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Two-center overlap integrals, three dimensional adaptive integration, and prolate ellipsoidal coordinates

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Abstract Numerical, adaptive algorithm evaluating the overlap integrals between the Numerical Type Orbitals (NTO) is presented. The described algorithm exploits the properties of the prolate ellipsoidal coordinates, which are the natural choice for two-center overlap integrals. The algorithm is designed for numerical atomic orbitals with the finite support. Since the cusp singularity of the atomic orbitals vanish in the prolate ellipsoidal coordinate system, the adaptive integration algorithm in $\mathbb{R}^3$ generates small number of subdivisions. The efficiency and reliability of the algorithm is demonstrated for the overlap integrals evaluated for the selected pairs of Slater Type Orbitals (STO).

Keywords Prolate ellipsoidal coordinates · Overlap integral · Numerical atomic orbital · Adaptive numerical integration

1 Introduction

The evaluation of the two-center overlap integrals is a longstanding problem. In the quantum chemistry, the overlap integrals are required if Linear Combination of Atomic Orbitals method is applied to Schroedinger or Kohn-Sham equation [1,2]. The required overlap integrals are evaluated between atomic orbitals defined as a product of the radial part and the spherical harmonic. Among the atomic orbitals the Gaussian Type Orbitals (GTO) are the most common, for which the overlap integrals are available analytically [3–5]. The Slater Type Orbitals (STO) have better chemical properties,

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however, the evaluation of the overlap integrals are more complicated [6–9]. The analytical expressions for the overlap integrals between Bessel Type Orbitals (BTO) are more concise [10–12], however BTO are rarely applied in the quantum mechanical calculations.

Recently, the researchers have focused their attention on the Numerical Type Orbitals (NTO), where the radial part need not be defined analytically [13–16]. The application of the sophisticated NTO can lead to the algorithms solving Kohn-Sham equation with linear cost, $\mathcal{O}(N)$, where N is the number of the atomic orbital [13,14,17,18]. Since the radial part of the atomic orbital is arbitrary, then, in order to evaluate the overlap integrals, new algorithms are required, which are based on the numerical integration.

Typically, the overlap integrals for NTO are evaluated based on the algorithm developed by Becke [19] and Delley [20] designed for multi-center function $h(\mathbf{r}) : \mathbb{R}^3 \mapsto \mathbb{R}$. First, the integrand $h(\mathbf{r})$ is decomposed into a sum of functions $h_i(\mathbf{r})$ related to centers (atoms):

$$h(\mathbf{r}) = \sum_i h_i(\mathbf{r}) \qquad h_i(\mathbf{r}) = w_i(\mathbf{r})h(\mathbf{r}) \tag{1}$$

The weight functions, $w_i(\mathbf{r}) : \mathbb{R}^3 \mapsto \mathbb{R}$, are required to fulfill two conditions for any $\mathbf{r} \in \mathbb{R}^3$:

$$w_i(\mathbf{r}) \geq 0 \qquad \text{and} \qquad \sum_i w_i(\mathbf{r}) = 1 \tag{2}$$

Moreover, it is required that:

- $w_i(\mathbf{r}) \approx 1$ near the ith center.
- $w_i(\mathbf{r}) \approx 0$ near the jth center for $j \neq i$.
- $w_i(\mathbf{r})$ should be smooth.

There were proposed many weight functions, which are discussed in [19–22]. The decomposition of many center integrand into a sum of the single center integrands, allows to apply the spherical coordinate system, where the singularity does not occur [23]. However, it was noticed that for the overlap integrals, the algorithm leads to the strong anisotropic single-centered components [24], which causes poor convergence of the numerical integration scheme.

In order to avoid the anisotropy caused by the weight function, we proposed the algorithm [25,26] based on the prolate ellipsoidal coordinates [27–30]. The usefulness of the prolate ellipsoidal coordinate system to evaluate the overlap integrals was proved in [31,32], where the analytical expressions of the overlap integral between STO were derived. In the previous two papers [25,26] we described the algorithm suitable to evaluate the overlap integrals between NTO with the finite support and the specific orientation of the coordinate system. In the present paper we describe the generalized algorithm. We assume that the atomic orbitals are defined in its own local coordinate system, which can be transformed one on each other by translation. This mutual orientation of the local coordinate systems is a typical situation in the molecular quantum calculations. Then, each of NTO is transformed to the prolate ellipsoidal coordinate systems, where the cusp singularity does not occur. Since the product of two NTO defined in the prolate coordinate system is a smooth function, the adaptive

integration procedure can be applied efficiently. The presented algorithm is valid for broad class of the atomic orbitals. It is particularly designed to the atomic orbitals with the finite support. Thus, it can be applied to the linearly scaling packages.

