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ORIGINAL PAPER

Molecular integrals for slater type orbitals using coulomb sturmians

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Abstract The use of Slater type orbitals in molecular calculations is hindered by the slowness of integral evaluation. In the present paper, we introduce a method for overcoming this problem by expanding STO's in terms of Coulomb Sturmians, for which the problem of evaluating molecular integrals rapidly has been satisfactorily solved using methods based on the theory of hyperspherical harmonics.

Keywords Slater type orbitals · STO molecular integrals · Coulomb Sturmians · Hyperspherical harmonics · Electronic structure theory · Molecular Coulomb Sturmians

1 Introduction

In recent years, much attention has been focused on the problem of evaluating molecular integrals with exponential type orbitals. This is because ETOs are intrinsically better suited to the synthesis of electronic wave functions than Gaussians, which are currently used in most quantum chemistry calculations. In fact, the only reason why Gaussians have until now dominated computational quantum chemistry is the ease with which the required many-center integrals can be calculated. However, rapid methods for calculating these integrals for ETOs are being developed, making way for a new wave in quantum chemistry.

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A general and simple form of the ETO is the Slater type orbital [1], which forms the basis for a wide variety of quantum chemical calculations. Before explaining the approach of the present paper, we would like to mention some of the important historical and recent development in STO integral evaluation. Pioneering work was done by Harris et al. [2]. While most quantum chemistry software is based on Gaussian orbitals, a number of software packages have been developed for quantum chemistry calculations using STOs, the most prominent being the STOP package [3], developed by Philip Hoggan et al., SMILES, developed by Fernandez Rico et al. [4] at Universidad Autónoma de Madrid, and ADF [5], by Baerends and Snijders in Amsterdam.

Hoggan [6] has recently been working with applications of the resolution of the Coulomb operator, a technique first introduced by Gill and his associates [7,8]. The results for solving the difficult molecular integrals by this method seem very promising. Levin and Sidi [9,10] have contributed importantly to Fourier transform methods, by developing methods for the accurate evaluation of highly oscillatory integrals involving spherical Bessel functions.

In the present paper we build on our previous work on Coulomb Sturmians and their Fourier transforms. In a remarkable early paper, V. Fock introduced a projection of momentum space onto the surface of the 4-dimensional unit sphere, and showed that the Fourier transformed Coulomb Sturmians are very simply related to the hyperspherical harmonics on this sphere. In our previous work [11], we have shown that molecular integrals for Coulomb Sturmians can be rapidly evaluated using the theory of hyperspherical harmonics.

In the present paper, we begin the work of extending this method to molecular integrals for Slater type orbitals by expanding them in terms of Coulomb Sturmians. Here, we only do the molecular overlap integrals, but all the remaining integrals follow in a similar way, and will be described in a later paper. In order to avoid overloading the reader with unfamiliar concepts, we do not describe in detail the methods employed for evaluating molecular integrals using the hyperspherical method, but we refer to our previous books and papers on the subject [12–20].

2 Definition of Coulomb Sturmians

Coulomb Sturmians are solutions to the one-electron wave equation [21,15,22–24]:

$$\left[-\frac{1}{2}\nabla^2 - \frac{nk}{r} + \frac{1}{2}k^2\right]\chi_{nlm}(\mathbf{x}) = 0 \tag{1}$$

The reader will recognize that this is just the wave equation obeyed by the familiar hydrogenlike orbitals, except that Z/n has been replaced by the constant k. Thus, if we start with a set of hydrogenlike orbitals and replace Z/n everywhere by the constant k, we will have generated a set of Coulomb Sturmians. They have the form

$$\chi_{nlm}(\mathbf{x}) = R_{nl}(r)Y_{lm}(\theta, \phi) \tag{2}$$

where the radial functions are given by

$$R_{nl}(r) = \mathcal{N}_{nl}(2kr)^l e^{-kr} F(l+1-n|2l+2|2kr) \tag{3}$$

with

$$\mathcal{N}_{nl} = \frac{2k^{3/2}}{(2l+1)!}\sqrt{\frac{(l+n)!}{n(n-l-1)!}} \tag{4}$$

