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OVERLAP INTEGRALS BETWEEN ATOMIC ORBITALS WITH PIECEWISE POLYNOMIAL RADIAL PART EVALUATED IN PROLATE SPHEROIDAL COORDINATES

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The algorithm evaluating the overlap integrals for the numerical atomic orbitals is presented. The general class of atomic orbitals is discussed, where the radial part of the atomic orbital is represented as a piecewise polynomial and the angular part is a complex spherical harmonic. The molecular problem is reduced to the diatomic case, which is solved in prolate spheroidal coordinate system. In the prolate spheroidal coordinates, the overlap integral is reduced to the integral over the polygon. The application of the piecewise polynomial representation of the radial part further reduces the complexity of the problem. Finally, it is shown that the integral can be obtained analytically for s, p, d orbitals.

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1. Introduction

The main result of Density Functional Theory (DFT) states that every physical/chemical property of the molecular system can be expressed as the functional of the electron density [1, 2]. In order to obtain the electron density Kohn–Sham eigenvalue problem must be solved. For molecular systems Kohn–Sham equation can be solved by Linear Combination of Atomic Orbitals (LCAO) method. This method reduces the Kohn–Sham eigenfunction problem to generalized algebraic eigenproblem $\boldsymbol{Hc} = \lambda \boldsymbol{Sc}$, where the elements of matrix $\boldsymbol{S}$ are the overlap integrals between the atomic orbitals.

The evaluation complexity of the elements of matrix $\boldsymbol{S}$ strongly depends on the chosen atomic orbitals. If cartesian GTO are selected, then the procedure is almost elementary [3]. If STO or B-type atomic orbitals are selected then the evaluation procedure is more involved [4,5]. Moreover, the selection of the proper atomic orbitals has important impact on the accuracy of the obtained results, like binding energy [1]. There is a common agreement, that the application of STO gives more accurate results than the application of GTO, if the same number of the atomic orbitals are applied [1]. Since the cost of the algebraic eigenproblem scales as N^3, where N is a number of the atomic orbitals [6], then the small number of the atomic orbitals saves the computational time. In order to obtain high accuracy with the small number of the atomic orbital in LCAO method, the numerical atomic orbitals has been proposed [7,8]. The radial part of the numerical orbital does not have any analytical form and can be represented as a sequence of the points interpolated by cubic splines [6].

1.1. Fourier transform method

The Fourier transform was successfully applied to evaluate the overlap integrals between STO [5,9] and BTO [4]. This method was also applied to evaluate the overlap integral between NTO [8]. Let us denote by $\psi(\boldsymbol{r})$ and $\bar{\psi}(\boldsymbol{k})$ the atomic orbital and its Fourier transform related each other by the equation [10]:

$$\bar{\psi}(\boldsymbol{k}) = \frac{1}{(2\pi)^{3/2}} \int \psi(\boldsymbol{r}) \exp(-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}) d\boldsymbol{r}\,. \tag{1}$$

The Fourier transform method is based on the convolution theorem [10], which transforms the overlap integral between the atomic orbitals $\psi_a(\boldsymbol{r})$, $\psi_b(\boldsymbol{r})$, separated by vector $\boldsymbol{q}$, to the integral in the reciprocal space:

$$\int \psi_a^\dagger(\boldsymbol{r})\psi_b(\boldsymbol{r}-\boldsymbol{q}) d\boldsymbol{r} = \int \bar{\psi}_a^\dagger(\boldsymbol{k})\bar{\psi}_b(\boldsymbol{k}) \exp(-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{q}) d\boldsymbol{k}\,, \tag{2}$$

where † denotes the conjugate complex. Let us assume that the atomic orbital is a product of the radial part and the complex spherical harmonic: $\psi(\boldsymbol{r}) = R(r)Y_\ell^m(\hat{\boldsymbol{r}})$, where $\boldsymbol{r} \equiv (r, \hat{\boldsymbol{r}})$. Then, based on the Rayleigh's formula [11]

$$\exp(\pm\mathrm{i}\boldsymbol{x}\cdot\boldsymbol{y}) = 4\pi \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} (\pm\mathrm{i})^\ell j_\ell(xy) Y_\ell^{m\dagger}(\hat{\boldsymbol{x}}) Y_\ell^{m\dagger}(\hat{\boldsymbol{y}}) \tag{3}$$

relating a plane wave with the spherical harmonics, the three dimensional integral (1) is reduced to one dimensional integral:

$$\bar{\psi}(\boldsymbol{k}) = (-\mathrm{i})^{\ell}\sqrt{2/\pi}Y_{\ell}^{m}(\hat{\boldsymbol{k}})\int\limits_{r=0}^{\infty} r^2 R(r) j_{\ell}(kr)dr\,, \tag{4}$$

where $j_\ell(x)$ denotes the spherical Bessel function [11]. Substituting Eqs. (3) and (4) into Eq. (2), the overlap integral is transform to the sum of the one-dimensional integrals (see Ref. [8, 9] for details). Thus, the problem is reduced from three dimensional to one dimensional. However, due to the presence of the spherical Bessel functions $j_\ell(kr)$, the integrand in Eq. (4) is highly oscillating function for large k and causes the numerical instability as was discussed in Ref. [4, 12, 13]. This algorithm is implemented in SIESTA program [8].

1.2. Presented method

The method outlined above, as well the algorithm developed by Delley [7] and Becke [14], evaluates the overlap integral between two atomic orbital with arbitrary radial part. However, the algorithms evaluate the overlap integral approximately, they do not return the exact results.

The purpose of the present manuscript is to described the algorithm which exactly (*i.e.* analytically) evaluates the overlap integral between atomic orbitals with the radial part represented by the piecewise polynomial. The performance of the algorithm is secondary aspect. It has been demonstrated that the piecewise polynomial approximation gives accurate results in Density Functional Theory (DFT) if applied to free atom [15, 16]. Thus, this kind of the atomic orbitals can be applied to represent the molecular orbitals in LCAO approach. Therefore, based on the present algorithm the accuracy of the approximated algorithms can be assessed. Typically, the performance and the accuracy of approximated algorithms have been assessed based on the analytical results of GTO [17], STO [4], BTO [5] and their linear combinations. This algorithm extends the class of the atomic orbitals with the analytically available overlap integrals.

In the present paper we propose the exact algorithm based on the prolate spheroidal coordinate system. The prolate spheroidal coordinates have been successfully applied to evaluate the molecular integrals between STO [18–23]. Although, the method described in Ref. [18–23] is designed for diatomic molecules, it can be applied to any molecular system, if the rotations of the complex spherical harmonics [24–26] are used.