The outline of the paper is as follows. In Sect. 2 the properties of the prolate ellipsoidal coordinate system are reviewed. In Sect. 3 the definition of the overlap integral in the prolate ellipsoidal coordinate system is derived. Section 4 is devoted to the adaptive integration algorithm over the cuboid. In Sect. 5 the efficiency and accuracy of the described algorithm is validated for overlap integrals evaluated for selected Slater orbitals.

2 Prolate ellipsoidal coordinate system

The prolate ellipsoidal coordinate system, $\mathcal{E}$, is a two-center orthogonal coordinate systems [27–30]. The orthogonal surfaces of this coordinate system consist of the confocal ellipsoids and hyperboloids of revolution and half-planes. The position of a point in $\mathbb{R}^3$ space in $\mathcal{E}$ is defined by three coordinates (η, ξ, ϕ), where $\eta \in [0, \infty)$, $\xi \in [0, \pi]$ and $\phi \in [0, 2\pi)$. Let us introduce the cartesian coordinate system, $\mathcal{C}$, and locate two foci at $A = (0, 0, -a)$ and $B = (0, 0, a)$, where $a > 0$. Then, the surface of constant value η is the ellipsoid defined in $\mathcal{C}$ by the equation:

$$\frac{x^2}{b_e^2} + \frac{y^2}{b_e^2} + \frac{z^2}{c_e^2} = 1 \tag{3}$$

where $b_e = a \sinh \eta$ and $c_e = a \cosh \eta$. The surface of constant value ξ is the hyperboloid of revolution defined in $\mathcal{C}$ by the equation:

$$-\frac{x^2}{b_h^2} - \frac{y^2}{b_h^2} + \frac{z^2}{c_h^2} = 1 \tag{4}$$

where $b_h = a \sin \eta$ and $c_h = a \cos \eta$. The surface of constant value ϕ defines the half-plane of Z axis as the edge.

If a point $V \in \mathbb{R}^3$ in $\mathcal{E}$ has the coordinates (η, ξ, ϕ), then its coordinates in the cartesian coordinate system $\mathcal{C}$ are given by:

$$x(\eta, \xi, \phi; a) = a \sinh \eta \ \sin \xi \ \cos \phi \tag{5a}$$
$$y(\eta, \xi, \phi; a) = a \sinh \eta \ \sin \xi \ \sin \phi \tag{5b}$$
$$z(\eta, \xi, \phi; a) = a \cosh \eta \ \cos \xi \tag{5c}$$

Let us denote by r_a, r_b the distance from the point V to foci A, B, respectively. Then, from Eq. (5), we obtain:

$$r_a(\eta, \xi; a) = \sqrt{x^2 + y^2 + (z + a)^2} = a(\cosh \eta + \cos \xi) \tag{6a}$$
$$r_b(\eta, \xi; a) = \sqrt{x^2 + y^2 + (z - a)^2} = a(\cosh \eta - \cos \xi) \tag{6b}$$

The volume element in the prolate ellipsoidal coordinate system, $\mathcal{E}$, has the form:

$$\begin{aligned} \mathrm{d}\mathbf{r} &= a r_a r_b \sinh\eta \ \sin\xi \ \mathrm{d}\eta \ \mathrm{d}\xi \ \mathrm{d}\phi \\ &= a^3(\sinh^2\eta + \sin^2\xi)\sinh\eta \ \sin\xi \ \mathrm{d}\eta \ \mathrm{d}\xi \ \mathrm{d}\phi \end{aligned} \tag{7}$$

3 Overlap integral

3.1 Definitions

Let us introduce two cartesian coordinate systems $\mathcal{C}_a$, $\mathcal{C}_b$ with origins located at two different points A and B separated by vector $\mathbf{q}$. Let us assume that X, Y, Z axes of systems $\mathcal{C}_a$, $\mathcal{C}_b$ are parallel, as is a common choice in the molecular quantum calculations. Let us introduce third right-hand cartesian coordinate system $\mathcal{C}$ with Z axes aligned with the vector $\mathbf{q}$ and the origin located in the middle of vector $\mathbf{q}$. The X and Y axes of $\mathcal{C}$ can be arbitrarily oriented. Let us consider any point $V \in \mathbb{R}^3$ and denote by $\mathbf{r}$, $\mathbf{r}_a$, $\mathbf{r}_b$ its coordinates in $\mathcal{C}$, $\mathcal{C}_a$, $\mathcal{C}_b$, respectively. Then, based on the mutual orientation of the coordinate systems, the relations hold:

$$\mathbf{r}_a = \mathbf{q} + \mathbf{r}_b \qquad \mathbf{r}_a = \mathbf{r} + \mathbf{q}/2 \qquad \mathbf{r}_b = \mathbf{r} - \mathbf{q}/2 \tag{8}$$

