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#### **RESEARCH ARTICLE**



## Derivation, properties and application of Coulomb Sturmians defined in spheroidal coordinates

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#### ABSTRACT

Coulomb Sturmian amplitude functions are derived in prolate spheroidal coordinates and are presented in a closed algebraic form. Spheroidal Sturnian functions are revealed to be related to the polynomial solutions of Heun's confluent equation. A reduction of symmetry from spherical to axial leads to the coupling of spherical polar orbitals and the formation of hybrid orbitals. The contribution of each spherical orbital into a hybrid orbital depends strongly on distance *R* from a nucleus to the dummy centre, and substantially alters when *R* varies. At two limiting cases R = 0 and  $R \rightarrow \infty$ spheroidal Sturmians are purely atomic orbitals, whereas at intermediate *R* they contain many features intrinsic to diatomic molecular orbitals. Applications of spheroidal Sturmian basis are discussed; Coulomb spheroidal Sturmians are asserted to be the most appropriate basis functions for diatomic molecular calculations.

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#### 1. Introduction

At an early stage of the development of wave mechanics, hydrogen-like amplitude or wave functions were considered to be satisfactory basis functions to build orbitals of many-electron atoms; it was soon revealed, however, that, unless the continuum is included, the hydrogenlike functions form an incomplete set, and thus fail to yield the proper atomic orbitals. To rectify this deficiency, Shull and Löwdin [1] proposed to construct basis functions in such a way as to be complete: i.e. any function obeying the appropriate boundary conditions was expandable in terms of the introduced basis functions. Basis sets of this type have been called a Sturmian basis [2,3] to emphasise their connection with Sturm–Liouville theory. Coulomb Sturmian amplitude functions obtained in spherical polar coordinates have found many applications in atomic physics. The completeness of Coulomb

Sturmians combined with their satisfactory properties of convergence makes them suitable to construct amplitude functions of many-electron atoms. The methods developed to calculate the spectra and properties of few-electron atoms and atomic ions, together with the obtained results, are presented elsewhere [4].

The efficient application of Coulomb Sturmians in atomic physics makes possible the use of this method in molecular calculations. For systems of one electron and many centres, calculations with Coulomb Sturmians are reported in several papers [5–11]. Coulomb Sturmians have been used to treat problems involving many centres and many electrons [12,13]; pilot calculations were performed for *N*-electron molecules using the generalised Sturmian method. Generalised Sturmian basis functions, their connection to hyperspherical harmonics and their application to solve many-electron



**Figure 1.** Prolate spheroidal coordinate system defined by Equations (2); an ellipsoidal surface (red) corresponds to constant  $\xi = 3/2$ ; two hyperboloids (blue surfaces) correspond to constant  $\eta = \pm 3/4$ ; a half-plane (green) is a surface of constant  $\varphi = \pi/4$ .

problems directly, without the use of the self-consistentfield approximation, are explored elsewhere [14].

Other than spherical polar coordinates, the nonrelativistic Schrödinger equation for the Kepler-Coulomb problem is separable in paraboloidal and prolate spheroidal (or ellipsoidal) coordinates [15,16]. The possibility to solve the obtained one-dimensional equations exactly and to express the amplitude functions in a closed form in paraboloidal coordinates allows one to generate the appropriate Sturmian sets, suitable as a complete orthonormal expansion basis in atomic and molecular calculations. Coulomb Sturmians in paraboloidal coordinates have been derived and investigated in detail [17,18]. In comparison with numerous applications of Coulomb spherical and paraboloidal amplitude functions, the spheroidal solutions have received little attention. This situation is attributed to the fact that solutions of the appropriate one-dimensional equations were not recognised to be expressed in terms of known special functions [19-21], although these equations are now understood to be solvable directly in terms of Heun's confluent functions, as we explain in Section 3.

The system of prolate spheroidal coordinates has two centres, corresponding to the foci of the respective ellipsoid, cf. Figure 1, and is most suitable for a study of the hydrogen molecular ion  $H_2^+$ . In the case of the hydrogen atom, one centre is at the atomic nucleus and another is located at distance *R* from the nucleus along positive axis *z*. The Schrödinger equation is reduced to three coupled equations, two of which contain *R* as a parameter; these equations become the familiar radial and angular equations when *R* tends to zero; the solutions of these equations are hence sometimes called the quasiradial and quasiangular functions. The third equation that does not contain *R* is common to spherical polar and paraboloidal coordinates. For arbitrary *R*, the quasiradial and quasiangular functions depend upon the distance between the centres of spheroidal coordinates, of which one has charge Z, and another, a dummy centre, has Z =0. When  $R \rightarrow \infty$ , the Coulomb spheroidal amplitude functions transform into the Coulomb paraboloidal amplitude functions [19].