The outline of the manuscript is as follows. In the first part the necessary definitions are given and the diatomic case is discussed. The analytical results for atomic orbitals with piecewise polynomial radial part is fully described. In the second part the rotation and the reflection of the complex spherical harmonics are applied to reduce the general case, which occurs in the molecular systems, to the case presented in the first part of the paper.

2. Diatomic molecule

In this section the application of the prolate spheroidal coordinate system to diatomic molecules is described.

2.1. Prolate spheroidal coordinate system

Let us create the prolate spheroidal coordinate system, $\mathcal{E}$, based on two spherical coordinate systems with specific mutual orientation [27–29]. Let us denote two spherical coordinate systems with origins at points A and B by $\mathcal{S}_a$ and $\mathcal{S}_b$. The system $\mathcal{S}_a$ is right-handed and the system $\mathcal{S}_b$ is left-handed. The XOY plane of $\mathcal{S}_a$ is parallel to the XOY plane of $\mathcal{S}_b$. Moreover, the YOZ planes of $\mathcal{S}_a$ and $\mathcal{S}_b$ are common and the axes Z of both systems have the opposite directions. Let us define a point $\boldsymbol{r} \in \mathbb{R}^3$ and denote its coordinates in $\mathcal{S}_a$ by $(r_a, \theta_a, \varphi_a)$ and in $\mathcal{S}_b$ by $(r_b, \theta_b, \varphi_b)$. Then, due to the mutual orientation of $\mathcal{S}_a$ and $\mathcal{S}_b$, the azimuth angles are identical $\varphi_a = \varphi_b = \varphi$, see Fig. 1.

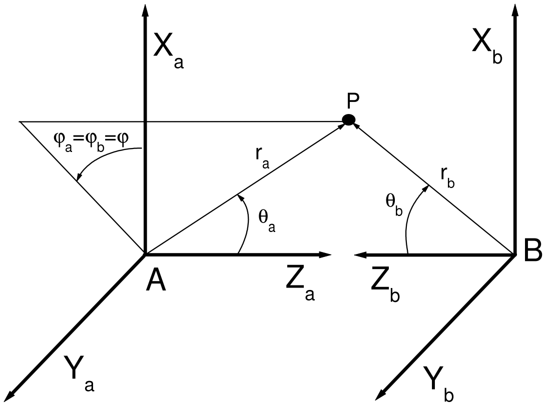

Fig. 1. Relative position of two spherical coordinate systems $\mathcal{S}_a$ and $\mathcal{S}_b$. The foci of prolate spheroidal coordinate are located at A and B. Azimuth angles are identical $\varphi_a = \varphi_b = \varphi$.

Let q be the distance between A and B. The coordinates of the point $\boldsymbol{r} \in \mathbb{R}^3$ in the prolate spheroidal coordinates system, $\mathcal{E}$, with foci located at A and B are denoted as (ξ, η, φ). The coordinates belong to the following ranges: $\xi \in [1, \infty]$ and $\eta \in [-1, 1]$ and $\varphi \in [0, 2\pi]$. Moreover, the coordinate

φ in $\mathcal{E}$ is equal to the coordinate φ in $\mathcal{S}_a$ and $\mathcal{S}_b$. The relations between the coordinates in $\mathcal{S}_a$, $\mathcal{S}_b$ and the coordinates in $\mathcal{E}$ are as follows [27–29]:

$$\begin{aligned} \mathcal{S}_a &\leftrightarrow \mathcal{E}\,, & \mathcal{S}_b &\leftrightarrow \mathcal{E}\,, \\ r_a(\xi,\eta;q) &= (\xi+\eta)\frac{q}{2}\,, & r_b(\xi,\eta;q) &= (\xi-\eta)\frac{q}{2}\,, \\ \cos(\theta_a(\xi,\eta)) &= \frac{(1+\xi\eta)}{(\xi+\eta)}\,, & \cos(\theta_b(\xi,\eta)) &= \frac{(1-\xi\eta)}{(\xi-\eta)}\,. \end{aligned} \tag{5}$$

The volume element in $\mathcal{E}$ is defined by:

$$d\boldsymbol{r} = \frac{q^3}{8}\left(\xi^2-\eta^2\right) d\xi d\eta d\varphi\,. \tag{6}$$

2.2. Atomic orbital

An atomic orbital $f(\boldsymbol{r}) : \mathbb{R}^3 \mapsto \mathbb{C}$ centered at the origin of the spherical coordinate system is a product of the radial part, $R(r) : \mathbb{R} \mapsto \mathbb{R}$, and the complex spherical harmonic:

$$f(\boldsymbol{r}) = R(r) Y_\ell^m(\theta,\varphi)\,. \tag{7}$$

The complex spherical harmonic is defined according to Condon–Shortley phase conventions [30]:

$$Y_\ell^m(\theta,\varphi) = N_\ell^m \mathcal{P}_\ell^m(\cos(\theta)) \mathrm{e}^{\mathrm{i}m\varphi}\,, \tag{8}$$

where N_ℓ^m is a normalization factor:

$$N_\ell^m = \mathrm{i}^{m+|m|}\left[\frac{2\ell+1}{4\pi}\frac{(\ell-|m|)!}{(\ell+|m|)!}\right]^{1/2} \tag{9}$$

and $\mathcal{P}_\ell^m(x)$ is an associated Legendre functions defined by Legendre polynomial $P_\ell(x)$, for $|x| \leq 1$:

$$\begin{aligned} \mathcal{P}_\ell^{|m|}(x) &= \left(1-x^2\right)^{|m|/2} \frac{d^{|m|}}{dx^{|m|}} P_\ell(x) \equiv \left(1-x^2\right)^{|m|/2} P_\ell^{(|m|)}(x)\,, & (10) \\ P_\ell(x) &= (2^\ell \ell!)^{-1} \frac{d^\ell}{dx^\ell}\left(x^2-1\right)^\ell\,, & (11) \end{aligned}$$

where $P_\ell^{(|m|)}(x)$ denotes the m-th derivative of the Legendre polynomial $P_\ell(x)$.

The radial part of the atomic orbital $R(r)$ can be any smooth function, like Gauss function, Slater function [1] or B-type function [5]. In the present paper we assume, that $R(r)$ is a piecewise polynomial function. Moreover, only the radial functions with the finite support are consider, *i.e.* functions, which vanish outside the specific ball.