Let us introduce two spherical coordinate systems $\mathcal{S}_a$, $\mathcal{S}_b$ associated with $\mathcal{C}_a$, $\mathcal{C}_b$, respectively. Let us denote by $\mathbf{r}_a = (r_a, \theta_a, \varphi_a)$ and $\mathbf{r}_b = (r_b, \theta_b, \varphi_b)$ the coordinates of the point $V \in \mathbb{R}^3$ in the systems $\mathcal{S}_a$ and $\mathcal{S}_b$, respectively. Further, let us introduce the two atomic orbitals $f_a(\mathbf{r})$, $f_b(\mathbf{r}) : \mathbb{R}^3 \mapsto \mathbb{C}$ centered at the points A and B (the origins on the $\mathcal{C}_a$ and $\mathcal{C}_b$):

$$f_a(\mathbf{r}_a) \equiv f_a(r_a, \theta_a, \varphi_a) \qquad f_b(\mathbf{r}_b) \equiv f_b(r_b, \theta_b, \varphi_b) \tag{9}$$

Then, the overlap integral between $f_a(\mathbf{r})$ and $f_b(\mathbf{r})$ is defined as:

$$I(\mathbf{q}) = \int_{\mathbb{R}^3} f_a^\dagger(\mathbf{r}_a) f_b(\mathbf{r}_b)\mathrm{d}\mathbf{r} = \int_{\mathbb{R}^3} f_a^\dagger(\mathbf{r}) f_b(\mathbf{r} - \mathbf{q})\mathrm{d}\mathbf{r} \tag{10}$$

where † denotes the conjugate complex. Finally, let us introduce prolate ellipsoidal coordinate system, $\mathcal{E}$, based on the cartesian system $\mathcal{C}$ with foci located at A and B, as described in Sect. 2. The coordinates of foci A and B in the system $\mathcal{C}$ are $(0, 0, -a)$ and $(0, 0, a)$, where $a = |\mathbf{q}|/2$.

Let us express the value of the atomic orbital $f_a(\mathbf{r}_a)$ and $f_b(\mathbf{r}_b)$ in the coordinates of the system $\mathcal{E}$. By construction, $\mathbf{r}_a$ in $\mathcal{S}_a$ and $\mathbf{r}_b$ in $\mathcal{S}_b$ define one point $V \in \mathbb{R}^3$. Let us denote the coordinates of the point $V \in \mathbb{R}^3$ in $\mathcal{C}$ as $\mathbf{r} = (x, y, z)$. Then, based on Eq. (8) and the relations between spherical and cartesian coordinate system,

we obtain:

$$\varphi_a(x, y; \mathbf{q}) = \tan^{-1} \frac{y + q_y/2}{x + q_x/2} \tag{11a}$$

$$\varphi_b(x, y; \mathbf{q}) = \tan^{-1} \frac{y - q_y/2}{x - q_x/2} \tag{11b}$$

$$\theta_a(x, y, z; \mathbf{q}) = \tan^{-1} \frac{\sqrt{(x + q_x/2)^2 + (y + q_y/2)^2}}{z + q_z/2} \tag{11c}$$

$$\theta_b(x, y, z; \mathbf{q}) = \tan^{-1} \frac{\sqrt{(x - q_x/2)^2 + (y - q_y/2)^2}}{z - q_z/2} \tag{11d}$$

where $\mathbf{q} = (q_x, q_y, q_z)$. In Eq. (5), the cartesian coordinates x, y, z are expressed by the prolate ellipsoidal coordinates (η, ξ, ϕ). Moreover, $a = |\mathbf{q}|/2 = \sqrt{q_x^2 + q_y^2 + q_z^2}/2$. Hence, the application of Eqs. (5), (6) and (11) transform the atomic orbitals $f_a(\mathbf{r}_a)$, $f_b(\mathbf{r}_b)$ to the prolate ellipsoidal coordinates. Let us denote the coordinates in $\mathcal{S}_a$ and $\mathcal{S}_b$ expressed by the coordinates of $\mathcal{E}$ as: $r_a(\eta, \xi; \mathbf{q})$, $\theta_a(\eta, \xi, \phi; \mathbf{q})$, $\varphi_a(\eta, \xi, \phi; \mathbf{q})$ and $r_b(\eta, \xi; \mathbf{q})$, $\theta_b(\eta, \xi, \phi; \mathbf{q})$, $\varphi_b(\eta, \xi, \phi; \mathbf{q})$.

