Exact Gaussian Expansions of Slater-Type Atomic Orbitals

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Abstract: Three exact Slater-type function (STO) integral transforms are presented. The STO-NG basis set can then be developed using either only 1s Gaussian functions, the same Gaussian exponents for each shell, or using the first Gaussian of each symmetry. The use of any of these three alternatives depends only on appropriate numerical integration techniques.


Key words: Slater-type orbital; integral transform; Gaussian expansion; numerical integration; STO-NG

Introduction

Expansion of wave functions in a Gaussian basis is one of the remarkable advances in ab initio quantum chemistry.\(^1\) The well-known deficiencies of Gaussians near nuclei or at large distances stimulated the development of an enormous variety of basis sets. One of the first and successful schemes was the Gaussian expansion of Slater basis functions

\[
\phi^{\text{S}}(\xi; \mathbf{r}) = \sum_{\mu=1}^{N} c_\mu \cdot \phi^{\text{G}}(\alpha_\mu; \mathbf{r})
\]

where \(\phi^{\text{S}}\) and \(\phi^{\text{G}}\) are Slater and Gaussian functions respectively, \(c_\mu\) are linear combination coefficients, \(\xi\) and \(\alpha_\mu\) are exponents of the functions and \(\mathbf{r}\) the spatial coordinates. The development of these contraction technique was undertaken to reproduce the correct asymptotic behavior of Slater functions and, consequently, to achieve accurate results for molecular properties. These basis sets were labeled STO-NG, and the initial sets were built with a small number of Gaussian primitives.\(^2-11\) However, with the recent developments in algorithms and numerical techniques,\(^12-15\) the interest in using Slater-type functions in quantum chemical calculations has been renewed. With the resurgence of Slater-type functions, STO-NG expansion are again valuable, because they can be used as reference in testing the accuracy of multicenter integrals calculated with the STO functions.

The common link between almost all the methods to develop STO-NG sets is the use of the least square techniques, where the \((c_\mu, \alpha_\mu)\) parameters are obtained through the minimization of the deviation of the fitness of the Gaussian expansion with STO. Two different schemes have been adopted to model these basis sets. The first one adopted 1s Gaussian functions for the expansion of all the s-type STO, 2p Gaussian functions for p-type STO, 3d Gaussian for d-type STO, and so on.\(^3-6\) The second method considers that the Gaussian \(\alpha_\mu\) exponents should be shared between \(ns\) and \(np\) functions.\(^7-11\) The exponent restriction was imposed for computational efficiency.

The source of inspiration for the elaboration of STO-NG was the exact representation of the 1s STO function as an integral transform, first suggested by Kikuchi;\(^16\)

\[
\exp(-r) = \frac{2}{\sqrt{\pi}} \int_{0}^{\infty} \exp[-(r/2t)^2 - t^2] dt.
\]

Despite the fact that exact STO integral transforms exist, Silver\(^17\) was the only one to use numerical techniques to generate a discrete expansion set to develop a particular STO-NG set. The lack of information about the use of other integral transforms can be associated with the success achieved by the traditional method and, as suggested by O-ohata et al.,\(^5\) “there is no guarantee that a mathematical sophistication infallibly brings in overall excellence or convenience.” However, accurate mathematical description of

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any system may lead to better comprehension of its nature and indicates possible alternatives for better numerical procedures. The objective of this article is to present three exact representations of the STO functions using Laplace transform, expressed in terms of Gaussian functions. A few quadrature methods are analyzed, and the adequacy of the approximated representations discussed.

Development of the STO Integral Transforms

The STO integral transforms developed in this article requires the previous definitions of five basic functions: (a) two Slater-type functions, (b) two Gaussian-type functions, and (c) a general integral transform.

The two normalized STO basis functions are those described in polar spherical and Cartesian coordinates, respectively. The product of a radial function \( R_\xi^S(\xi; r) \) and the normalized spherical harmonic \( Y_\ell^m(\theta, \phi) \) describes the first STO function as

\[
\phi_{S_{\ell m}}^S(\xi; r, \theta, \phi) = R_\xi^S(\xi; r)Y_\ell^m(\theta, \phi) \tag{3}
\]

where

\[
R_\xi^S(\xi; r) = N_\ell^S(\xi)r^{\ell+1}\exp(-\xi r) \tag{4}
\]

and

\[
N_\ell^S(\xi) = \left(\frac{2\xi^{2\ell+1}}{(2\ell)!}\right)^{1/2} \tag{5}
\]

where \( n, \ell, \) and \( m \) are the well-known quantum numbers.