Let us define the atomic orbitals centered at the points A and B as:

$$f_a(\boldsymbol{r}) = R_a(r_a)Y_{\ell_a}^{m_a}(\theta_a,\varphi_a)\,, \qquad f_b(\boldsymbol{r}) = R_b(r_b)Y_{\ell_b}^{m_b}(\theta_b,\varphi_a)\,. \tag{12}$$

If the spherical coordinates, defined by prolate coordinates, Eq. (5), are inserted into the definition of the atomic orbitals, Eq. (12), we obtain:

$$\tilde{f}_a(\xi,\eta,\varphi;q) \;=\; N_{\ell_a}^{m_a} R_a\Big(\tfrac{(\xi+\eta)q}{2}\Big)\mathcal{P}_{\ell_a}^{m_a}\Big(\tfrac{1+\xi\eta}{\xi+\eta}\Big)e^{\mathrm{i}m_a\varphi}\,, \tag{13a}$$

$$\tilde{f}_b(\xi,\eta,\varphi;q) \;=\; N_{\ell_b}^{m_b} R_b\Big(\tfrac{(\xi-\eta)q}{2}\Big)\mathcal{P}_{\ell_b}^{m_b}\Big(\tfrac{1-\xi\eta}{\xi-\eta}\Big)e^{\mathrm{i}m_b\varphi}\,, \tag{13b}$$

where q is the distance between point A and B. In the present paper the atomic orbitals with the finite support are considered. Let us denote by r_a^*, r_b^* the support of $f_a(\boldsymbol{r})$, $f_b(\boldsymbol{r})$. Then, the atomic orbitals $f_a(\boldsymbol{r})$, $f_b(\boldsymbol{r})$ are non zero only inside the balls $\mathcal{B}_a$, $\mathcal{B}_b$ centered at A, B and radiuses r_a^*, r_b^*:

$$\mathcal{B}_a = \{\boldsymbol{v}\in\mathbb{R}^3 : |\boldsymbol{v}-\boldsymbol{r}_A| \le r_a^*\}\,, \qquad \mathcal{B}_b = \{\boldsymbol{v}\in\mathbb{R}^3 : |\boldsymbol{v}-\boldsymbol{r}_B| \le r_b^*\}\,, \tag{14}$$

where $\boldsymbol{r}_A$, $\boldsymbol{r}_B$ denote the coordinates of points A, B. Based on these definitions and the relations between spherical and prolate spheroidal coordinate systems, Eq. (5), the balls $\mathcal{B}_a$, $\mathcal{B}_b$ in prolate spheroidal coordinate system are:

$$\tilde{\mathcal{B}}_a \;=\; \{(\eta,\xi,\varphi)\in[-1,1]\times[1,\infty]\times[0,2\pi] : (\xi+\eta)q/2 \le r_a^*\}\,, \tag{15}$$

$$\tilde{\mathcal{B}}_b \;=\; \{(\eta,\xi,\varphi)\in[-1,1]\times[1,\infty]\times[0,2\pi] : (\xi-\eta)q/2 \le r_b^*\}\,. \tag{16}$$

The balls $\tilde{\mathcal{B}}_a$ and $\tilde{\mathcal{B}}_b$ in two dimensional domain (η,ξ) are depicted in Fig. 2. It is seen that, $\tilde{\mathcal{B}}_a$ and $\tilde{\mathcal{B}}_b$ in domain (η,ξ) are the polygons. The center of $\tilde{\mathcal{B}}_a$ has the coordinates $(\eta,\xi) = (-1,1)$ and the center of $\tilde{\mathcal{B}}_b$ has the coordinates $(\eta,\xi) = (1,1)$. The polygon representing $\tilde{\mathcal{B}}_a$ in plane (η,ξ) has the vertices A, B, C_a and D_a. The polygon representing $\tilde{\mathcal{B}}_b$ in plane (η,ξ) has the vertices A, B, C_b and D_b. The coordinates of C_a, D_a and C_b, D_b can be obtained from Eqs. (15) and (16). The lines passing through the pair of points (C_a,D_a) and the pair (C_b,D_b) are defined by:

$$\xi+\eta = \frac{2r_a^*}{q}\,, \qquad \xi-\eta = \frac{2r_b^*}{q}\,. \tag{17}$$

The vertices C_a, C_b lie on the vertical edges ($\eta=-1$ or $\eta=1$) and have the coordinates:

$$C_a(\eta,\xi) = \left(-1, \frac{2r_a^*}{q}+1\right)\,, \qquad C_b(\eta,\xi) = \left(1, \frac{2r_b^*}{q}+1\right)\,. \tag{18}$$

The position of vertices D_a, D_b depends on the relation between r_a^*, r_b^* and q:

$$D_a(\eta, \xi) = \begin{cases} \left(2\frac{r_a^*}{q} - 1, 1\right) & \text{if} \quad r_a^* \le q\,, \\ \left(1, 2\frac{r_a^*}{q} - 1\right) & \text{if} \quad r_a^* > q\,, \end{cases} \tag{19a}$$

$$D_b(\eta, \xi) = \begin{cases} \left(1 - 2\frac{r_b^*}{q}, 1\right) & \text{if} \quad r_b^* \le q\,, \\ \left(-1, 2\frac{r_b^*}{q} - 1\right) & \text{if} \quad r_b^* > q\,. \end{cases} \tag{19b}$$

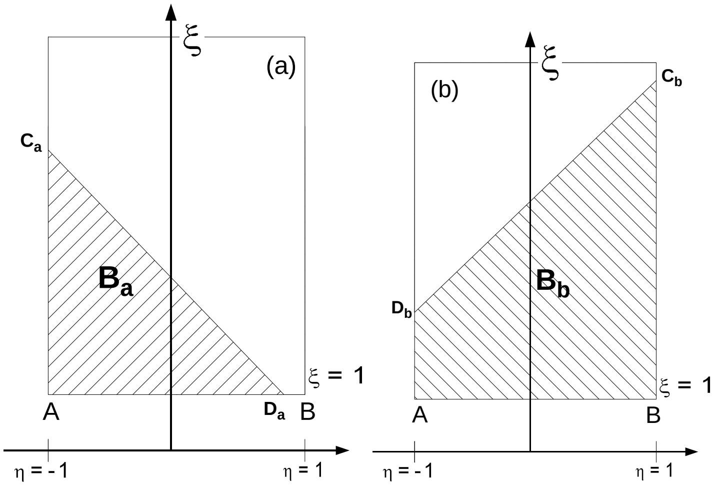

Fig. 2. (a) Ball $\tilde{\mathcal{B}}_a$, Eq. (15), in plane (η, ξ) of prolate coordinate system. (b) Ball $\tilde{\mathcal{B}}_b$, Eq. (16), in plane (η, ξ) of prolate coordinate system. Both $\tilde{\mathcal{B}}_a$ and $\tilde{\mathcal{B}}_b$ are polygons.