and

$$F(a|b|x) \equiv \sum_{j=0}^{\infty} \frac{a^{\overline{j}}}{j!b^{\overline{j}}}x^j = 1 + \frac{a}{b}x + \frac{a(a+1)}{2b(b+1)}x^2 + \cdots \tag{5}$$

is the confluent hypergeometric function of the first kind. Notice that the series in (5) only sums up to $n-l-1$ in our case. The first few Coulomb Sturmian radial functions are

$$\begin{aligned} R_{1,0}(r) &= 2k^{3/2}e^{-kr} \\ R_{2,0}(r) &= 2k^{3/2}(1-kr)e^{-kr} \\ R_{2,1}(r) &= \frac{2k^{3/2}}{\sqrt{3}}\, kr\; e^{-kr} \end{aligned} \tag{6}$$

These become the familiar hydrogenlike orbitals if k is replaced by Z/n, where Z is the nuclear charge and n is the principal quantum number. It can be shown that the Coulomb Sturmians obey a set of potential-weighted orthonormality relations of the form:

$$\int d^3x\; \chi^*_{n'l'm'}(\mathbf{x})\frac{n}{kr}\chi_{nlm}(\mathbf{x}) = \delta_{n'n}\delta_{l'l}\delta_{m'm} \tag{7}$$

A Coulomb Sturmian basis set is isoenergetic. All the members of the set correspond to the energy

$$\epsilon = -\frac{1}{2}k^2 \tag{8}$$

The potential in the wave equation obeyed by the members of the basis set is especially weighted so that all the basis functions will correspond to this energy. We can rewrite Eq. (1) in the form

$$\left[-\frac{1}{2}\nabla^2 - \beta_n\frac{Z}{r} + \frac{1}{2}k^2\right]\chi_{nlm}(\mathbf{x}) = 0 \tag{9}$$

where the weighting factor $\beta_n = nk/Z$ is especially chosen in such a way as to make all the members of the basis set correspond to the energy $-k^2/2$.

3 Definition of STO's

Slater-Type Orbitals have a radial part of the form [25]:

$$\mathbb{R}_{n,\zeta}(r) = N_{n,\zeta}\ r^{n-1}e^{-\zeta r} \tag{10}$$

where $N_{n,\zeta}$ is a normalizing constant:

$$N_{n,\zeta} = (2\zeta)^n\sqrt{\frac{2\zeta}{(2n)!}} = \frac{(2\zeta)^{n+\frac{1}{2}}}{\sqrt{(2n)!}} \tag{11}$$

It is common to use spherical harmonics as the angular parts of STO's. Thus we can write:

$$\Phi_{n,\zeta,l,m}(\mathbf{x}) = \mathbb{R}_{n\zeta}(r)Y_{l,m}(\hat{\mathbf{x}}) \equiv \Phi_{\bar{\mu}}(\mathbf{x}) \tag{12}$$

where

$$\bar{\mu} \equiv (n,\zeta,l,m) \tag{13}$$

(Although STO's are often denoted by the symbol χ, we denote them here by Φ in order to distinguish them from Coulomb Sturmians, which we have consistently called χ in our books and papers.)

4 Expansion of an arbitrary function of $s = kr$ in terms of Coulomb Sturmian radial functions

Why is it not trivial to expand STO's in terms of Coulomb Sturmians? Why not just let $k = \zeta$? The reason is that for the hyperspherical method to work, k must be the same for all the Sturmian orbitals involved in the integral. But in general, the molecular integrals that we wish to evaluate involve several values of ζ on different centers. Thus, in general, k will not be equal to ζ, and therefore the expansion is not a trivial one.

