. In such a case, the four-center integral involving s type orbitals yields the following semi-infinite integral,

$$\mathcal{S}_{\mathrm{FIT}}=\int_{z=0}^{+\infty}\frac{B_{n_1+n_2+1}[\beta(u,z)\overrightarrow{AB}]}{\beta(u,z)^{2(n_1+n_2)+1}} \times\frac{B_{n_3+n_4+1}[\gamma(v,z)\overrightarrow{DC}]}{\gamma(v,z)^{2(n_3+n_4)+1}}j_0(\|\vec{v}\|z)\,dz \tag{28}$$

where,

$$j_0(z)=\frac{\sin(z)}{z} \tag{29}$$

$$\vec{v}=(1-v)\overrightarrow{DC}-(1-u)\overrightarrow{AB}+\overrightarrow{AD} \tag{30}$$

$$\beta(u,z)=\sqrt{(1-u)\alpha_1^2+u\alpha_2^2+u(1-u)z^2} \tag{31}$$

$$\gamma(v,z)=\sqrt{(1-v)\alpha_3^2+v\alpha_4^2+v(1-v)z^2} \tag{32}$$

In order to carry out a comparative study between the efficiency of the procedures used to evaluate multicenter within the framework of the FIT and the GIT, it suffices to compare the complexity of the algorithms used to evaluate the innermost integrals in the earlier equations. The rationale behind this restriction is the due to the similarity of the outer integrals, i.e. over u and v, in both GIT and FIT, and this will likely to involve a similar number of elementary operations. In the case of the FIT, the $S\bar{D}$ transformation is probably the most suitable procedure for integrals involving a product of an oscillatory Bessel function $j_0(\alpha x)$ and exponentially decreasing

Table 3. Counting the Number of Elementary Operations Required to Compute the Semiinfinite Integral (25) by Means of the SK Series.

Coefficients of the Hermite polynomials[a]	Number of operations
$x_1=\alpha_1 p\sqrt{(1-w)/u}$	Computed before stepping into summation over a [cf. eq. (25)].
$(-1)^a/[a!(n_1-2a)!]x_1^a$	Computed and stored in a one-dimension array. This requires $2(n_1-1)+1$ operations.
A similar approach is applied to the Hermite polynomials H_{n_2}, H_{n_3}, and H_{n_4}, hence leading to a total of $2(n_1+n_2+n_3+n_4-4)$ operations.	
Other terms[a]	**Number of operations**
$1/\Gamma(l+p+3/2)$	Computed and appropriately stored as part of the initialization of the system.
$T_p=\sqrt{\tau/(1+\sigma)}^{p+1/2}K_{p+1/2}(2\sqrt{\tau(1+\sigma)})$	Computed before stepping into the summations over a, b, c, and d in eq. (25). This requires $(4p_{\max})$[b] operations.
$1/\Gamma(\alpha+p+3/2)\times T_p$	This is computed inside the innermost summation in eq. (25). This requires $(p_{\max}+\alpha+1)$[c] operations.
Total (required inside the innermost summation)[c]	$p_{\max}+l+1$

[a] $p_{\max}$ denotes the number of terms required to ensure convergence of the SK series.
[b] The three-term recurrence relation, $U_{p+1}=1/(1+\sigma)[\tau U_{p-1}+(p+1/2)U_p]$ is used to compute the product in question.
[c] This product requires only one multiplication that needs to be performed inside the innermost summation of eq. (25).

term. According to Safouhi, the $S\bar{D}$ transformation can be written as,

$$S\bar{D}_n^{(2,j)} = \frac{\sum_{i=0}^{n+1} \left(\begin{array}{c} n+1 \\ i \end{array} \right) (1+i+j)^n F(x_{i+j}) / \left[x_{i+j}^2 G(x_{i+j}) \right]}{\sum_{i=0}^{n+1} \left(\begin{array}{c} n+1 \\ i \end{array} \right) (1+i+j)^n / \left[x_{i+j}^2 G(x_{i+j}) \right]} \quad (33)$$

where $x_{i+j} = (i+j+1)\pi$ and $F(x) = \int_0^x G(t)\sin(t)dt$. In the case under study the function $G(t)$ is defined as,

$$G(t) = \frac{1}{\|\vec{v}\| z} \frac{B_{n_1+n_2+1}[\beta(u,z)\overrightarrow{AB}]}{\beta(u,z)^{2(n_1+n_2)+1}} \frac{B_{n_3+n_4+1}[\gamma(v,z)\overrightarrow{DC}]}{\gamma(v,z)^{2(n_3+n_4)+1}} \quad (34)$$

Following the analysis given previously in Table 2 of ref. 19, the number of elementary operations required by the evaluation of the semi-infinite integral (28) using the $S\bar{D}$ can be written as,

$$N_{S\bar{D}} = [(j+1)+(n+1)]N_{\text{Leg}}[19+3(n_1+n_2+n_3+n_4)] \quad (35)$$

where n and j are the parameters of the $S\bar{D}$ transformation. As for the term N_{Leg}, it stands for the order of the Legendre quadrature used to compute the integral $F(x)$ occurring in (33). Interestingly, it can be seen from eqs. (35) and (24) that the number of elementary operations involves the same dependence on the quantum numbers, i.e. $3(n_1+n_2+n_3+n_4)$. This clearly shows that the complexity of both the $S\bar{D}$-and the GB based algorithms is similar, provided that the roots and weights of the GB quadrature are not computed on the fly.

Conclusion

In the course of this work, we have highlighted two major aspects of the algorithm using the GIT. First, it was shown that when the SK series is used to compute the semi-infinite integral, its convergence can be dramatically slow for small values of σ. In this respect, a convergence accelerator such as the Levin u transformation can be used to accelerate the convergence but may suffer severely due to numerical instabilities. Second, from a complexity perspective, it was shown that a GB based algorithms (for which the roots and weights were stored beforehand) performs better than the SK-series, especially for large values of the principal quantum numbers. For the purpose of the present work, the roots and weights of the special GB quadrature using $\mathcal{W}(1,\beta;z)$ were stored for values of β ranging from 0.05 to 10^4 with a stepsize of 0.05. The first numerical experiments conducted on small systems such as CH_4, C_2H_2, and C_2H_4 showed that an algorithm fully based on the GB quadrature appears to be comparable to that build on the $S\bar{D}$ method in the framework of the FIT approach. At this point, the remaining unknown is to determine the optimal number of points N_z and N_w that will allow the double integral, i.e. over w and z, to be evaluated accurately with the least amount of elementary operations and a thorough comparison of accuracy. However, for a general purpose algorithm, we expect that a tradeoff between speed and accuracy needs to be found in order to accommodate extreme cases, e.g. medium to large screening distances and medium to large interatomic distances.

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