The second definition of normalized STO in Cartesian coordinates can be written as

\[
\phi_{S_{\ell m}}^C(\xi; x, y, z) = N_{S_{\ell m}}^C(\xi)x^ay^bz^c\xi^{\ell+1}\exp(-\xi r), \tag{6}
\]

with

\[
N_{S_{\ell m}}^C(\xi) = \left[\frac{(2\xi^{2\ell+1})}{(2\ell)!}\frac{(2a + 2b + 2c + 1)!}{4\pi(2a - 1)!(2b - 1)!(2c - 1)!}\right]^{1/2} \tag{7}
\]

where \( k = n - (a + b + c) \) and \( a, b, \) and \( c \) are integers. The sum \( a + b + c = l \) is usually referred to as \( s, p, \) \( d, \) etc., even though they generally contain components of lower angular momentum.

The definition of the two Gaussians-type functions is based on the polar spherical coordinates and Cartesian coordinates. The Gaussian function in polar spherical coordinates is similar to eq. (3).

\[
\phi_{S_{\ell m}}^G(\xi; r, \theta, \phi) = R_\xi^G(\alpha; r)Y_\ell^m(\theta, \phi). \tag{8}
\]

The difference is the radial function, which is taken to be

\[
R_\xi^G(\alpha; r) = N_\ell^G(\alpha)r^{\ell+1}\exp(-\alpha r^2) \tag{9}
\]

with

\[
N_\ell^G(\alpha) = \left(\frac{2^{4\ell+3}\alpha^{2\ell+1}}{(2\ell-1)!!\pi^{1/4}}\right)^{1/2} \tag{10}
\]

The Cartesian Gaussian functions are also similar to eq. (6) and can be written as

\[
\phi_{S_{\ell m}}^G(\alpha; x, y, z) = N_{S_{\ell m}}^G(\alpha)x^ay^bz^c\exp(-\alpha r^2) \tag{11}
\]

with

\[
N_{S_{\ell m}}^G(\alpha) = \left[\frac{2^{4\ell+3}\alpha^{2\ell+1}}{(2\ell-1)!!(2a - 1)!(2b - 1)!(2c - 1)!!\pi^{1/4}}\right]^{1/2} \tag{12}
\]

The rigorous correlation between Slater and Gaussian functions can be carried out through the general transform derived by Wright, and given by

\[
r^{\ell+1}\exp(-\xi r) = \frac{1}{2^\ell\sqrt{\pi}}\int_0^\infty \alpha^{-(\ell+1/2)}H_\ell\left(\frac{\xi}{\sqrt{\alpha}}\right) \times \exp\left(-\frac{\xi^2}{4\alpha}\right)\exp(-\alpha r^2)\,da \tag{13}
\]

where \( H_\ell(x) \) is a Hermite polynomial. Equation (13) can be substituted into eqs. (4) and (6) yielding two new definitions of Slater functions as

\[
R_\xi^S(\xi; r) = \frac{N_\ell^S(\xi)}{2^\ell\sqrt{\pi}}\int_0^\infty \alpha^{-(\ell+1/2)}H_\ell \ 	imes \left(\frac{\xi}{\sqrt{\alpha}}\right)\exp\left(-\frac{\xi^2}{4\alpha}\right)\exp(-\alpha r^2)\,da \tag{14}
\]

or

\[
\phi_{S_{\ell m}}^G(\alpha; x, y, z) = \frac{N_{S_{\ell m}}^G(\xi)x^ay^bz^c}{2^\ell\sqrt{\pi}}\int_0^\infty \alpha^{-(\ell+1/2)}H_\ell \ 	imes \left(\frac{\xi}{\sqrt{\alpha}}\right)\exp\left(-\frac{\xi^2}{4\alpha}\right)\exp(-\alpha r^2)\,da \tag{15}
\]

Suitable substitutions of Gaussian functions [eqs. (9) or (11)] into eq. (14) and eq. (15), provide the Laplace transforms as

\[
\phi_{S_{\ell m}}^G(\xi; x, y, z) = \int_0^\infty f(\alpha, \xi; a, b, c, k)\phi_{S_{\ell m}}^G(\alpha; x, y, z)\,\frac{da}{\alpha} \tag{16}
\]

where
Expansions of Slater-Type Atomic Orbitals

\begin{align}
    f(\alpha, \xi; a, b, c, k) &= \frac{N_{\text{h}}^{\text{H}}(\alpha)}{N_{\text{h}}^{\text{H}}(a)} \frac{\alpha^{-1(1/2)}}{2^3 \sqrt{\pi}} H_i\left(\frac{\xi}{2 \sqrt{\alpha}}\right) \exp\left(-\frac{\xi^2}{4\alpha}\right) \\
\end{align}

and

\begin{align}
    R_{\text{n}}(\xi; r) &= \int_0^\infty f(\alpha, \xi; n) R_{\text{n}}(\alpha; r) \frac{d\alpha}{\alpha} \\
\end{align}