Let us first discuss how to expand an arbitrary function of $s = kr$ in terms of Coulomb Sturmian radial functions. It follows from Eqs. (3)–(6) that if we divide the radial parts of Coulomb Sturmians by a factor of $k^{\frac{3}{2}}$ we will obtain a function

$$\tilde{R}_{n,l}(s) \equiv \frac{1}{k^{\frac{3}{2}}}R_{n,l}(r) \tag{14}$$

which is a pure function of $s = kr$. For example,

$$\begin{aligned}\tilde{R}_{1,0}(s) &= 2e^{-s}\\ \tilde{R}_{2,0}(s) &= 2(1-s)e^{-s}\\ \tilde{R}_{2,1}(s) &= \frac{2}{\sqrt{3}}\ s\ e^{-s}\end{aligned} \tag{15}$$

and so on. From the potential-weighted orthonormality relation (7), it then follows that

$$\int_0^\infty ds\ s\ \tilde{R}_{n',l}(s)\tilde{R}_{n,l}(s) = \frac{1}{n}\delta_{n'n} \tag{16}$$

Now suppose that we wish to expand a function $f(s)$ in a series of the form:

$$f(s) = \sum_{n>l} \tilde{R}_{n,l}(s)\ c_n \tag{17}$$

In Eqs. (18)–(29), the symbol c_n retains this meaning: It is the coefficient corresponding to n in the expansion of some function of s in terms of Coulomb Sturmian radial functions. But the functions being expanded differ in the various equations. Making use of the orthonormality relation (7), we obtain

$$\begin{aligned} n\int_0^\infty ds\ s\ \tilde{R}_{n,l}(s)f(s) &= \sum_{n'>l}\int_0^\infty ds\ s\ \tilde{R}_{n',l}(s)\tilde{R}_{n,l}(s)\ c_{n'} \\ &= \sum_{n'>l}\delta_{n',n}c_{n'} = c_n \end{aligned} \tag{18}$$

Thus, for example, in the series

$$e^{-\rho s} = \sum_n \tilde{R}_{n,0}(s)\ c_n \tag{19}$$

the coefficients c_n are given by

$$c_n = n\int_0^\infty ds\ s\ \tilde{R}_{n,0}(s)\ e^{-\rho s} \tag{20}$$

We can evaluate this integral exactly, for example using Mathematica [26], and the surprisingly simple result is

$$c_n = n\int_0^\infty ds\ s\ \tilde{R}_{n,0}(s)\ e^{-\rho s} = 2n\,\frac{(\rho-1)^{n-1}}{(\rho+1)^{n+1}} \tag{21}$$

From (18) and (21), it follows that the coefficients c_n in the series

$$s^j\ e^{-\rho s} = \sum_{n>0} \tilde{R}_{n,0}(s)\ c_n \tag{22}$$

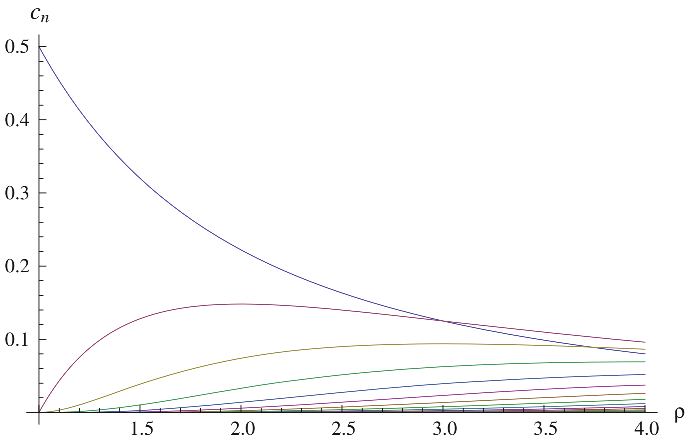

Fig. 1 The coefficients c_n of Eq. (19) are plotted as functions of the parameter ρ in the range $1 < \rho < 4$. When $\rho = 1$, only c_1 is nonzero. As ρ increases above 1, more and more coefficients contribute significantly to the series in Eq. (19)

are given by

$$c_n = n\left(-\frac{\partial}{\partial\rho}\right)^j \int_0^\infty ds\; s\; \tilde{R}_{n,0}(s)\; e^{-\rho s} = 2n\left(-\frac{\partial}{\partial\rho}\right)^j \frac{(\rho-1)^{n-1}}{(\rho+1)^{n+1}} \tag{23}$$

The completeness properties of the Coulomb Sturmians are such that the series defined by Eqs. (22) and (23) are exact for the full, infinite sum, regardless of the non-negative integer value of j and of $\rho > 0$. Our pilot calculations show that when $1/4 < \rho < 4$, and for moderate values of j, convergence is rapid (see Figs. 1 and 2). Convergence of the series becomes progressively less rapid as j increases, and for values of ρ outside the range just mentioned.