Recent attention to the solution of the hydrogen atom problem in spheroidal coordinates [22-28] revived interest in solutions of this type, which have in turn stimulated interest in the Coulomb Sturmians basis set, obtained in spheroidal coordinates. In [17,18], the Coulomb Sturmian amplitude functions are derived in two limiting cases, at small and large R. The results were obtained on representing the unknown functions in terms of Coulomb spherical (small R) and Coulomb paraboloidal (at large R) Sturmians. The main spheroidal corrections to spherical and paraboloidal Coulomb Sturmian amplitude functions are found in [17,18]. Our paper [29] suggests a simple and straightforward scheme of calculation; Coulomb spheroidal Sturmians for some states are obtained in an explicit algebraic form at arbitrary separation R. An important conclusion is that Coulomb Sturmian amplitude functions derived in spheroidal coordinates constitute the most appropriate basis functions for calculations on diatomic molecules. Knowledge of the complete set of Coulomb spheroidal Sturmians is hence desirable.

The purpose of the present work is twofold. The first objective is to develop optimally a method of calculation [29]; explicitly, we seek the spheroidal Sturmians in an entirely closed form for use in calculations on diatomic molecules involving several electrons. The second objective is to express spheroidal Sturmians through known special functions, specifically, in terms of Heun's confluent functions and to reveal the properties of derived functions.

This article is organised as follows. After this review of the main results of preceding authors and stating the purpose of the present work, Section 2 presents briefly the basic equations and explicit expressions for Coulomb Sturmian amplitude functions in spheroidal coordinates. Section 3 reveals the relation of Coulomb spheroidal Sturmians to Heun's confluent functions. Sections 4 and 5 present illustrations of the derived amplitude functions and discuss their application, before a conclusion in Section 6. Atomic units, in which e = m = h = 1 are used throughout this article.

# 2. Coulomb Sturmian functions in spheroidal coordinates

The main characteristics of the Coulomb Sturmian basis become evident by reference to the hyrogenic basis. By definition, the Coulomb Sturmian amplitude functions  $\Psi(\vec{r})$  satisfy the equation [12,13]

$$\left(-\frac{1}{2}\Delta - \frac{Z}{r} - E\right)\Psi(\vec{r}) = 0, \qquad (1)$$

in which  $E = -k^2/2 < 0$  is a fixed parameter, Z = nk and n = 1, 2, ... The solutions of Equation (1) are  $\Psi_{nlm}(\vec{r}) = R_{nl}(r)Y_{lm}(\vartheta, \varphi)$ , in which appear radial function  $R_{nl}(r)$  and spherical harmonic  $Y_{lm}(\vartheta, \varphi)$ . The radial functions of states with  $n \le 3$  and  $l \le 1$  are given in [13].

We seek the solutions of Equation (1) in prolate spheroidal coordinates,

$$\xi = \frac{r_a + r_b}{R} \quad \eta = \frac{r_a - r_b}{R} \quad \varphi = \arctan \frac{y}{x}.$$
 (2)

In (2)  $r_a$  and  $r_b$  denote the distances from an electron to the left and right centres of spheroidal coordinate system and x, y are Cartesian coordinates; the variables are defined in these domains:  $1 \le \xi < \infty$ ,  $-1 \le \eta \le 1$  and  $0 \le \varphi \le 2\pi$ ; a nucleus is located at the left centre of spheroidal coordinates ( $\xi = 1, \eta = -1$ ). Figure 1 shows surfaces of constant values of these coordinates.

On presenting the Coulomb Sturmian amplitude function  $\psi(\xi, \eta, \varphi)$  as a product of three functions

$$\psi(\xi,\eta,\varphi) = X(\xi)Y(\eta)e^{\pm im\varphi},\tag{3}$$

in which m = 0, 1, 2, ... is the magnetic quantum number, Equation (1) becomes expressed in this form

$$\frac{d}{d\xi} \left(\xi^{2} - 1\right) \frac{dX}{d\xi} + \left[\lambda - \frac{k^{2}R^{2}}{4} \left(\xi^{2} - 1\right) + nkR\xi - \frac{m^{2}}{\xi^{2} - 1}\right] X = 0,$$
(4.a)

$$\frac{d}{d\eta} (1 - \eta^2) \frac{dY}{d\eta} + \left[ -\lambda - \frac{k^2 R^2}{4} (1 - \eta^2) - nkR\eta - \frac{m^2}{1 - \eta^2} \right] Y = 0.$$
(4.b)