For the particular case of \( n = 1 \), eq. (13) can be simplified providing a transform for the exponential function similar to that obtained by Kikuchi [eq. (1)]. In this case, substituting this simpler integral transform into eq. (4) and using the Gaussian function from eq. (9), we obtain a third definition for a STO

\begin{align}
    R_{\text{n}}(\xi; r) &= \int_0^\infty f(\alpha, \xi; n) R_{\text{n}}(\alpha; r) \frac{d\alpha}{\alpha} \\
\end{align}

where the weight function \( f(\alpha, \xi, r) \) is described as

\begin{align}
    f(\alpha, \xi; n) &= \frac{N_{\text{h}}^{\text{H}}(\alpha)}{N_{\text{h}}^{\text{H}}(n)} \frac{\alpha^{-1(1/2)}}{2^3 \sqrt{\pi}} H_i\left(\frac{\xi}{2 \sqrt{\alpha}}\right) \exp\left(-\frac{\xi^2}{4\alpha}\right). \\
\end{align}

The three integrals present particular characteristics. The first case [eq. (16)] can be used to expand STO functions in terms of Cartesian Gaussian functions presenting the same symmetry. The second [eq. (18)] and third [eq. (20)] transforms act specifically upon the radial functions. Equation (18) provides discrete expansions of any STO radial function from the 1s Gaussian function. Equation (20) yields expansions in terms of radial Gaussian functions with the same principal quantum number \( n \) of the STO functions.

### The STO-NG Contraction

Equations (16), (18), and (20) are exact representations of STO in terms of Gaussian functions. A more manageable form can be obtained by applying a suitable numerical quadrature scheme in eqs. (16), (18), and (20), yielding expressions such as

\begin{align}
    \phi^\text{H}(\xi; r) &= \sum_{\mu=1}^N \omega_{\mu} f(\xi, \alpha_{\mu}) \phi^\text{H}(\alpha_{\mu}; r) \\
\end{align}

where \( \omega_{\mu} \) and \( \alpha_{\mu} \) are characteristic of the numerical integration. A comparison of eq. (22) with the conventional expansion of the Slater functions as linear combination of Gaussians (STO-NG) shows that the coefficients \( c_{\mu} \) are related to the discretized weight function by

\begin{align}
    c_{\mu} &= \omega_{\mu} f(\xi, \alpha_{\mu}). \\
\end{align}

The methods discussed in the literature to develop STO-NG basis sets, determine \( c_{\mu} \) and \( \alpha_{\mu} \) in the least square sense by minimizing the deviation \( V(\xi, \alpha) \) represented by

\begin{align}
    V(\xi, \alpha; r) &= \int_0^\infty [\phi^\text{H}(\xi; r) - \sum_{\mu=1}^N c_{\mu} \phi^\text{H}(\alpha_{\mu}; r)]^2 d\tau. \\
\end{align}

As pointed out by Silver, eq. (22) shows that none of the parameters of the discretization is unknown when integral transforms are used. The quadrature method and the precise definition of the weight functions by eqs. (17), (19), and (21) provide sufficient information to determine both sets of parameters \( c_{\mu} \) [eq. (24)] and \( \alpha_{\mu} \).

The range of the Laplace transform suggests the use of Gauss–Laguerre or Gauss–Hermite methods. However, a graphical analysis of the weight functions obtained from eqs. (17), (19), and (21) shows that the significant interval for the numerical integration can be drastically reduced. To better visualize the weight functions, a change of the coordinate system is required. The integral transforms [eqs. (16), (18), and (20)] are then written as

\begin{align}
    \phi^\text{H}(\xi; r) &= \int_{-\infty}^{\infty} f(\alpha, \xi) \phi^\text{H}(\alpha; r) d\ln \alpha, \\
\end{align}

where the space of the exponents is now spanned from \(-\infty \to \infty\).