3.2 Finite support

In the present paper, the atomic orbitals $f_a(\mathbf{r}_a)$, $f_b(\mathbf{r}_b)$ with the finite support are considered, i.e. functions which vanish outside the sphere. Let us denote by $r_a^*, r_b^* > 0$ the support of the atomic orbitals $f_a(\mathbf{r})$, $f_b(\mathbf{r})$, respectively. Then, $f_a(\mathbf{r})$, $f_b(\mathbf{r})$ are non zero only inside the balls $\mathcal{B}_a$, $\mathcal{B}_b$ centered at A, B and radiuses r_a^*, r_b^*. The balls $\mathcal{B}_a$, $\mathcal{B}_b$ in cartesian coordinate systems $\mathcal{C}$ are defined as:

$$\mathcal{B}_a = \{\mathbf{u} \in \mathbb{R}^3 : |\mathbf{u} - \mathbf{r}_A| \leq r_a^*\} \qquad \mathcal{B}_b = \{\mathbf{u} \in \mathbb{R}^3 : |\mathbf{u} - \mathbf{r}_B| \leq r_b^*\} \tag{12}$$

where $\mathbf{r}_A = -\mathbf{q}/2$, $\mathbf{r}_B = \mathbf{q}/2$ denote the coordinates of the points A, B in $\mathcal{C}$. Since $f_a(\mathbf{r})$ vanishes outside $\mathcal{B}_a$ and $f_b(\mathbf{r})$ vanishes outside $\mathcal{B}_b$, the product $f_a^\dagger(\mathbf{r}) f_b(\mathbf{r} - \mathbf{q})$ is non zero only over the intersection $\mathcal{B}_a \cap \mathcal{B}_b$. Further, since $f_a(\mathbf{r})$ and $f_b(\mathbf{r})$ are centered at the points A and B, then there exists the ellipsoid of revolution with foci located at A and B which contains two balls $\mathcal{B}_a$ and $\mathcal{B}_b$ and hence the intersection $\mathcal{B}_a \cap \mathcal{B}_b$. Therefore, the integral (10) over space $\mathbb{R}^3$ can be restricted to the finite space. Moreover, the ellipsoid of revolution in $\mathcal{E}$ is defined as $\{\mathbf{u} = (\eta, \xi, \phi) \in \mathbb{R}^3 : \eta \in [0, \eta^*], \xi \in [0, \pi], \phi \in [0, 2\pi)\}$, where η^* defines the size of the ellipsoid. Let us choose η^* to be the smallest ellipsoid, which contains the balls $\mathcal{B}_a$ and $\mathcal{B}_b$. Then, the overlap integral, Eq. (10), has the form:

$$I(\mathbf{q}) = a^3 \int_{\eta=0}^{\eta^*} \int_{\xi=0}^{\pi} \int_{\phi=0}^{2\pi} \alpha(\eta, \xi, \phi; \mathbf{q}) (\sinh^2 \eta + \sin^2 \xi) \sinh \eta \ \sin \xi \ \mathrm{d}\eta \, \mathrm{d}\xi \, \mathrm{d}\phi \tag{13}$$

where the integrand is defined as:

$$\alpha(\eta,\xi,\phi;\mathbf{q}) = f_a\Big(r_a(\eta,\xi;\mathbf{q}),\ \theta_a(\eta,\xi,\phi;\mathbf{q}),\ \varphi_a(\eta,\xi,\phi;\mathbf{q})\Big) \times f_b\Big(r_b(\eta,\xi;\mathbf{q}),\ \theta_b(\eta,\xi,\phi;\mathbf{q}),\ \varphi_b(\eta,\xi,\phi;\mathbf{q})\Big) \tag{14}$$

The integration domain of the integral (13) is the cuboid $[0,\eta^*]\times[0,2\pi]\times[0,\pi]$ defined in the prolate ellipsoid coordinate system $\mathcal{E}$. Hence, in order to evaluate the integral (13), the adaptive numerical integration scheme can be applied, which is described in Sect. 4. The value η^* can be obtained from Eq. (6), which must hold for any ξ. Thus, we have:

$$r_a^* \le a(\cosh\eta^* - 1) \qquad \text{and} \qquad r_b^* \le a(\cosh\eta^* - 1) \tag{15}$$