Here  $\lambda$  is a separation parameter, energy  $E = -Z^2/2n^2$ is the same for all solutions and charge *Z* is chosen to make the solutions isoenergetic. We consider *m* to be positive without loss of generality, so as to avoid writing |m|in the formulae. In (4.a) and (4.b) the eigenvalues are the separation parameters  $\lambda$  associated with each amplitude function. In this case, in contrast with the cases for spherical and paraboloidal basis sets, neither spheroidal eigenfunctions  $\psi(\xi, \eta, \varphi)$  nor eigenvalues  $\lambda$  are expressible in closed form [17,18].

It follows from (4) that the functions  $X(\xi) \equiv W(t)$ and  $Y(\eta) \equiv W(t)$  satisfy the same equation with distinct domains for the variables:

$$\frac{d}{dt} (1-t^2) \frac{dW}{dt} - \left[\lambda + \frac{k^2 R^2}{4} (1-t^2) + nkRt + \frac{m^2}{1-t^2}\right] W = 0.$$
(5)

Representing W(t) as

$$W(t) = e^{-\frac{kR(t-1)}{2}} (t^2 - 1)^{\frac{m}{2}} \Phi(t), \quad (t = \xi)$$
 (6.a)

$$W(t) = e^{-\frac{kR}{2}(1+t)} (1-t^2)^{\frac{m}{2}} \Phi(t), \quad (t=\eta)$$
 (6.b)

and substituting (6.a) and (6.b) into (5), we obtain the equation for unknown function  $\Phi(t)$ :

$$(1-t^2)\frac{d^2\Phi}{dt^2} - \left[2(m+1)t + kR(1-t^2)\right]\frac{d\Phi}{dt} - \left[\lambda + m^2 + m + kR(n-m-1)t\right]\Phi = 0.$$
 (7)

The solutions of the hydrogen atom in spheroidal coordinates, i.e. the familiar Coulomb spheroidal amplitude functions, are polynomials [19,28]. It is hence natural to suppose that the solutions of Equations (4.a) and (4.b) are also polynomials at all separations. In accordance with this assumption, we represent the solution of Equation (7) as

$$\Phi(t) = \sum_{i=0}^{s} d_{s-i}(R) t^{s-i}, \quad (d_s = 1)$$
(8)

in which *s* defines the degree of the polynomial and  $d_{s-i}$  are polynomial coefficients that depend on *R*.

Substituting (8) into (7) and introducing the new separation parameter  $h = \lambda + (m + s)(m + s + 1)$  one obtains that polynomial coefficients  $d_{s-i}$  must satisfy the equation:

$$\sum_{i=0}^{s} \left\{ kR \left[ s - i - n + m + 1 \right] t^{s-i+1} - \left[ h + i \left( i - 2s - 2m - 1 \right) \right] t^{s-i} - kR \left( s - i \right) t^{s-i-1} + \left( s - i \right) \left( s - i - 1 \right) t^{s-i-2} \right\} d_{s-i} = 0.$$
(9)

Setting equal to zero the coefficients before each power of t, we evaluate polynomial coefficients  $d_{s-i}$ . For given m and  $s = 0, 1, \ldots$ , we obtain that n = s + m + 1 and

$$d_{s} = 1,$$

$$d_{s-1} = -\frac{1}{kR}hd_{s},$$

$$d_{s-2} = -\frac{1}{2kR}\left\{\left[h - 2(m+s)\right]d_{s-1} + skRd_{s}\right\},$$

$$d_{s-3} = -\frac{1}{3kR}\left\{\left[h - 4(m+s) + 2\right]d_{s-2} + (s-1)kRd_{s-1} - s(s-1)d_{s}\right\},$$

$$d_{s-4} = -\frac{1}{4kR}\left\{\left[h - 6(m+s) + 6\right]d_{s-3} + (s-2)kRd_{s-2} - (s-1)(s-2)d_{s-1}\right\},$$

$$d_{s-5} = -\frac{1}{5kR}\left\{\left[h - 8(m+s) + 12\right]d_{s-4} + (s-3)kRd_{s-3} - (s-2)(s-3)d_{s-2}\right\},$$

$$d_{s-6} = -\frac{1}{6kR}\left\{\left[h - 10(m+s) + 20\right]d_{s-5} + (s-4)kRd_{s-4} - (s-3)(s-4)d_{s-3}\right\}.$$
 (10)

Further polynomial coefficients are readily evaluated.