Figure 1 shows some of the weight functions obtained from eqs. (17), (19), and (21) vs. \ln \alpha with the Slater parameter \( \xi \) set to unity. Some important aspects can be obtained from Figure 1. The first one is the fact that the weight functions present a smooth behavior vanishing at the boundaries of the \( \alpha \) space. A second one is that the significant outermost (lower \( \alpha \) or \( \ln \alpha < 0 \)) and innermost (greater \( \alpha \) or \( \ln \alpha > 0 \)) range of the exponents is apparently well defined. Although the lowest values of \( \alpha \) can be satisfactorily determined, numerical tests show that the greatest values require caution.

Based on the smaller effective limits of integration for eqs. (16), (18), and (20), three different procedures were used to discretize the defined integral transforms: (1) a Gauss–Legendre quadrature,\(^{19}\) (2) an even-tempered geometric set of exponents, and (3) a modified even-tempered geometric set. Gauss–Legendre is a well-known method, and suitable description can be found in the literature.\(^{19}\) The even-tempered set of exponents is based on the geometric set

\begin{align}
    \alpha_{\mu} = ab^{\mu-1}, \quad \mu = 1, \ldots, N, \\
\end{align}
where $N_i$ is the number of primitive functions, and the parameters $a$ and $b$ are optimized to minimize eq. (25). The use of this option is based on the successful and widespread even-tempered basis set developed by Raffenetti and Feller and Ruedenberg. Inspection of the tendency of the exponents of STO-NG optimized by Huizenga also suggests that this set can represent the space spanned by the exponents. An important characteristic of the even-tempered sequence is that the exponents are equally distributed in $\ln$.

To provide a better fitting of the exponents and evaluate the adequacy of the even-tempered sequence, a more flexible set was also examined. The third discretization considers that

$$\ln \alpha_i = \sum_{i=1}^{4} d_i (\mu - 1)^{i-1}, \mu = 1, \ldots, N,$$  \hspace{1cm} (28)

where the parameters $d_i$ were optimized in the least square sense [minimization of eq. (25)].

All the optimizations were carried out with the simplex method of Nelder and Mead. The computational package from ref. 19 was used to search for the best values of all the variables through the minimum of $V(\xi, \alpha, \mathbf{r})$ [eq. (25)]. The vertices of the starting simplex were fixed as 0.05 or 0.10 times the initial value of the parameters. Initial calculations indicated that a value between $10^{-7}$ and $10^{-8}$ should be used as tolerance in the least square function for the simplex procedure.

Results and Discussion

The traditional methods do not take into account the explicit STO integral transforms and consider that coefficients and exponents [eq. (23)] should be optimized to minimize the least square function. To evaluate the accuracy of eqs. (27), (28), and Gauss-Legendre quadratures, the same procedures were used, but constraining the exponents to the three discretization techniques. The coefficients were obtained from the minimization of the least-square function [eq. (25)]. The results are compared with those obtained with the fully optimized exponents. Table 1 shows the least-square deviation where radial Gaussian functions fit some STO functions. Equation (28) provides the best fit of the exponents in the least-square sense. This behavior is due to the larger number of optimized parameters in comparison with the other fitting functions. Despite the accuracy of eq. (28) extrapolation or inclusion of diffuse and inner functions is not as simple as for eq. (27). The results calculated with eq. (27) are reasonably accurate, and the mathematical structure of the basis set shows that it can be expanded and easily modified due to its dependence of only two optimized parameters. Gauss-Legendre quadrature provides the least accurate mesh, although the limits of integration have been optimized. Table 1 also shows that any of the three discretization methods converge to the exact fitting for large number of Gaussian functions.

The degree of accuracy of each discretization method can be understood observing the behavior of the exponents. Figure 2 shows the set exponents in a logarithmic scale for the STO-6G basis set obtained by the methods discussed in Table 1. The region of low exponents $[\ln(\alpha) < 0]$ is very similar for any of the discretization methods. The most significant difference is found in the innermost exponents $[\ln(\alpha) > 0]$. The basis set with lowest least square deviation is the one presenting the largest exponent and vice versa. Similarly, the optimized basis set with respect to the energy indicates that the fully optimized exponents in an STO-NG tend to concentrate primitives in the region near the center of the Slater function. The order of accuracy of the discretization is clearly dependent of the flexibility with which Gaussian functions can be included in the neighborhood of the center of the Slater function. Fully optimized basis can provide a reasonable description of the innermost and outermost region while the other methods tend to constrain the flexibility of the primitive set not allowing for an appropriate description of the region with large exponents.