2.3. Overlap integral

For the atomic orbitals $f_a(\boldsymbol{r})$ and $f_b(\boldsymbol{r})$ with the finite support, the overlap integral is over the finite space, which is the intersection $\mathcal{B}_a \cap \mathcal{B}_b$ of balls defined by Eq. (14):

$$I(q) = \int\limits_{\mathbb{R}^3} f_a^\dagger(\boldsymbol{r}) f_b(\boldsymbol{r}) d\boldsymbol{r} = \int\limits_{\mathcal{B}_a \cap \mathcal{B}_b} f_a^\dagger(\boldsymbol{r}) f_b(\boldsymbol{r}) d\boldsymbol{r}\,, \tag{20}$$

where † denotes the conjugate complex. This integral can be expressed in prolate spheroidal coordinate system. Substituting Eq. (13) and volume element, Eq. (6), into Eq. (20) we obtain:

$$\begin{aligned} I(q) &= \frac{q^3}{8} \int\limits_{\varphi=0}^{2\pi} \int\limits_{\eta=-1}^{1} \int\limits_{\xi=1}^{\infty} \tilde{f}_a^{\dagger}(\xi,\eta,\varphi;q)\tilde{f}_b(\xi,\eta,\varphi;q)(\xi^2-\eta^2)d\xi d\eta d\varphi \\ &= \frac{q^3}{8} N_{\ell_a}^{m_a} N_{\ell_b}^{m_b} I_1(q) I_2 \end{aligned} \tag{21}$$

with

$$I_1(q) = \int\limits_{\eta=-1}^{1} \int\limits_{\xi=1}^{\infty} \alpha(\xi,\eta;q)d\xi d\eta = \int\limits_{\tilde{\mathcal{B}}_a \cap \tilde{\mathcal{B}}_b} \alpha(\xi,\eta;q)d\xi d\eta \tag{22}$$

and

$$I_2 = \int\limits_{\varphi=0}^{2\pi} \mathrm{e}^{\mathrm{i}(m_b-m_a)\varphi} d\varphi = 2\pi\delta_{m_a,m_b} , \tag{23}$$

where δ_{m_a,m_b} is a Kronecker delta. The integrand in Eq. (22) is given by:

$$\alpha(\xi,\eta;q) = R_a\Big(\tfrac{(\xi+\eta)q}{2}\Big)\mathcal{P}_{\ell_a}^{m_a}\Big(\tfrac{1+\xi\eta}{\xi+\eta}\Big)R_b\Big(\tfrac{(\xi-\eta)q}{2}\Big)\mathcal{P}_{\ell_b}^{m_b}\Big(\tfrac{1-\xi\eta}{\xi-\eta}\Big)(\xi^2-\eta^2) \tag{24}$$

and the integration domain is the intersection of balls in prolate coordinate system $\tilde{\mathcal{B}}_a \cap \tilde{\mathcal{B}}_b$. Since $I(q)$ is a product of $I_1(q)$ and I_2, then based on Eq. (23) the overlap integral is nonzero only for $m_a = m_b$. Moreover, due to the application of prolate spheroidal coordinate system, the three dimensional integral, Eq. (20), is reduced to two dimensional integral, Eq. (22).

If $R_a(r)$ and $R_b(r)$ are any smooth function, then the numerical integration must be performed to evaluate the integral $I_1(q)$. It has been demonstrated [31], that the adaptive integration schema gives the accurate results. In the following Sections we present the algorithm evaluating the integral $I_1(q)$ analytically, when the radial part of the atomic orbitals are polynomials and piecewise polynomials.

2.4. Polynomial approximation

Let us consider the case when the radial part of the atomic orbitals is a polynomial. Since any polynomial $\sum_k c_k x^k$ is a linear combination of monomials x^k, the results for

$$R_a(r_a) = r_a^{n_a} , \qquad R_b(r_b) = r_b^{n_b} , \qquad n_a, n_b = 0, 1, 2, \ldots \tag{25}$$

are only studied. Substituting Eq. (25) into Eq. (24) we get:

$$\alpha(\xi,\eta;q) = \left(\frac{q}{2}\right)^{n_a+n_b}(\xi+\eta)^{n_a+1}(\xi-\eta)^{n_b+1}\mathcal{P}_{\ell_a}^{m_a}\left(\tfrac{1+\xi\eta}{\xi+\eta}\right)\mathcal{P}_{\ell_b}^{m_b}\left(\tfrac{1-\xi\eta}{\xi-\eta}\right). \quad (26)$$

Due to Kronecker delta in Eq. (23), the overlap integral $I(q)$ is only non zero for $m_a = m_b = m$. Substituting this condition into Eq. (26) we get:

$$\begin{aligned}\alpha(\xi,\eta;q) \;=\; &\left(\frac{q}{2}\right)^{n_a+n_b}(\xi+\eta)^{n_a+1}(\xi-\eta)^{n_b+1}\left(\frac{(1-\eta^2)(\xi^2-1)}{\xi^2-\eta^2}\right)^{|m|}\\ &\times P_{\ell_a}^{(|m|)}\left(\tfrac{1+\xi\eta}{\xi+\eta}\right)P_{\ell_b}^{(|m|)}\left(\tfrac{1-\xi\eta}{\xi-\eta}\right), \end{aligned} \quad (27)$$

where $P_\ell^{(|m|)}(x)$ denotes $|m|$-th derivative of Legendre polynomial, see Eq. (10). In many practical applications s, p, d atomic orbitals are mainly considered, *i.e.* $\ell_a, \ell_b \le 2$. For these cases, Eq. (27) simplifies considerably. The explicit expressions for $\alpha(\xi,\eta;q)\,(2/q)^{n_a+n_b}$ are given in Table I. For $n_a, n_b \ge 1$ the expressions in Table I are polynomials, hence the integral $\iint \alpha(\xi,\eta;q)d\xi d\eta$ can be easily obtained. If $n_a = 0$ or $n_b = 0$, then the integral is expressed by $\log(\cdot)$. If $n_a = n_b = 0$ the integral is expressed by $\tan^{-1}(\cdot)$. Thus, for each case listed in Table I the integral $\iint \alpha(\xi,\eta;q)d\xi d\eta$

TABLE I

Explicit expressions for $\alpha(\xi,\eta;q)\,(2/q)^{n_a+n_b}$, Eq. (27), with radial functions being the monomials $R_a(r_a) = r_a^{n_a}$ and $R_b(r_b) = r_b^{n_b}$. Results are presented for $\ell_a, \ell_b \le 2$ and $0 \le m \le \min\{\ell_a, \ell_b\}$, what corresponds to s, p, d atomic orbitals.