Since $\cosh x$ is an increasing function for $x \ge 0$, then we obtain:

$$\eta^* = \cosh^{-1}(\max\{r_a^*, r_b^*\})/a + 1 \tag{16}$$

Let us define the smallest cuboid $[x_{\min}, x_{\max}]\times[y_{\min}, y_{\max}]\times[z_{\min}, z_{\max}]$ in the cartesian coordinate system $\mathcal{C}$, which contains the intersection $\mathcal{B}_a \cap \mathcal{B}_b$: $x_{\min} = y_{\min} = \max\{-r_a^*, -r_b^*\}$ and $x_{\max} = y_{\max} = \min\{r_a^*, r_b^*\}$ and $z_{\min} = \max\{-r_a^* - a, -r_b^* + a\}$ and $z_{\max} = \min\{r_a^* - a, r_b^* + a\}$. Then, the overlap integral (10) can be expressed as:

$$I(\mathbf{q}) = \int_{x=x_{\min}}^{x_{\max}} \int_{y=y_{\min}}^{y_{\max}} \int_{z=z_{\min}}^{z_{\max}} \beta(x,y,z;\mathbf{q})\ \mathrm{d}x\ \mathrm{d}y\ \mathrm{d}z \tag{17}$$

where the integrand is defined as: $\beta(x,y,z;\mathbf{q}) = f_a\big(r_a(x,y,z;\mathbf{q}),\ \theta_a(x,y,z;\mathbf{q}),\ \varphi_a(x,y,z;\mathbf{q})\big) \times f_b\big(r_b(x,y,z;\mathbf{q}),\ \theta_b(x,y,z;\mathbf{q}),\ \varphi_b(x,y,z;\mathbf{q})\big)$. Let us consider the typical case, where the radial part of the atomic orbitals have the exponential cusp: $R_a(r_a) = \exp(-c_a r_a)$ and $R_b(r_b) = \exp(-c_b r_b)$ where $c_a, c_b > 0$. Then, the application of the adaptive integration scheme to evaluate the overlap integral (17) in the cartesian coordinate system is not efficient, as was proved in [33,34]. The inefficiency of the adaptive algorithm is caused by the occurrence of two cusp located at the points A and B.

However, the cusps do not occur in the coordinate system $\mathcal{E}$. The smoothness of the functions $R_a(r_a) = \exp(-c_a r_a)$ and $R_b(r_b) = \exp(-c_b r_b)$ can be proved, if Eq. (6) is used and the Taylor expansion applied:

$$r_a = a(\cosh\eta + \cos\xi) = 2a - a(\xi^2 + \eta^2)/2 + \mathcal{O}(\xi^3) + \mathcal{O}(\eta^3) \tag{18a}$$

$$r_b = a(\cosh\eta - \cos\xi) = a(\xi^2 + \eta^2)/2 + \mathcal{O}(\xi^3) + \mathcal{O}(\eta^3) \tag{18b}$$

Hence, the application of the prolate ellipsoidal coordinate system removes the cusp singularity and transforms the non-differentiable function $\beta(x,y,z)$ in cartesian coordinate system, $\mathcal{C}$, to the smooth function $\alpha(\eta,\xi,\phi)$ in prolate ellipsoidal coordinate system, $\mathcal{E}$. Moreover, in both cases, the integration domain is the finite cuboid, what facilitate the application of the adaptive integration algorithm.

4 Adaptive integration over cuboid

In this section the numerical, adaptive algorithm evaluating the integral over the cuboid $\mathbb{R}^3 \supset C = [x_1, x_2] \times [y_1, y_2] \times [z_1, z_2]$ for function $f(\mathbf{r}) : \mathbb{R}^3 \mapsto \mathbb{R}$ is presented:

$$\int_C f(x, y, z)\, \mathrm{d}x\, \mathrm{d}y\, \mathrm{d}z = \int_{x=x_1}^{x_2} \int_{y=y_1}^{y_2} \int_{z=z_1}^{z_2} f(x, y, z)\, \mathrm{d}x\, \mathrm{d}y\, \mathrm{d}z \tag{19}$$

The broad class of the adaptive integration meta-algorithms are discussed in [35,36], where the number of the available adaptive algorithms is estimated to be about 10^6. However, in this paper only the ADAPT-like algorithm is considered, dedicated to N-dimensional cube [33,34]. Before the structure of the ADAPT-like algorithm is presented, the notation is introduced.