Setting equal to zero the coefficients before  $t^0$  in (9), one obtains that the separation parameter *h* is a solution of the following algebraic equations:

$$h = 0 \quad s = 0 \tag{11.a}$$

$$[h - 2(m+1)] d_0 + kRd_1 = 0 \quad s = 1$$
(11.b)

$$[h - s(2m + s + 1)] d_0 + kRd_1 - 2d_2 = 0 \quad s = 2, 3, \dots$$
(11.c)

Substituting in each of these equations the above derived explicit expressions for  $d_0$ ,  $d_1$ ,  $d_2$  corresponding to given *m* and *s*, we produce an equation of order (n - m) that has (n - m) real and distinct roots  $h_1 < h_2 < h_3 < \cdots h_{n-m}$  (cf. Appendix A).

It remains to specify amplitude functions  $\psi(\xi, \eta, \varphi)$ with spheroidal quantum numbers  $(n_{\xi}, n_{\eta}, m)$ , in which  $n_{\xi}$  and  $n_{\eta}$  denote the number of nodes of the quasiradial  $X_{n_{\xi}m}(\xi)$  and quasiangular  $Y_{n_{\eta}m}(\eta)$  functions, respectively. Substituting in turn the roots  $h_1, h_2, \ldots h_{n-m}$  into  $X_{n_{\xi}m}(\xi)$  and  $Y_{n_{\eta}m}(\eta)$ , we obtain that, when  $h = h_1 n_{\xi} = 0$ and  $n_{\eta} = n - m - 1$ , when  $h = h_2 n_{\xi} = 1$  and  $n_{\eta} = n - m - 2$ , when  $h = h_3 n_{\xi} = 2$  and  $n_{\eta} = n - m - 3$  and so on [29]. The spheroidal quantum numbers are hence related with a condition  $n = n_{\xi} + n_{\eta} + m + 1$ . When  $R \to \infty, n = n_{\xi} + n_{\eta} + m + 1$  transforms into the condition  $n = n_1 + n_2 + m + 1$  in which  $(n_1, n_2, m)$  are the paraboloidal quantum numbers. To summarise these results, we state that, for given m and s ( $s \equiv n - m - 1 = 0, 1, ...$ ), the Coulomb Sturmian amplitude functions obtained in spheroidal coordinates are expressible as

$$\psi_{n_{\xi}n_{\eta}m} = C_{n_{\xi}n_{\eta}m} e^{-\frac{kR(\xi+\eta)}{2}} \left[ (\xi^{2} - 1)(1 - \eta^{2}) \right]^{\frac{m}{2}} \\ \times \sum_{i=0}^{s} d_{s-i}\xi^{s-i} \sum_{j=0}^{s} d_{s-j}\eta^{s-j} e^{\pm im\varphi}, \quad (12)$$

in which

$$d_{s} = 1,$$
  

$$d_{s-i} = -\frac{1}{ikR} \{ [h_{l} + (i-1)(i-2-2m-2s)] d_{s-i+1} + (s-i+2)kRd_{s-i+2} - (s-i+2) \times (s-i+3)d_{s-i+3} \}, \quad (i = 1, 2, \dots s)$$
(13)

 $h_l$  is root l  $(1 \le l \le s + 1)$  of Equation (11) corresponding to the spheroidal quantum numbers  $n_{\xi} = l - 1$ ,  $n_{\eta} = s - l + 1$  and m;  $C_{n_{\xi}n_{\eta}m}$  is a normalising factor (cf. Appendix B).

Amplitude functions (12) with varied *m* are orthogonal because of factor  $\exp(\pm im\varphi)$ . The quasiradial  $X_{n_{\xi}m}(\xi)$  and quasiangular  $Y_{n_{\eta}m}(\eta)$  functions are defined with Equation (5), in which separation parameter  $\lambda$  plays the role of an eigenvalue. For given *n* and *m*, all solutions of Equation (5) are hence mutually orthogonal, provided only that  $\lambda$  are distinct; in Appendix A, we show that  $\lambda$  are all real and distinct. Hence  $\langle X_{n'_{\xi}m}|X_{n_{\xi}m}\rangle = 0$ and  $\langle Y_{n'_{\eta}m}|Y_{n_{\eta}m}\rangle = 0$  if  $n_{\xi} + n_{\eta} = n'_{\xi} + n'_{\eta}$  and  $n'_{\xi} \neq n_{\xi}$ ,  $n'_{\eta} \neq n_{\eta}$ .