(ℓ_a, ℓ_b, m)	$\alpha(\xi,\eta;q)\,(2/q)^{n_a+n_b}$
$(0,0,0)$	$(\xi-\eta)^{n_b}(\xi+\eta)^{n_a}(\xi^2-\eta^2)$
$(1,0,0)$	$(\xi-\eta)^{n_b+1}(\xi+\eta)^{n_a}(1+\eta\xi)$
$(0,1,0)$	$(\xi-\eta)^{n_b}(\xi+\eta)^{n_a+1}(1-\eta\xi)$
$(1,1,1)$	$(\xi-\eta)^{n_b}(\xi+\eta)^{n_a}(1-\eta^2)(\xi^2-1)$
$(2,0,0)$	$(\xi-\eta)^{n_b+1}(\xi+\eta)^{n_a-1}[3+4\eta\xi-\xi^2+\eta^2(3\xi^2-1)]/2$
$(0,2,0)$	$(\xi-\eta)^{n_b-1}(\xi+\eta)^{n_a+1}[3-4\eta\xi-\xi^2-\eta^2(1-3\xi^2)]/2$
$(2,1,0)$	$(\xi-\eta)^{n_b}(\xi+\eta)^{n_a-1}(1-\eta\xi)[3+4\eta\xi-\xi^2+\eta^2(3\xi^2-1)]/2$
$(1,2,0)$	$(\xi-\eta)^{n_b-1}(\xi+\eta)^{n_a}(1+\eta\xi)[3-4\eta\xi-\xi^2+\eta^2(3\xi^2-1)]/2$
$(2,1,1)$	$3(\xi-\eta)^{n_b}(\xi+\eta)^{n_a-1}(1+\eta\xi)(1-\eta^2)(\xi^2-1)$
$(1,2,1)$	$3(\xi-\eta)^{n_b-1}(\xi+\eta)^{n_a}(1-\eta\xi)(1-\eta^2)(\xi^2-1)$
$(2,2,0)$	$(\xi-\eta)^{n_b-1}(\xi+\eta)^{n_a-1}[3-4\eta\xi-\xi^2+\eta^2(3\xi^2-1)]$ $\times[3+4\eta\xi-\xi^2+\eta^2(3\xi^2-1)]/4$
$(2,2,1)$	$9(\xi-\eta)^{n_b-1}(\xi+\eta)^{n_a-1}(1-\eta^2)(\xi^2-1)(1-\eta\xi)(1+\eta\xi)$
$(2,2,2)$	$9(\xi-\eta)^{n_b-1}(\xi+\eta)^{n_a-1}(1-\eta^2)^2(1-\xi^2)^2$

can be obtained analytically. The required integrals can be obtained by symbolic algebra packages like Mathematica (`http://www.wolfram.com/`) or Maple (`http://www.maplesoft.com/`).

2.5. The intersection $\tilde{\mathcal{B}}_a \cap \tilde{\mathcal{B}}_b$ in (η, ξ) plane

In order to obtain the value of integral $I(q)$ the intersection $\tilde{\mathcal{B}}_a \cap \tilde{\mathcal{B}}_b$ must be explicitly given. The intersection $\mathcal{B}_a \cap \mathcal{B}_b$, and hence the intersection $\tilde{\mathcal{B}}_a \cap \tilde{\mathcal{B}}_b$, depends on the mutual relation of radius r_a^*, r_b^* and the inter-center distance q. There are seven mutually exclusive cases listed below:

1. if $r_a^* + r_b^* < q$, then $\tilde{\mathcal{B}}_a \cap \tilde{\mathcal{B}}_b = \emptyset$.
2. If $r_a^* \geq r_b^* + q$, then $\tilde{\mathcal{B}}_a \cap \tilde{\mathcal{B}}_b = \tilde{\mathcal{B}}_b$.
3. If $r_b^* \geq r_a^* + q$, then $\tilde{\mathcal{B}}_a \cap \tilde{\mathcal{B}}_b = \tilde{\mathcal{B}}_a$.
4. If $r_a^* \leq q$ and $r_b^* \leq q$, then $\tilde{\mathcal{B}}_a \cap \tilde{\mathcal{B}}_b$ in plane (η, ξ) is a isosceles triangle, see Fig. 3 (a), with vertices D_a, D_b and G.
5. If $r_a^* \leq q$ and $r_b^* > q$, then $\tilde{\mathcal{B}}_a \cap \tilde{\mathcal{B}}_b$ in plane (η, ξ) is a quadrilateral, see Fig. 3 (b), with vertices D_b, A, D_a and G.
6. If $r_a^* > q$ and $r_b^* \leq q$, then $\tilde{\mathcal{B}}_a \cap \tilde{\mathcal{B}}_b$ in plane (η, ξ) is a quadrilateral, see Fig. 3 (c), with vertices D_b, B, D_a and G.
7. If $r_a^* > q$ and $r_b^* > q$, then $\tilde{\mathcal{B}}_a \cap \tilde{\mathcal{B}}_b$ in plane (η, ξ) is a pentagon, see Fig. 3 (d), with vertices D_b, A, B, D_a and G.

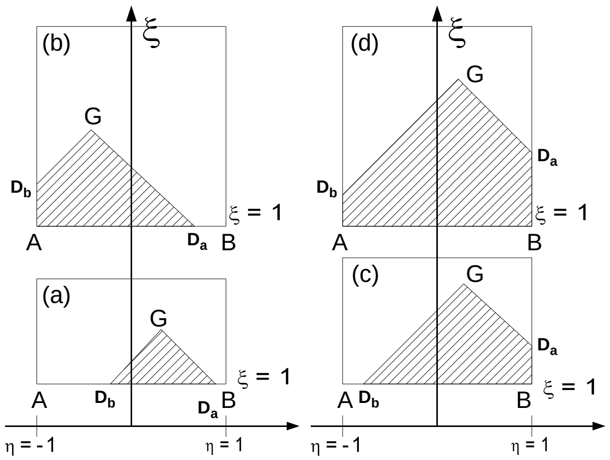

Fig. 3. Intersection $\tilde{\mathcal{B}}_a \cap \tilde{\mathcal{B}}_b$ in plane (η, ξ) denoted by hatched region. The intersection depends on the mutual relation of r_a^*, r_b^* and q: (a) $r_a^* \leq q$ and $r_b^* \leq q$, (b) $r_a^* \leq q$ and $r_b^* > q$, (c) $r_a^* > q$ and $r_b^* \leq q$, (d) $r_a^* > q$ and $r_b^* > q$.