If we make an expansion in terms of Coulomb Sturmian radial functions corresponding to $l = 1$, i.e. an expansion of the form

$$se^{-\rho s} = \sum_{n>1} \tilde{R}_{n,1}(s)\; c_n \tag{24}$$

we again obtain a simple result for the expansion coefficients:

$$c_n = n\int_0^\infty ds\; s\; \tilde{R}_{n,1}(s)\; se^{-\rho s} = 4n\sqrt{(n-1)(n+1)}\; \frac{(\rho-1)^{n-2}}{(\rho+1)^{n+2}} \tag{25}$$

and we can again write down equations analogous to (22) and (23):

$$s^{j+1}\; e^{-\rho s} = \sum_{n>1} \tilde{R}_{n,1}(s)\; c_n \tag{26}$$

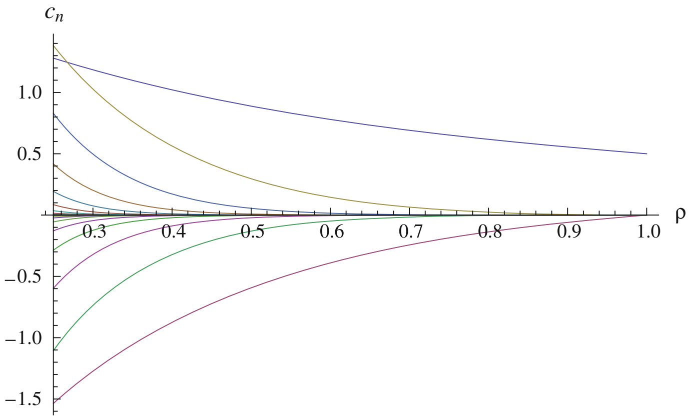

Fig. 2 This figure is the same as Fig. 1, except that the coefficients c_n are shown in the range $1/4 < \rho < 1$. The series in (19) converges for all real and positive values of ρ. The rate of convergence can be judged in the two figures by the number of coefficients markedly different from zero

$$\begin{aligned} c_n &= n\left(-\frac{\partial}{\partial\rho}\right)^j \int_0^\infty ds\ s\ \tilde{R}_{n,1}(s)\ se^{-\rho s} \\ &= 4n\sqrt{(n-1)(n+1)}\left(-\frac{\partial}{\partial\rho}\right)^j \frac{(\rho-1)^{n-2}}{(\rho+1)^{n+2}} \end{aligned} \tag{27}$$

Similarly simple and rapidly-convergent series are obtained when we expand in terms of $\tilde{R}_{n,l}(s)$ for higher values of l. In general we find that the expansion

$$s^{j+l}\ e^{-\rho s} = \sum_{n>l} \tilde{R}_{n,l}(s)\ c_n \tag{28}$$

leads to expansion coefficients of the form

$$c_n = n\left(-\frac{\partial}{\partial\rho}\right)^j \int_0^\infty ds\ s\ \tilde{R}_{n,l}(s)\ s^l e^{-\rho s} = a_{n,l}\left(-\frac{\partial}{\partial\rho}\right)^j \frac{(\rho-1)^{n-l-1}}{(\rho+1)^{n+l+1}} \tag{29}$$

Table 1 shows the first few coefficients $a_{n,l}$ for $l = 2, 3, 4$ and $n = 3, 4, \ldots, 10$. $a_{n,0} = 2n$, while for $a_{n,1} = 4n\sqrt{(n-1)(n+1)}$. Higher coefficients are easy to obtain, since the integral in Eq. (29) can readily be evaluated by Mathematica. It seems that a closed form formula exists, but we have not yet found it.