The spheroidal Sturmians  $\psi_{n_{\xi}n_{\eta}m} = X_{n_{\xi}m}(\xi)Y_{n_{\eta}m}(\eta)e^{\pm im\varphi}$  derived above correspond to the location of a nucleus at the left centre of spheroidal coordinates ( $\xi = 1, \eta = -1$ ). If a nucleus is located at the right centre ( $\xi = 1, \eta = 1$ ), the quasiradial function  $X_{n_{\xi}m}(\xi)$  remains unchanged whereas  $\eta \to -\eta$  in the quasiangular function  $Y_{n_{\eta}m}(\eta)$ .

#### 3. Relation with Heun's confluent functions

In this section we demonstrate that the solutions of onedimensional equation (7) and accordingly Equation (5) are related to the solutions of Heun's confluent equation. In its standard canonical normal form the Heun's equation is expressed as [30–32]

$$\begin{cases} x(x-1)(x-\mu)\frac{d^2}{dx^2} + [c(x-1)(x-\mu) + dx(x-\mu) + (a+b+1-c-d)x(x-1)]\frac{d}{dx} + (abx-\alpha) \end{cases} \chi \ (x) = 0. \tag{14}$$

This equation has three regular singularities x = 0, x = 1,  $x = \mu$  and one irregular singularity  $x = \infty$ ; *a*, *b*, *c*, *d* are local parameters,  $\mu$  is a scaling parameter that determines the location of one singular point;  $\alpha$  is an accessory parameter that typically plays a role of spectral parameter.

Heun's (singly) confluent equation is obtained from the general Heun equation (14) through a confluence, i.e. a process according to which two singularities coalesce, performed by redefining parameters and taking limits. Coalescing singular points  $x = \mu$  and  $x = \infty$  ( $\mu = 1/\varepsilon$ ,  $b = p/\varepsilon$ ,  $\alpha = \beta/\varepsilon$ ,  $\varepsilon \to 0$ ,  $p = \mu$ ,  $\beta = \alpha$ ), we obtain [31,32]

$$\left\{ x(x-1)\frac{d^2}{dx^2} + [c(x-1) + dx - \mu x(x-1)]\frac{d}{dx} - (a\mu x - \alpha) \right\} \chi(x) = 0.$$
 (15)

Performing Möbius transformation  $x \rightarrow t$  where t = 2x - 1 [31,32], Heun's confluent equation (15) becomes written in this form:

$$\left\{ (1-t^2)\frac{d^2}{dt^2} - \left[ (c+d)t - c + d + \frac{\mu}{2} \left( 1 - t^2 \right) \right] \frac{d}{dt} - \left[ \alpha - \frac{\mu a}{2} \left( 1 + t \right) \right] \right\} \chi(t) = 0.$$
 (16)

Assuming that

$$a = -n + m + 1, c = d = m + 1, \mu = 2kR, \alpha = \lambda + m^{2} + m - kR(n - m - 1),$$
(17)

Equation (16) converts into Equation (7). The solutions of confluent Heun's equation (15) with parameters defined in Equation (17) are hence expected to coincide with the solutions of Equation (7).

For any singular points x = 0, x = 1 and  $x = \infty$ , two solutions of Equation (15) exist, which are characterised by the particular behaviour at these singular points [32]. Near singular point x = 0 the regular solution is represented as an expansion in power series

$$\chi(a, c, d; x) = \sum_{i=0}^{\infty} g_i x^i, \qquad g_0 = 1.$$
 (18)

For this to be a solution of (15) the expansion coefficients must satisfy the three-term recurrence relation [32]

$$(i+1)(i+c)g_{i+1} - [i(i+c+d+\mu-1)+\alpha]g_i + \mu (i+a-1)g_{i-1} = 0.$$
(19)

When parameters *a*, *c*, *d*,  $\mu$  and accessory parameter  $\alpha$  are defined with Equations (17), (19) transforms into the following three-term recurrence relation:

$$(i+1)(i+m+1)g_{i+1} - [i(i+2m+1+2kR) - kR(n-m-1) + \lambda + m^2 + m]g_i + 2kR(i-n+m)g_{i-1} = 0.$$
(20)

Recurrence relation (20) yields a continued-fraction equation in  $\lambda$ , the roots of which determine the expansion coefficients in (18). For the non-polynomial solutions of Equation (15), the algorithm of the calculation is discussed elsewhere [31,32].