The coordinates of vertices C_a, C_b, D_a, D_b are given by Eqs. (18) and (19). The point G lies on the intersection of lines defined by Eq. (17) and has the coordinates $G(\eta,\xi) = ((r_a^* - r_b^*)/q, (r_a^* + r_b^*)/q)$. Since the integral $\iint \alpha(\xi,\eta;q)d\xi d\eta$ and the intersection $\tilde{\mathcal{B}}_a \cap \tilde{\mathcal{B}}_b$ in (η,ξ) are determined, then the integral $I_1(q)$ and hence the overlap integral $I(q)$ for s, p, d atomic orbitals with polynomial radial parts can be obtained analytically.

The results obtained in this Section for atomic orbital with polynomial radial part are applied in the following Section, when the radial part of the atomic orbital is represented as a piecewise polynomial function.

2.6. Piecewise polynomial functions

The piecewise polynomial function $h(x) : [\mu,\nu] \mapsto \mathbb{R}$ is defined on the partition $\mu = x_0 < x_1 < \ldots < x_N = \nu$, where N is the number of the nodes in the partition [6]. On each interval $[x_j, x_{j+1}]$ the function $h(x)$ is a polynomial. It has been demonstrated that polynomial approximation is very powerful [32, 33] and has been successfully applied to the quantum mechanical calculation in density functional framework [15].

Let us assume, that radial parts $R_a(r)$, $R_b(r)$ of the atomic orbitals

$$f_a(\boldsymbol{r}) = R_a(r)Y_{\ell_a}^{m_a}(\theta,\varphi)\,, \qquad f_b(\boldsymbol{r}) = R_b(r)Y_{\ell_b}^{m_b}(\theta,\varphi) \tag{28}$$

are piecewise polynomials. Further, let us assume, that $R_a(r)$ is defined on the partition $0 = r_{a,0} < r_{a,1} < \ldots < r_{a,N_a} = r_a^*$ and $R_b(r)$ is defined on the partition $0 = r_{b,0} < r_{b,1} < \ldots < r_{b,N_b} = r_b^*$. The intervals $[0, r_a^*]$ and $[0, r_b^*]$ define the supports of the atomic orbitals and N_a, N_b are the number of the nodes in the partitions. Let us introduce the functions:

$$p_{a,i}(r) = \begin{cases} w_{a,i}(r) & \text{if } r \in [r_{a,i-1}, r_{a,i})\,, \\ 0 & \text{otherwise}\,, \end{cases} \tag{29a}$$

$$p_{b,j}(r) = \begin{cases} w_{b,j}(r) & \text{if } r \in [r_{b,j-1}, r_{b,j})\,, \\ 0 & \text{otherwise}\,, \end{cases} \tag{29b}$$

where $w_{a,i}(r)$, $w_{b,i}(r)$ are the polynomials defining the functions $R_a(r)$, $R_b(r)$, on the intervals $[r_{a,i-1}, r_{a,i})$, $[r_{b,j-1}, r_{b,j})$, respectively. Since the supports of $p_{a,i}(r)$, $p_{b,j}(r)$ are disjointed, then the radial functions are represented as a sums:

$$R_a(r) = \sum_{i=1}^{N_a} p_{a,i}(r)\,, \qquad R_b(r) = \sum_{j=1}^{N_b} p_{b,j}(r)\,. \tag{30}$$

Further, let us introduce the functions:

$$u_{a,i}(r) = \begin{cases} w_{a,i}(r) & \text{if } r \in [0, r_{a,i})\,, \\ 0 & \text{otherwise}\,, \end{cases} \tag{31a}$$

$$u_{b,j}(r) = \begin{cases} w_{b,j}(r) & \text{if } r \in [0, r_{b,j})\,, \\ 0 & \text{otherwise}\,. \end{cases} \tag{31b}$$

The functions $u_{a,i}(r)$ and $u_{b,j}(r)$ are the polynomials on the intervals $[0, r_{a,i})$, $[0, r_{b,j})$. Based on the above definitions and Eq. (29), we have:

$$p_{a,i}(r) = u_{a,i}(r) - u_{a,i-1}(r)\,, \qquad p_{b,j}(r) = u_{b,j}(r) - u_{b,j-1}(r)\,. \tag{32}$$

Hence, the functions $R_a(r)$ and $R_b(r)$ can be represented as a sum and difference of the polynomials defined on the finite intervals with the begin at zero:

$$R_a(r) = \sum_{i=1}^{N_a} [u_{a,i}(r) - u_{a,i-1}(r)]\,, \qquad R_b(r) = \sum_{j=1}^{N_b} [u_{b,j}(r) - u_{b,j-1}(r)]\,. \tag{33}$$

Let us define two auxiliary atomic orbitals:

$$g_{a,i}(\boldsymbol{r}) = u_{a,i}(r_a) Y_{\ell_a}^{m_a}(\theta_a, \varphi_a)\,, \qquad g_{b,j}(\boldsymbol{r}) = u_{b,j}(r_b) Y_{\ell_b}^{m_b}(\theta_b, \varphi_b)\,. \tag{34}$$

Then, the functions $f_a(\boldsymbol{r})$, $f_b(\boldsymbol{r})$, defined in Eq. (28), can be expressed as:

$$f_a(\boldsymbol{r}) = \sum_{i=1}^{N_a} [g_{a,i}(\boldsymbol{r}) - g_{a,i-1}(\boldsymbol{r})]\,, \qquad f_b(\boldsymbol{r}) = \sum_{j=1}^{N_b} [g_{b,j}(\boldsymbol{r}) - g_{b,j-1}(\boldsymbol{r})]\,. \tag{35}$$