- $\delta > 0$. The tolerance of the integral evaluation.
- p. The iteration index of the adaptive procedure.
- $C_k = [x_{k,1}, x_{k,2}] \times [y_{k,1}, y_{k,2}] \times [z_{k,1}, z_{k,2}]$. The k-th cuboid, the element of the partition.
- $\mathcal{S}_p$. The set of cuboids C_k at p-th iteration. The partition C is built from the cuboids C_k belonging to the set $\mathcal{S}_p$, i.e. $C = \bigcup_{C_k \in \mathcal{S}_p} C_k$ and $C_k \cap C_{k'} = \emptyset$ for $k \neq k'$.
- $\hat{I}(f, C_k)$. Returns the integral approximation of function f over the cuboid C_k.
- $\hat{\varepsilon}(f, C_k)$. Returns the error approximation of $\hat{I}(f, C_k)$.
- $I_p(f) = \sum_{C_k \in \mathcal{S}_p} \hat{I}(f, C_k)$. At p-th iteration, returns the integral approximation of function f over the cuboid C with partition $\mathcal{S}_p$.
- $\varepsilon_p(f) = \sum_{C_k \in \mathcal{S}_p} \hat{\varepsilon}(f, C_k)$. At p-th iteration, returns the error approximation of I_p.

Using the above notation, the structure of the ADAPT-like algorithm evaluating adaptively the integral over cuboid C for function f is as follows:

1. Initialization: $p = 0$ and $\mathcal{S}_0 = \{C\}$.
2. Select C_k from $\mathcal{S}_p$ with the largest $\hat{\varepsilon}(f, C_k)$.
3. $\mathcal{S}_p := \mathcal{S}_p - \{C_k\}$.
4. Bisect C_k into $C_{k,1}$ and $C_{k,2}$ perpendicular to the direction of the largest forth divided difference.
5. Calculate $\hat{I}(f, C_{k,1})$, $\hat{\varepsilon}(f, C_{k,1})$ and $\hat{I}(f, C_{k,2})$, $\hat{\varepsilon}(f, C_{k,2})$.
6. $\mathcal{S}_p := \mathcal{S}_p \cup \{C_{k,1}\} \cup \{C_{k,2}\}$.
7. Stop condition: if $\varepsilon_p(f) < \delta$, then $\int_C f(x, y, z)\mathrm{d}x\mathrm{d}y\mathrm{d}z \approx I_p(f)$. END.
8. $p := p + 1$ and go to point (2).

The above listed algorithm does not specify the procedures evaluating the approximations $\hat{I}(f, C_k)$ and $\hat{\varepsilon}(f, C_k)$ over the cuboid C_k. In this paper we study procedures based on the quadrature, i.e. $\hat{I}(f, C_k) = \sum_i w_i f(x_i, y_i, z_i)$, where $w_i \in \mathbb{R}$ are weights and $x_i, y_i, z_i \in \mathbb{R}$ are the nodes of the quadrature [37,38]. There exist the quadratures of low orders, fully symmetric with small number of nodes [39–41]. The quadratures are so designed that the polynomials are integrated exactly. In the present paper, we apply the quadratures designed in the [33,34], where the quadrature of order seven over the unit cuboid has the form $Q_7(f) = w_7^{(1)} f(0, 0, 0) + w_7^{(2)} \sum^* f(\lambda_2, 0, 0) +$

$w_7^{(3)} \sum^* f(\lambda_3, 0, 0) + w_7^{(4)} \sum^* f(\lambda_4, \lambda_4, 0) + w_7^{(5)} \sum^* f(\lambda_5, \lambda_5, \lambda_5)$. All sums $\sum^*$ are fully symmetric over all permutations of coordinates, sign changes included. In [34] the quadrature coordinates $\lambda_1, \ldots, \lambda_5$ were obtained. Moreover, two sets of weights (with the same coordinates $\lambda_1, \ldots, \lambda_5$) were proposed, corresponding to the quadrature of degree seven, $Q_7(f)$, and degree five $Q_5(f) = w_5^{(1)} f(0, 0, 0) + w_5^{(2)} \sum^* f(\lambda_2, 0, 0) + w_5^{(3)} \sum^* f(\lambda_3, 0, 0) + w_5^{(4)} \sum^* f(\lambda_4, \lambda_4, 0)$. Based on these two quadratures the integral approximation and the error approximation are defined as:

$$\hat{I}(f, \Omega_k) = Q_7(f) \qquad \hat{\varepsilon}(f, \Omega_k) = |Q_7(f) - Q_5(f)| \tag{20}$$