We seek the solutions of Heun's confluent equation (15) in a polynomial form. When i = 0, (18) is a polynomial of degree zero,  $\chi(a, c, d; x) = 1$ . In this case (20) converts into the equation  $kR(n - m - 1) - \lambda - m^2 - m = 0$ . To satisfy this equation for arbitrary *R*, conditions n = m + 1 and  $\lambda = m^2 + m$  must be fulfilled. The obtained solution of Equation (15) hence coincides with the solution of Equation (7) derived in Section 2 at s = 0.

When i = 0, 1, (18) converts into a polynomial of first degree,  $\chi$  (a, c, d; x) = 1 +  $g_1x$ . Recurrence relation (20) yields two equations for  $g_1$ . To satisfy these equations simultaneously  $\lambda$  must be the solution of the quadratic equation with n = m + 2. A small calculation shows that the obtained equation coincides with the quadratic equation derived in Section 2 at s = 1; the solutions of Equation (15) coincide with those of Equation (7).

When i = 0, 1, 2, (18) converts into a polynomial of second degree,  $\chi(a, c, d; x) = 1 + g_1 x + g_2 x^2$ . Recurrence relation (20) yields three equations for  $g_1$  and  $g_2$ . To satisfy these equations simultaneously  $\lambda$  must be the solution of the cubic equation with n = m + 3. This cubic equation coincides with the analogous one derived in Section 2 at s = 2; the solutions of Equation (15) coincide with the solutions of Equation (7). The same effect can be shown for polynomials of third, fourth,... degrees. We have thus derived that the solutions of Equation (7) coincide with the polynomial solutions of Heun's confluent equation (15),  $\Phi(t) = \chi(a, c, d; (t + 1)/2)$ , if parameters  $a, c, d, \mu$  and accessory parameter  $\alpha$  are defined with Equation (17).

#### 4. Properties of spheroidal Sturmian functions

Spheroidal Sturmian amplitude functions  $\psi_{n_{\xi}n_{\eta}m}(\xi, \eta, \varphi)$ , derived above, can be represented as linear combinations of Coulomb spherical Sturmians  $\Psi_{nlm}(r_a, \vartheta_a, \varphi)$ . This result is achievable on representing  $r_b$  in Equations (2) as  $r_b = (r_a^2 - 2r_aR\cos\vartheta_a + R^2)^{1/2}$ , in which  $\vartheta_a$  denotes the angle between radius vector  $\vec{r_a}$ 

and axis *z*, and on representing spheroidal coordinates through spherical ones  $(r_a, \vartheta_a, \varphi)$  in  $\psi_{n_{\xi}n_{\eta}m}(\xi, \eta, \varphi)$ . Performing the appropriate calculation, we obtain that, at all separations,  $\psi_{n_{\xi}n_{\eta}m}(\xi, \eta, \varphi)$  is a linear combination of spherical Sturmians  $\Psi_{nlm}(r_a, \vartheta_a, \varphi)$  orbitals with  $n = m + 1, m + 2, \dots n_{\xi} + n_{\eta} + m + 1$  and l = m,  $m + 1, \dots n_{\xi} + n_{\eta} + m$  (cf. Appendix C).

We thus obtain that, with the exception of functions  $\psi_{00m}$ , the introduced spheroidal Sturmians  $\psi_{n_{\xi}n_{\eta}m}$  are hybrid orbitals; such a hybrid orbital is more stretched towards a neighbour atom and yields greater overlap of orbitals, and accordingly a stronger bond of atoms involved in a molecule. From equations (C.1)–(C.3) it follows that, when  $R \rightarrow 0$  spheroidal orbital  $\psi_{n_{\xi}n_{\eta}m}$  converts into spherical  $\Psi_{nlm}$  with  $n = n_{\xi} + n_{\eta} + m + 1$  and  $l = n_{\eta} + m$ ; at limit  $R \rightarrow \infty$ ,  $\psi_{n_{\xi}n_{\eta}m}$  converts into paraboloidal orbital  $\Psi_{n_{1}n_{2}m}$  with quantum numbers  $n_{1} = n_{\xi}$  and  $n_{2} = n_{\eta}$ , as appropriate.