Substituting Eq. (35) into the definition of $I(q)$, Eq. (20), we obtain:

$$\begin{aligned} I(q) \;=\; & \sum_{i=1}^{N_a} \sum_{j=1}^{N_b} \int_{\mathbb{R}^3} \Big[g_{a,i}^{\dagger}(\boldsymbol{r}) g_{b,j}(\boldsymbol{r}) - g_{a,i}^{\dagger}(\boldsymbol{r}) g_{b,j-1}(\boldsymbol{r}) \\ & - g_{a,i-1}^{\dagger}(\boldsymbol{r}) g_{b,j}(\boldsymbol{r}) + g_{a,i-1}^{\dagger}(\boldsymbol{r}) g_{b,j-1}(\boldsymbol{r}) \Big] d\boldsymbol{r}\,. \end{aligned} \tag{36}$$

Since the radial part of each atomic orbital occurred in the above equation is a polynomial with the finite support starting at zero, then the algorithm described in Section 2.4 can be applied. Thus, the overlap integral between the atomic orbitals with the radial parts represented by the piecewise polynomial functions in diatomic case are obtained analytically for $\ell_a, \ell_b \leq 2$.

3. Molecular systems

In the molecular systems the local, atomic coordinates have specific orientation, which differs from the orientation discussed for the diatomic case. In this section it is shown how to reduce the overlap integral defined for general case to the diatomic case described in Section 2. Before we proceed, the rotation and reflection of the complex spherical harmonics are outlined.

3.1. Rotation of complex spherical harmonics

The rotation of the complex spherical harmonics was described in Refs. [24–26]. In these papers the rotation in $\mathbb{R}^3$ space is defined by Euler angles. Let us denote a coordinates of point $\boldsymbol{r}$ in fixed and rotated coordinate system as (r, θ, φ), (r, θ', φ'), respectively. Then it was proved that the relation holds:

$$Y_\ell^m(\theta, \varphi) = \sum_{M=-\ell}^{\ell} \boldsymbol{D}^{(\ell)}_{M,m}(\alpha, \beta, \gamma) Y_\ell^M(\theta', \varphi')\,, \tag{37}$$

where the summation runs only over the magnetic quantum number M. The expansion coefficients are so called Wigner D-matrix:

$$\boldsymbol{D}^{(\ell)}_{M,m}(\alpha, \beta, \gamma) = e^{-i\alpha M} \boldsymbol{d}^{(\ell)}_{M,m}(\beta) e^{-i\gamma m} \tag{38}$$

with

$$\begin{aligned} \boldsymbol{d}^{(\ell)}_{M,m}(\beta) \;&=\; (-1)^{M-m} \left[\frac{(\ell+M)!(\ell-M)!}{(\ell+m)!(\ell-m)!} \right]^{1/2} \\ &\quad \times \sum_{k=k_{\min}}^{k_{\max}} \Big\{ (-1)^k \binom{\ell+m}{k} \binom{\ell-m}{\ell-M-k} \\ &\quad \times \big(\cos(\beta/2)\big)^{2\ell-M+m-2k} \big(\sin(\beta/2)\big)^{M-m+2k} \Big\}, \end{aligned} \tag{39}$$

where $k_{\min} = \max\{0, m-M\}$ and $k_{\max} = \min\{\ell-M, \ell+m\}$. For numerical calculations, recursion relations of the $\boldsymbol{d}^{(\ell)}_{M,m}(\beta)$ are important and can be found if Ref. [25, 34, 35].

3.2. Reflection of complex spherical harmonics

Let us consider two coordinate systems with common axes OX, OY and common plane XOY, one left-handed, $\mathcal{S}_{\rm L}$, and one right-handed, $\mathcal{S}_{\rm R}$. Let us denote the coordinates of a point $\boldsymbol{r}$ in $\mathcal{S}_{\rm R}$, $\mathcal{S}_{\rm L}$ by (x, y, z), $(\tilde{x}, \tilde{y}, \tilde{z})$, respectively. Then, the relations (for cartesian and spherical coordinates) hold:

$$\begin{aligned} \tilde{x} &= x\,, & \tilde{y} &= y\,, & \tilde{z} &= -z\,, \\ \tilde{r} &= r\,, & \tilde{\theta} &= \pi + \theta\,, & \tilde{\phi} &= \phi\,. \end{aligned} \tag{40}$$

Since $\cos(\pi+\theta) = -\cos(\theta)$, then based on the definition of complex spherical harmonics, Eq. (8), one can prove:

$$Y_\ell^m(\tilde{\theta},\tilde{\varphi}) = Y_\ell^m(\pi+\theta,\varphi) = (-1)^{\ell+m} Y_\ell^m(\theta,\varphi)\,. \tag{41}$$

Thus, the complex spherical harmonic defined in $\mathcal{S}_\mathrm{L}$ is expressed by the complex spherical harmonic defined in $\mathcal{S}_\mathrm{R}$.

3.3. Reduction to diatomic case

Let us consider two atoms A and B in $\mathbb{R}^3$ space. The atomic orbitals for atom A and B are defined in their local spherical coordinate systems $\mathcal{S}_a$ and $\mathcal{S}_b$ with origins located at A and B, respectively. The systems $\mathcal{S}_a$ and $\mathcal{S}_b$ have parallel coordinate axes and the distance between A and B is $\boldsymbol{q}$. The pair of the coordinates systems $\mathcal{S}_a$ and $\mathcal{S}_b$ can be transformed to the pair of the coordinate systems $\mathcal{S}'_a$ and $\mathcal{S}'_b$ constituting the prolate spheroidal coordinate system (described in Section 2.1) by three transformations:

1. Rotate $\mathcal{S}_a$ around point A such that its Z axis align $\boldsymbol{q}$.
2. Rotate $\mathcal{S}_b$ around point B such that its Z axis align $\boldsymbol{q}$.
3. Change the rotated right-handed system $\mathcal{S}_b$ to the left-handed system.

Since the atomic orbital is a product of the radial part and the complex spherical harmonic, Eq. (7), and the radial part does not change during the transformations (1)–(3), then only complex spherical harmonics are transformed.