5 Evaluation of molecular integrals

This expansion allows us to apply to STO's our previously-developed methods for the evaluation of molecular integrals by means of the theory of hyperspherical harmonics.

Table 1 The coefficients $a_{n,l}$ of Eq. (29). $a_{n,0} = 2n$, while $a_{n,1} = 4n\sqrt{(n-1)(n+1)}$

n	$l = 2$	$l = 3$	$l = 4$
3	$48\sqrt{10}$		
4	$192\sqrt{5}$	$384\sqrt{35}$	
5	$240\sqrt{14}$	$1{,}920\sqrt{14}$	$11{,}520\sqrt{14}$
6	$192\sqrt{70}$	$1{,}152\sqrt{210}$	$23{,}040\sqrt{42}$
7	$625\sqrt{15}$	$13{,}440\sqrt{6}$	$80{,}640\sqrt{22}$
8	$384\sqrt{105}$	$3{,}840\sqrt{231}$	$92{,}160\sqrt{77}$
9	$288\sqrt{385}$	$3{,}456\sqrt{770}$	$34{,}560\sqrt{2002}$
10	$960\sqrt{66}$	$1{,}920\sqrt{6,006}$	$161{,}280\sqrt{286}$

We can evaluate the coefficients C_{n,n_1} by writing the STO radial function on the form:

$$\begin{aligned}
\mathbb{R}_{n_1,\zeta_1}(r) &= N_{n_1,\zeta_1}\, r^{n_1-1} e^{-\zeta_1 r} \\
&= \frac{(2\zeta_1)^{n_1+\frac{1}{2}}}{\sqrt{(2n_1)!}}\, r^{n_1-1} e^{-\zeta_1 r} \\
&= \frac{(2\zeta_1)^{n_1+\frac{1}{2}}}{k^{n_1-1}\sqrt{(2n_1)!}}\, s^{n_1-1} e^{-\rho_1 s} \qquad s \equiv kr \qquad k \equiv \sqrt{\zeta_1\zeta_2} \\
&= k^{3/2}\frac{(2\rho_1)^{n_1+\frac{1}{2}}}{\sqrt{(2n_1)!}}\, s^{n_1-1} e^{-\rho_1 s} \qquad \rho_1 \equiv \frac{\zeta_1}{k} \equiv \sqrt{\frac{\zeta_1}{\zeta_2}}
\end{aligned} \tag{30}$$

When the STO radial function is expanded in terms of Coulomb Sturmian radial functions in a series of the form:

$$\begin{aligned}
\mathbb{R}_{n_1,\zeta_1}(r) &= k^{3/2}\sum_{n>l_1} \tilde{R}_{n,l_1}(s)\, C_{n,n_1}^{(l_1,\rho_1)} \qquad s \equiv kr \\
\mathbb{R}_{n_2,\zeta_2}(r) &= k^{3/2}\sum_{n>l_2} \tilde{R}_{n,l_2}(s)\, C_{n,n_2}^{(l_2,\rho_2)}
\end{aligned} \tag{31}$$

we can write the expansion as

$$\frac{(2\rho_1)^{n_1+\frac{1}{2}}}{\sqrt{(2n_1)!}}\, s^{n_1-1} e^{-\rho_1 s} = \sum_{n>l_1} \tilde{R}_{n,l_1}(s)\, C_{n,n_1}^{(l_1,\rho_1)} \tag{32}$$