The bisection of the cuboid C_k in point (4) of the algorithm is based on the fourth difference value, as proposed in [33]. The fourth difference in direction X, Y, Z are:

$$\begin{aligned}
\Delta_x &= v|[f(-\lambda_2, 0, 0) - u + f(\lambda_2, 0, 0)] - [f(-\lambda_1, 0, 0) - u + f(\lambda_1, 0, 0)]| \\
\Delta_y &= v|[f(0, -\lambda_2, 0) - u + f(0, \lambda_2, 0)] - [f(0, -\lambda_1, 0) - u + f(0, \lambda_1, 0)]| \\
\Delta_z &= v|[f(0, 0, -\lambda_2) - u + f(0, 0, \lambda_2)] - [f(0, 0, -\lambda_1) - u + f(0, 0, \lambda_1)]|
\end{aligned}$$

where $v = \lambda_1^2/\lambda_2^2$, $u = 2f(0, 0, 0)$ and λ_1, λ_2 are the coordinates of the quadrature nodes. The number of the integrand evaluation for each cuboid C_k is 33.

5 Exemplary results

In this section the numerical result obtained by the described algorithm are presented. The overlap integrals are calculated for STO. The normalized STO centered at the origin of the spherical coordinate system is defined as [1]:

$$\Psi(r, \theta, \varphi; n, \ell, m, \alpha) = \frac{(2\alpha)^{n+1/2}}{[(2n)!]^{1/2}} r^{n-1} \mathrm{e}^{-\alpha r} Y_\ell^m(\theta, \varphi) \tag{21}$$

The above applied complex spherical harmonics, $Y_\ell^m(\theta, \varphi)$, is defined according to Condon-Shortley phase [42,43] for $|m| \leq \ell$:

$$Y_\ell^m(\theta, \varphi) = \mathrm{i}^{m+|m|} \Big[\frac{2\ell + 1}{4\pi} \frac{(\ell - |m|)!}{(\ell + |m|)!} \Big]^{1/2} \mathcal{P}_\ell^{|m|}(\cos\theta) \mathrm{e}^{\mathrm{i}m\varphi} \tag{22}$$

where $\mathcal{P}_\ell^m(x)$ is an associated Legendre functions defined for $|x| \leq 1$ and $m \geq 0$:

$$\mathcal{P}_\ell^m(x) = (1 - x^2)^{m/2} \frac{\mathrm{d}^\ell}{\mathrm{d}x^\ell} P_\ell(x) = \frac{(1 - x^2)^{m/2}}{2^\ell \ell!} \frac{\mathrm{d}^{\ell+m}}{\mathrm{d}x^{\ell+m}} (x^2 - 1)^\ell \tag{23}$$

Let us introduce two Slater orbitals $\Psi(\mathbf{r}; n_a, \ell_a, m_a, \alpha_a)$, $\Psi(\mathbf{r}; n_b, \ell_b, m_b, \alpha_b)$ centered at points separated by vector $\mathbf{q}$. Then, according to the definition (10), we have:

$$I_{\mathrm{STO}}(\mathbf{q}) = \int_{\mathbb{R}^3} \Psi^\dagger(\mathbf{r}; n_a, \ell_a, m_a, \alpha_a) \Psi(\mathbf{r} - \mathbf{q}; n_b, \ell_b, m_b, \alpha_b) \mathrm{d}\mathbf{r} \tag{24}$$