An important property, which follows also from equations presented in Appendix C, is that the shape of spheroidal Sturmian orbitals depends on distance R from a nucleus to a dummy centre and significantly alters when *R* varies. As graphic illustrations of the progression of spheroidal amplitude functions  $\psi_{n_k n_n m}$  as distance R increases along axis z from the spherical polar limit at R = 0 to the paraboloidal limit as  $R \to \infty$ , we display plots of surfaces of constant  $\psi_{n_k n_n m}$  functions at a magnitude that is 1/20 of the maximum magnitude. Whereas these amplitude functions are expressed in terms of prolate spheroidal coordinates, the figures are plotted in the customary Cartesian coordinates. At any value of R, the surface for function  $\psi_{000}$  is a sphere (is not shown); for  $\psi_{010}$  and  $\psi_{100}$ , the shapes vary with *R* as shown in Figures 2(a)-(d) and 3(a)-(d).

Figure 2(a) shows that, at R = 0, the shape of spheroidal orbital  $\psi_{010}$  coincides with the shape of spherical polar orbital  $\Psi_{2p0}$ . When *R* increases, this shape alters: as follows from Figure 2(b), the two lobes of spheroidal orbital  $\psi_{010}$  lack a clear gap implying a planar nodal surface between them; the negative lobe along axis *z* is perceptibly smaller than the positive lobe along axis *z*. The same tendency is observable in Figure 2(c), in which the negative lobe is much smaller than the positive lobe. When R = 50 (Figure 2(d)), the negative lobe disappears; the shape of positive lobe resembles strongly the shape of a paraboloidal amplitude function with quantum numbers  $n_1 = 0$ ,  $n_2 = 1$  and m = 0.

For  $\psi_{100}$  at R = 0, in Figure 3(a) the inner (positive) lobe has a spherical shape with its centre on a nucleus; the negative lobe also has a spherical shape and occupies the volume between the inner and another (negative) lobe of spherical shape of much larger size. This negative lobe is cut open to depict the inner structure of the positive

lobe. The shape of this contour of the amplitude function  $\psi_{100}$  thus coincides at R = 0 with the shape of spherical polar amplitude function  $\Psi_{2s0}$ . When *R* increases, the inner and outer lobes of amplitude function  $\psi_{100}$  substantially alter, as shown in Figure 3(b)–(d). At R = 1, in Figure 3(b) the inner (positive) lobe of spheroidal orbital  $\psi_{100}$  has its centre clearly displaced along positive axis z approximately 1 unit from the origin at which the nucleus is located; its shape is no longer spherical but prolate spheroidal. At R = 2 in Figure 3(c), the positive lobe of spheroidal orbital  $\psi_{100}$  has entirely escaped from enclosure within the negative lobe. When R = 50 in Figure 3(d), the negative lobe disappears; the shape of the remaining positive lobe resembles strongly the shape of a paraboloidal amplitude function with the quantum numbers  $n_1 = 1$ ,  $n_2 = 0$  and m = 0. According to Figure 2(d) and 3(d), at R = 50 the shapes of spheroidal orbitals  $\psi_{010}$ an  $\psi_{100}$  are practically identical, but oriented oppositely along axis z. We refrain from presenting amplitude function  $\psi_{001}$  because it has no dependence on R and at any separation coincides with spherical polar amplitude function  $\Psi_{2p1}$ .

These algebraic and graphical results thus reveal that, for R > 0,  $\psi_{010}$  and  $\psi_{100}$  are hybrid orbitals formed of spherical polar orbitals  $\Psi_{2p0}$ ,  $\Psi_{2s0}$  and  $\Psi_{1s0}$ . Unlike hybrid orbitals introduced earlier, in  $\psi_{010}$  and  $\psi_{100}$  the weight of each of the spherical polar orbital depends on the distance between a nucleus and the dummy centre, and substantially alters when *R* varies.

In Figures 4–6 is shown the transformation of spheroidal amplitude functions  $\psi_{020}$ ,  $\psi_{110}$  and  $\psi_{011}$  as distance *R* increases from R = 0 to R = 50; tendencies analogous to those shown in Figures 2 and 3 are observable in these figures. Amplitude functions  $\psi_{020}$ ,  $\psi_{110}$  and  $\psi_{200}$  (not shown) are hybrid orbitals formed of spherical polar orbitals  $\Psi_{3d0}$ ,  $\Psi_{3p0}$ ,  $\Psi_{3s0}$ ,  $\Psi_{2p0}$ ,  $\Psi_{2s0}$  and  $\Psi_{1s0}$ . Amplitude functions  $\psi_{011}$  and  $\psi_{101}$  (not shown) are hybrid orbitals formed of spherical polar orbitals  $\Psi_{3d1}$ ,  $\Psi_{3p1}$  and  $\Psi_{2p1}$ . At R = 50,  $\psi_{011}$  and  $\psi_{101}$  resemble strongly the paraboloidal amplitude function with quantum numbers (011) and (101). Figures 4–6 confirm an important property of spheroidal orbitals – their shape strongly depends on the location of the dummy centre.