Comparing this with Eqs. (28) and (29), we can see that we need to make the identification $j = n_1 - l_1 - 1$, and that

$$C_{n,n_1}^{(l_1,\rho_1)} = a_{n,l_1}\frac{(2\rho_1)^{n_1+\frac{1}{2}}}{\sqrt{(2n_1)!}}\left(-\frac{\partial}{\partial\rho_1}\right)^{n_1-l_1-1}\frac{(\rho_1-1)^{n-l_1-1}}{(\rho_1+1)^{n+l_1+1}} \qquad \rho_1 \equiv \frac{\zeta_1}{k} \equiv \sqrt{\frac{\zeta_1}{\zeta_2}} \tag{33}$$

and similarly,

$$C_{n,n_2}^{(l_2,\rho_2)} = a_{n,l_2}\frac{(2\rho_2)^{n_2+\frac{1}{2}}}{\sqrt{(2n_2)!}}\left(-\frac{\partial}{\partial\rho_2}\right)^{n_2-l_2-1}\frac{(\rho_2-1)^{n-l_2-1}}{(\rho_2+1)^{n+l_2+1}} \qquad \rho_2 \equiv \frac{\zeta_2}{k} \equiv \sqrt{\frac{\zeta_2}{\zeta_1}} \tag{34}$$

Equation (31) sums over infinitely many values of n, but in practice will be truncated and thus not an identity but an approximation. However, as shown in Figures 1 and 2, the convergence is rapid in the indicated range. The following table shows the L_2-error

$$||\mathbb{R}_{exact} - \mathbb{R}_{approx}|| = \left(\int_0^\infty (\mathbb{R}_{exact}(r) - \mathbb{R}_{approx}(r))^2\, dr\right)^{1/2} \tag{35}$$

for the synthesis of Slater 3d-orbitals by Eq. (31) as a function of ρ, using 30 Coulomb Sturmians in the expansion:

ρ_1	1	3/2	2	5/2	3	7/2	4
L_2-error	0	3.0×10^{-19}	1.5×10^{-12}	2.9×10^{-9}	2.9×10^{-7}	6.6×10^{-6}	6.3×10^{-5}

6 STO overlap integrals

From Eqs. (12) and (31) we have

$$\begin{aligned}\Phi_{\bar{\mu}_1}(\mathbf{x}-\mathbf{X}_1) &= \sum_{n>l_1}\chi_{n,l_1,m_1}(\mathbf{x}-\mathbf{X}_1)C_{n,n_1}^{(l_1,\zeta_1)}\\ \Phi_{\bar{\mu}_2}(\mathbf{x}-\mathbf{X}_2) &= \sum_{n>l_2}\chi_{n,l_2,m_2}(\mathbf{x}-\mathbf{X}_2)C_{n,n_2}^{(l_2,\zeta_2)}\end{aligned} \tag{36}$$

Therefore the STO overlap integral can be written as

$$\begin{aligned}&\int d^3x\ \Phi_{\bar{\mu}_1}^*(\mathbf{x}-\mathbf{X}_1)\Phi_{\bar{\mu}_2}(\mathbf{x}-\mathbf{X}_2)\\ &= \sum_{n'>l_1}\sum_{n>l_2} C_{n',n_1}^{(l_1,\rho_1)}C_{n,n_2}^{(l_2,\rho_2)}\int d^3x\ \chi_{n',l_1,m_1}^*(\mathbf{x}-\mathbf{X}_1)\chi_{n,l_2,m_2}(\mathbf{x}-\mathbf{X}_2)\end{aligned} \tag{37}$$

Since we are able to evaluate overlap integrals between Coulomb Sturmians rapidly, and in closed form, by using a method based on the theory of hyperspherical harmonics [11]–[17], this gives us a rapid and accurate method for evaluating STO overlap integrals. The Coulomb Sturmian overlap matrix $m(\mathbf{S})$ is precalculated, and is the same regardless of which Slater type orbitals enter the computation. The coefficients $C_{n',n}^{(l,\rho)}$