To evaluate the usefulness of the analytical weight functions presented in eqs. (17), (19), and (21), a final test was carried out eliminating the step where the linear combination coefficients were adjusted to minimize the least-square function. The exponents of each discretization method were again optimized satisfying the specific constraints of each method and the coefficients were determined from eq. (24) in association with the respective analytical weight function [eqs. (17), (19), and (21)]. Table 2 shows the least-square deviation for the same tests presented in Table 1. Comparison of results from both tables shows that the rigid structure of the analytical weight functions introduce a significant error. Small deviations are 10 times larger than those obtained by the fully optimized exponents and coefficients. The large magnitude of the least-square errors are obviously associated with the numerical
treatment of the discretized weight functions. The tendency in the degree of accuracy reached by the three methods is the same observed by fully optimized parameters. In other words, the modified even-tempered set yields better fitting functions, whereas the Gauss–Legendre quadrature yields the less effective one. An interesting behavior is observed for the STO-4G expansion, which shows smaller deviations for the Gauss–Legendre quadrature than the even-tempered set when the linear coefficients are obtained from the analytical expressions. Apparently, the even-tempered meshes are more effective than the Gauss–Legendre exponents for sets containing more than four Gaussians.

Nevertheless, calculations of the radial distribution functions employing any of the discretized analytical weight functions present results as adequate as the fully optimized bases. As expected, the differences between the discretized analytical functions and the optimized one tend to diminish when the number of primitives tends to infinity. Applications of STO-6G obtained by the methods described above in the calculation of molecular properties presented good agreement among the discretization techniques.

**Conclusion**

The difficulties to obtain analytical solutions for multicenter integrals involving Slater-type functions (STO) inspired the development of the STO-NG basis sets. The literature has usually presented STO-NG from fully optimized exponents and coefficients in the least-square sense. In this article we show that there are at least three different representations of the STO-NG through the

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**Table 1. Least-Square Deviation for Four Different Discretization Methods Optimizing the Linear Combination Coefficients.**