Table 1 Overlap integrals for normalized Slater Type Orbitals

n_a	ℓ_a	m_a	n_b	ℓ_b	m_b	α_a	α_b	Cub	Numerical	Exact	Diff
1	0	0	1	0	0	0.1	0.1	84	0.9983372913	0.9983372846	6.7[−9]
1	0	0	1	0	0	1.0	0.1	57	0.1870516151	0.1870519193	3.0[−7]
1	0	0	1	0	0	5.0	0.1	31	0.2016802799[−1]	0.2016803717[−1]	2.8[−8]
1	0	0	1	0	0	1.0	1.0	77	0.8583853802	0.8583853617	1.9[−8]
1	0	0	1	0	0	5.0	1.0	75	0.2399400308	0.2399400177	1.3[−8]
1	0	0	1	0	0	5.0	5.0	54	0.9657724481[−1]	0.9657724032[−1]	2.4[−7]
8	0	0	8	0	0	0.1	0.1	89	0.9998889123	0.9998889017	1.1[−8]
8	0	0	8	0	0	1.0	0.1	12	0.8449070688[−4]	0.8450810273[−4]	1.7[−8]
8	0	0	8	0	0	5.0	0.1	12	0.7152244882[−9]	0.7155374435[−9]	3.2[−13]
8	0	0	8	0	0	1.0	1.0	84	0.9890157808	0.9890157213	6.0[−8]
8	0	0	8	0	0	5.0	1.0	35	0.1074383155[−1]	0.1074373417[−1]	1.7[−7]
8	0	0	8	0	0	5.0	5.0	147	0.7852308528	0.7852308500	2.8[−9]
5	4	0	5	4	0	0.1	0.1	597	0.9974698856	0.9974698507	3.5[−8]
5	4	4	5	4	4	0.1	0.1	3580	0.9995455834	0.9995455808	2.6[−9]
5	4	0	5	4	0	1.0	0.1	84	0.2213266808[−2]	0.2213276772[−2]	3.3[−8]
5	4	4	5	4	4	1.0	0.1	434	0.2259642893[−2]	0.2259647731[−2]	4.3[−8]
5	4	0	5	4	0	5.0	0.1	12	0.6431401088[−6]	0.6667585746[−6]	2.4[−8]
5	4	4	5	4	4	5.0	0.1	12	0.1191450793[−5]	0.7294559035[−6]	4.6[−7]
5	4	0	5	4	0	1.0	1.0	641	0.7686170134	0.7686170156	2.2[−9]
5	4	4	5	4	4	1.0	1.0	3474	0.9557787935	0.9557787463	4.7[−8]
5	4	0	5	4	0	5.0	1.0	214	0.9002656170[−2]	0.9002623092[−2]	5.6[−8]
5	4	4	5	4	4	5.0	1.0	1209	0.3180040281[−1]	0.3180037457[−1]	4.0[−7]
5	4	0	5	4	0	5.0	5.0	505	−0.1382570115	−0.1382570116	7.0[−11]
5	4	4	5	4	4	5.0	5.0	2273	0.3568259972	0.3568259868	1.0[−8]

The overlap integrals are evaluated for selected cases with centers separated by vector $\mathbf{q} = (0, 0, 1)$. In column 'Numerical' the result obtained by the present algorithm are listed. Column 'Cub' contains the number of cuboids generated by present, adaptive procedure. In column 'Exact' the analytical results obtained in [8] are copied. Numbers in square brackets represent powers of 10

In Table 1 the values of the integral $I_{\mathrm{STO}}(\mathbf{q})$ for $\mathbf{q} = (0, 0, 1)$ are listed. The exact values for the selected parameters are brought from [8]. Since the present algorithm requires the atomic orbitals with the finite support, then STO was neglected if its radial value dropped below 10^{-13}. The values listed in Table 1 were obtained with the absolute accuracy of the adaptive algorithm set to $\delta = 10^{-6}$.

The column Diff of Table 1 contains the absolute difference between the numerical values obtained by the present method (column Numerical) and the exact values (column Exact). It is seen that for all studied cases, the difference is less than the set absolute accuracy δ. The column Cub contains the number of generated cuboids by the adaptive integration procedure. Due to the smoothness of the integrand $\Psi^{\dagger}(\mathbf{r}; n_a, \ell_a, m_a, \alpha_a)\Psi(\mathbf{r} - \mathbf{q}; n_b, \ell_b, m_b, \alpha_b)$ represented in the prolate ellipsoidal coordinates, the number of the generated cuboids is small for STO with cups, i.e. for $n_a = 1$ or $n_b = 1$. The largest number of the generated cuboids corresponds to $n_a = n_b = 5$, $\ell_a = \ell_b = m_a = m_b = 4$ and $\alpha_a = \alpha_b = 0.1$. The large number of cuboids is caused by the small value of coefficients $\alpha_a = \alpha_b = 0.1$. The small value of coefficients α_a, α_b give the large radius of the restricting balls, and hence large integration space, which requires many subdivisions.

The number of the generated cuboids is the measure of the efficiency of the adaptive integration algorithm. The Slater orbitals possess the cusp singularity for $n = 1$. It is seen from Table 1, that the presented algorithm is reliable and efficient for this case, since the number of generated cuboids is less than 100.

6 Summary

The numerical algorithm evaluating the overlap integrals between the atomic orbitals was presented. The algorithm is based on the ADAPT-like adaptive integration procedure. The adaptive integration procedure is applied to the integrand transformed from two spherical coordinate systems to one prolate ellipsoidal coordinate system, where the integrand does not possess the cusp singularity. The discussed algorithm is designed to the atomic orbitals with the finite support. The efficiency and accuracy of the algorithm was demonstrated for STO with the finite support.

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