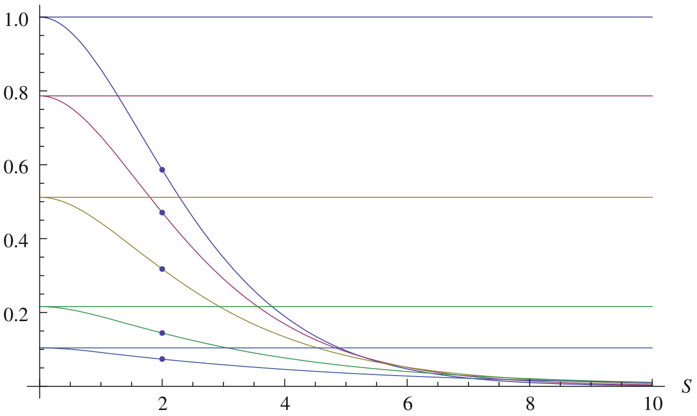

Fig. 3 Overlap integrals for STO 1s orbitals. The overlap integrals are shown as functions of the parameter $S = \sqrt{\zeta_1 \zeta_2}\,|\mathbf{X}_1 - \mathbf{X}_2|$. The *top curve* shows the case where $\zeta_1 = \zeta_2$, which is exact. The *next four curves* show the cases where $\sqrt{\zeta_1/\zeta_2}$ is $3/2$, 2, 3, and 4. The *dots* at $S = 2$ were calculated with three-dimensional numerical integrals. The numerical integrals were calculated with 8–10 significant digits, and agreed with the calculated curves up to that precision

are pre-evaluated and stored as functions of ρ; for a particular STO calculation, they are instantiated with the particular $\rho = \sqrt{\frac{\zeta_1}{\zeta_2}}$ required for the computation. Examples are shown in Figs. 3 and 4. This requires only evaluating a very small polynomial in ρ and one division per coefficient. Equation (37) can be written on the form of a matrix-vector product and a dot product

$$\mathbf{c}_{\mu_1} \cdot (\mathbf{M}\mathbf{c}_{\mu_2}) \tag{38}$$

Thus, computing all overlap integrals requires us to perform one small matrix-vector product for each STO basis function, and for each integral only the final dot-product is needed. Our current implementation is not yet optimized and ready for benchmarking, but we expect similar performance to the results presented in Ref. [11]. There, tens to few hundreds nanoseconds were required per multicentre electron repulsion integral on current consumer hardware, which is comparable to the efficiency of Gaussian type orbitals.

7 Discussion

In this paper we have presented a method for the evaluation of overlap integrals involving Slater-type orbitals. The method works extremely rapidly, with an accuracy of at least 8 significant figures, provided that the Slater exponents fall into the range

$$\frac{1}{4} < \rho < 4, \qquad \rho \equiv \sqrt{\frac{\zeta_1}{\zeta_2}} \tag{39}$$

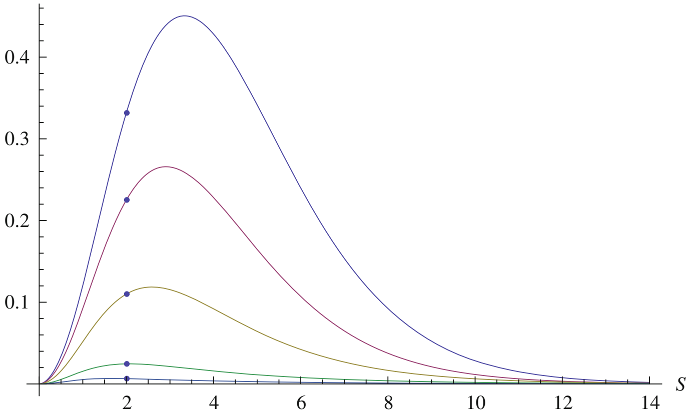

Fig. 4 STO overlap integrals between 1s and 3d orbitals (with $m = 0$) shown with the same parameters as in Fig. 3. The displacement is in the z-direction. As before, the overlap integrals are correct at least up to 8–10 digits, which is the number of significant digits in the numerically calculated integrals

or

$$\frac{1}{16} < \frac{\zeta_1}{\zeta_2} < 16 \tag{40}$$

The calculation of kinetic energy integrals and nuclear attraction integrals goes through in a closely analogous manner, as we plan to discuss in a future paper. Finally, we plan to show in a future article that interelectron repulsion integrals involving STO's can also be treated by expanding the STO's in terms of Coulomb Sturmians and afterwards making use of Fock's projection and the theory of hyperspherical harmonics to evaluate the 2-electron integrals.

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