Let us denote the coordinates of a point $\boldsymbol{r}$ in $\mathcal{S}_a$, $\mathcal{S}'_a$ as (r_a,θ_a,φ_a) and $(r_a,\theta'_a,\varphi'_a)$. Identically, let us denote the coordinates of a point $\boldsymbol{r}$ in $\mathcal{S}_b$, $\mathcal{S}'_b$ as (r_b,θ_b,φ_b) and $(r_b,\theta'_b,\varphi'_b)$. Further, let us denote the atomic orbitals defined in $\mathcal{S}_a$, $\mathcal{S}_b$ as

$$f_{\ell_a}^{m_a}(\boldsymbol{r}) = R_a(r_a) Y_{\ell_a}^{m_a}(\theta_a,\varphi_a)\,, \qquad f_{\ell_b}^{m_b}(\boldsymbol{r}) = R_b(r_b) Y_{\ell_b}^{m_b}(\theta_b,\varphi_b)\,. \tag{42}$$

Then, based on Section 3.1 and Section 3.2 we obtain:

$$Y_{\ell_a}^{m_a}(\theta_a,\varphi_a) = \sum_{M_a=-\ell_a}^{\ell_a} \boldsymbol{a}_{M_a,m_a}^{(\ell_a)} Y_{\ell_a}^{M_a}(\theta'_a,\varphi'_a)\,, \tag{43}$$

$$Y_{\ell_b}^{m_b}(\theta_b,\varphi_b) = \sum_{M_b=-\ell_b}^{\ell_b} \boldsymbol{b}_{M_b,m_b}^{(\ell_b)} Y_{\ell_b}^{M_b}(\theta'_b,\varphi'_b) \tag{44}$$

with

$$\begin{aligned} \boldsymbol{a}^{(\ell_a)}_{M_a,m_a} &= \boldsymbol{D}^{(\ell_a)}_{M_a,m_a}(\alpha,\beta,\gamma)\,, && \text{(45a)}\\ \boldsymbol{b}^{(\ell_b)}_{M_b,m_b} &= (-1)^{\ell_b+M_b}\boldsymbol{D}^{(\ell_b)}_{M_b,m_b}(\alpha,\beta,\gamma)\,. && \text{(45b)} \end{aligned}$$

Let us denote by

$$h^{m_a}_{\ell_a}(\boldsymbol{r}) = R_a(r_a)Y^{m_a}_{\ell_a}(\theta'_a,\varphi'_a) \quad \text{and} \quad h^{m_b}_{\ell_b}(\boldsymbol{r}) = R_b(r_b)Y^{m_b}_{\ell_b}(\theta'_b,\varphi'_b)$$

the atomic orbitals in $\mathcal{S}'_a$ and $\mathcal{S}'_b$, respectively. Then, multiplying Eq. (43) by $R_a(r_a)$ and multiplying Eq. (44) by $R_b(r_b)$, we obtain:

$$f^{m_a}_{\ell_a}(\boldsymbol{r}) = \sum_{M_a=-\ell_a}^{\ell_a} \boldsymbol{a}^{(\ell_a)}_{M_a,m_a} h^{M_a}_{\ell_a}(\boldsymbol{r})\,, \qquad f^{m_b}_{\ell_b}(\boldsymbol{r}) = \sum_{M_b=-\ell_b}^{\ell_b} \boldsymbol{b}^{(\ell_b)}_{M_b,m_b} h^{M_b}_{\ell_b}(\boldsymbol{r})\,. \tag{46}$$

Substituting Eq. (46) into the definition of the overlap integral, Eq. (20), we obtain:

$$\int_{\mathbb{R}^3} f^{m_a\dagger}_{\ell_a}(\boldsymbol{r}) f^{m_b}_{\ell_b}(\boldsymbol{r}) d\boldsymbol{r}^3 = \sum_{M_a=-\ell_a}^{\ell_a} \boldsymbol{a}^{(\ell_a)\dagger}_{M_a,m_a} \sum_{M_b=-\ell_b}^{\ell_b} \boldsymbol{b}^{(\ell_b)}_{M_b,m_b} \int_{\mathbb{R}^3} h^{M_a\dagger}_{\ell_a}(\boldsymbol{r}) h^{M_b}_{\ell_b}(\boldsymbol{r}) d\boldsymbol{r}^3\,. \tag{47}$$

Hence, the overlap integral between $f^{m_a}_{\ell_a}(\boldsymbol{r})$ and $f^{m_b}_{\ell_b}(\boldsymbol{r})$ is a sum of the overlap integrals between $h^{M_a}_{\ell_a}(\boldsymbol{r})$ and $h^{M_b}_{\ell_b}(\boldsymbol{r})$. Due to the mutual orientation of $\mathcal{S}'_a$ and $\mathcal{S}'_b$, the overlap integral between $h^{M_a}_{\ell_a}(\boldsymbol{r})$ and $h^{M_b}_{\ell_b}(\boldsymbol{r})$ atomic orbitals can be evaluated in prolate spheroidal coordinate system. Since the overlap integral between $h^{M_a}_{\ell_a}(\boldsymbol{r})$ and $h^{M_b}_{\ell_b}(\boldsymbol{r})$ is only non-zero for $M_a = M_b = M$, see Section 2.3, then the double sum reduce to the single sum:

$$\int_{\mathbb{R}^3} f^{m_a\dagger}_{\ell_a}(\boldsymbol{r}) f^{m_b}_{\ell_b}(\boldsymbol{r}) d\boldsymbol{r}^3 = \sum_{M=M_{\min}}^{M_{\max}} \boldsymbol{a}^{(\ell_a)\dagger}_{M,m_a} \boldsymbol{b}^{(\ell_b)}_{M,m_b} \int_{\mathbb{R}^3} h^{M\dagger}_{\ell_a}(\boldsymbol{r}) h^{M}_{\ell_b}(\boldsymbol{r}) d\boldsymbol{r}^3\,, \tag{48}$$

where $M_{\min} = \max\{-\ell_a, -\ell_b\}$ and $M_{\max} = \min\{\ell_a, \ell_b\}$.

4. Summary

In the present paper we discussed the algorithm evaluating of the overlap integral of the atomic orbitals with the radial part represented as a piecewise polynomial. The algorithm based on the prolate spheroidal coordinate system was presented. First, the integration over $\mathbb{R}^3$ was reduced to $\mathbb{R}^2$, due to the application of the prolate spheroidal coordinates in diatomic case. Second, the overlap integral was split into sum of the overlap integrals between “thick spheres”. It was proved that the intersection of two “thick spheres” is a polygon in prolate spheroidal coordinates. Moreover, the integrand function over the intersection can be calculated analytically for s, p, d atomic orbitals. In the second part of the manuscript the general overlap integral is described. The application of rotations and reflections reduced the general case to diatomic case discussed in the first part of the paper. The presented algorithm is exact and easy to implement, although applicable to broad class of atomic orbitals useful in the molecular LCAO-DFT calculations.

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