<table>
<thead>
<tr>
<th>Gaussian expansion</th>
<th>STO-4G</th>
<th>STO-6G</th>
<th>STO-8G</th>
<th>STO-10G</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_e^G \leftarrow R_n^G$</td>
<td>$4.3762 \times 10^{-5}$</td>
<td>$1.387 \times 10^{-6}$</td>
<td>$5.4111 \times 10^{-9}$</td>
<td>$4.3721 \times 10^{-9}$</td>
</tr>
<tr>
<td>$R_i^G \leftarrow R_1^G$</td>
<td>$2.6971 \times 10^{-5}$</td>
<td>$3.2090 \times 10^{-7}$</td>
<td>$1.2279 \times 10^{-8}$</td>
<td>$&lt;10^{-9}$</td>
</tr>
<tr>
<td>$R_o^G \leftarrow R_2^G$</td>
<td>$1.7254 \times 10^{-6}$</td>
<td>$1.2596 \times 10^{-7}$</td>
<td>$2.5127 \times 10^{-9}$</td>
<td>$&lt;10^{-9}$</td>
</tr>
<tr>
<td>$R_p^G \leftarrow R_3^G$</td>
<td>$2.9039 \times 10^{-5}$</td>
<td>$5.6027 \times 10^{-7}$</td>
<td>$1.7645 \times 10^{-8}$</td>
<td>$&lt;10^{-9}$</td>
</tr>
<tr>
<td>$R_n^G \leftarrow R_4^G$</td>
<td>$2.1116 \times 10^{-5}$</td>
<td>$2.8993 \times 10^{-7}$</td>
<td>$9.4432 \times 10^{-9}$</td>
<td>$&lt;10^{-9}$</td>
</tr>
<tr>
<td>Fully optimized exponents</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$R_e^G \leftarrow R_1^G$</td>
<td>$2.3184 \times 10^{-4}$</td>
<td>$3.1867 \times 10^{-5}$</td>
<td>$2.4439 \times 10^{-6}$</td>
<td>$3.1761 \times 10^{-7}$</td>
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<tr>
<td>$R_i^G \leftarrow R_1^G$</td>
<td>$1.7015 \times 10^{-4}$</td>
<td>$5.2183 \times 10^{-5}$</td>
<td>$4.0857 \times 10^{-6}$</td>
<td>$3.2506 \times 10^{-7}$</td>
</tr>
<tr>
<td>$R_o^G \leftarrow R_1^G$</td>
<td>$9.4709 \times 10^{-5}$</td>
<td>$1.3684 \times 10^{-5}$</td>
<td>$5.9620 \times 10^{-7}$</td>
<td>$1.6476 \times 10^{-8}$</td>
</tr>
<tr>
<td>$R_p^G \leftarrow R_2^G$</td>
<td>$2.4997 \times 10^{-4}$</td>
<td>$1.9825 \times 10^{-5}$</td>
<td>$1.2444 \times 10^{-6}$</td>
<td>$1.8833 \times 10^{-7}$</td>
</tr>
<tr>
<td>$R_n^G \leftarrow R_3^G$</td>
<td>$2.6853 \times 10^{-4}$</td>
<td>$1.3379 \times 10^{-5}$</td>
<td>$7.4403 \times 10^{-7}$</td>
<td>$1.2749 \times 10^{-7}$</td>
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<td>Gauss-Legendre quadrature</td>
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<td>$R_e^G \leftarrow R_1^G$</td>
<td>$1.2894 \times 10^{-4}$</td>
<td>$8.1992 \times 10^{-6}$</td>
<td>$6.9016 \times 10^{-7}$</td>
<td>$7.3168 \times 10^{-8}$</td>
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<td>$2.1884 \times 10^{-6}$</td>
<td>$1.9161 \times 10^{-7}$</td>
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<tr>
<td>$R_o^G \leftarrow R_1^G$</td>
<td>$1.1633 \times 10^{-4}$</td>
<td>$3.5213 \times 10^{-6}$</td>
<td>$1.2707 \times 10^{-7}$</td>
<td>$5.7436 \times 10^{-9}$</td>
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<td>$3.9863 \times 10^{-6}$</td>
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<td>$2.3793 \times 10^{-8}$</td>
</tr>
<tr>
<td>$R_n^G \leftarrow R_3^G$</td>
<td>$7.0327 \times 10^{-5}$</td>
<td>$2.2684 \times 10^{-5}$</td>
<td>$1.1820 \times 10^{-7}$</td>
<td>$1.4164 \times 10^{-8}$</td>
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<tr>
<td>Even-tempered set [eq. (27)]</td>
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<td></td>
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<td>$R_e^G \leftarrow R_1^G$</td>
<td>$4.3762 \times 10^{-5}$</td>
<td>$1.3975 \times 10^{-6}$</td>
<td>$6.6965 \times 10^{-8}$</td>
<td>$5.8872 \times 10^{-9}$</td>
</tr>
<tr>
<td>$R_i^G \leftarrow R_1^G$</td>
<td>$6.6380 \times 10^{-5}$</td>
<td>$1.8177 \times 10^{-7}$</td>
<td>$7.7938 \times 10^{-8}$</td>
<td>$&lt;10^{-9}$</td>
</tr>
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<td>$R_o^G \leftarrow R_1^G$</td>
<td>$1.9078 \times 10^{-5}$</td>
<td>$2.4020 \times 10^{-7}$</td>
<td>$4.0275 \times 10^{-9}$</td>
<td>$&lt;10^{-9}$</td>
</tr>
<tr>
<td>$R_p^G \leftarrow R_2^G$</td>
<td>$2.9039 \times 10^{-5}$</td>
<td>$6.5324 \times 10^{-7}$</td>
<td>$2.2170 \times 10^{-9}$</td>
<td>$2.3865 \times 10^{-9}$</td>
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<td>$R_n^G \leftarrow R_3^G$</td>
<td>$2.1116 \times 10^{-5}$</td>
<td>$3.5255 \times 10^{-7}$</td>
<td>$1.1373 \times 10^{-8}$</td>
<td>$1.2962 \times 10^{-9}$</td>
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<tr>
<td>Modified even-tempered set [eq. (28)]</td>
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</table>
use of integral transform. Considering this possibility, the development of STO-NG is a matter of appropriate numerical integration. Four different discretization techniques were tested regarding the determination of the set of exponents and coefficients: (1) fully optimized systems, (2) Gauss–Legendre quadrature, (3) even-tempered exponents, and (4) modified even-tempered exponents. Items (2), (3), and (4) were compared with item (1), and showed expected results. A sufficient large number of Gaussian primitives provide equivalent results with any of the methods considered. Smaller contraction schemes are strongly dependent of the degree of flexibility of the discretization method. Method (4) presents the best results when compared with the fully optimized basis set. Finally, discretized analytical weight functions can be used to model STO-NG presenting asymptotic behavior compatible with fully optimized STO-NG.

References