#### 5. Application

In the introduction we state that Coulomb Sturmian amplitude functions defined in spheroidal coordinates are the most appropriate basis functions for calculations on diatomic molecules. This statement is based on the results obtained in [29], in which the spheroidal Sturmian basis was used to calculate energy terms



**Figure 2.** Coulomb spheroidal Sturmian  $\psi_{010}$  at distance *R* from a nucleus to the dummy centre: (a) R = 0, (b) R = 1, (c) R = 2 and (d) R = 50. Parameter *k* is taken to have value unity.

and amplitude functions of diatomic molecules with one electron. The similarity of one- and two-centre orbitals in spheroidal coordinates, combined with the completeness and effective convergence properties of Coulomb spheroidal Sturmians, substantially speeds convergence and brings the calculated results nearer the exact ones.

We suggest that Coulomb spheroidal Sturmians are useful basis functions for calculations on diatomic molecules with several electrons; we expect that an application of Coulomb Sturmians defined in spheroidal coordinates yields results better than analogous calculations employing Coulomb Sturmians defined in spherical coordinates, as in the case of diatomic molecules with one electron. We proceed to describe briefly a scheme of calculation *ab initio* for a diatomic homonuclear molecule involving two electrons.

We introduce Coulomb а spheroidal functions Sturmian basis amplitude in as two sets,  $\{\psi_{jm}^a \equiv X_{n_{\xi}}(\xi)Y_{n_{\eta}}(\eta)e^{\pm im\varphi}\}$  and  $\{\psi_{jm}^b \equiv X_{n_{\xi}}(\xi)Y_{n_{\eta}}(-\eta)e^{\pm im\varphi}\}$ . Amplitude functions in the former set correspond to the location of a nucleus at the left centre; the latter set corresponds to the location of a nucleus at the right centre of spheroidal coordinates. For diatomic molecules formed of two identical atoms the basic functions are constructed as functions symmetric  $\psi_{jm}^{(+)} = 2^{-1/2}(\psi_{jm}^a + \psi_{jm}^b)$  and antisymmetric  $\psi_{jm}^{(-)} = 2^{-1/2}(\psi_{jm}^a - \psi_{jm}^b)$  with respect to reflection



**Figure 3.** As in Figure 2 but for Coulomb spheroidal Sturmian  $\psi_{100}$ .

in the plane normal to and bisecting molecular axis  $\vec{R}$   $(r_a \leftrightarrow r_b \text{ or equivalently } \eta \rightarrow -\eta).$ 

In the approximation with fixed nuclei, the amplitude function of two electrons with the total spin S = 0 and 1 can be represented at all separations as

$$\Psi_{pm}^{(s=0)} = \sum_{i,j} C_{pij}(R) \left( \psi_{im_i}(1)\psi_{jm_j}(2) + \psi_{im_i}(2)\psi_{jm_j}(1) \right),$$
  

$$\Psi_{pm}^{(s=1)} = \sum_{i,j} C_{pij}(R) \left( \psi_{im_i}(1)\psi_{jm_j}(2) - \psi_{im_i}(2)\psi_{jm_j}(1) \right),$$
(21)

in which  $C_{pij}(R)$  are expansion coefficients and  $m = m_i + m_j$ . Amplitude functions (21) are symmetric if both electrons are in the symmetric or antisymmetric state; (21) are antisymmetric if one electron is in the symmetric and another is in the antisymmetric state.

In the amplitude function (21), summation is performed over all two-electron configurations of a given symmetry. This amplitude function can be simplified considering only four configurations  $\psi_{10}^{(+)}(1)\psi_{10}^{(+)}(2)$ ,  $\psi_{10}^{(-)}(1)\psi_{10}^{(-)}(2)$ ,  $\psi_{10}^{(+)}(1)\psi_{10}^{(-)}(2)$  and  $\psi_{10}^{(-)}(1)\psi_{10}^{(+)}(2)$ 



**Figure 4.** Coulomb spheroidal Sturmian  $\psi_{020}$  at distance *R* from a nucleus to the dummy centre: (a) R = 0, (b) R = 2, (c) R = 5 and (d) R = 50. Parameter *k* is taken to have value unity.

in the summation. In this case, we obtain two symmetric amplitude functions with total spin S = 0

$$\begin{split} \Psi_{p0}^{(+)} &= X_{00}(\xi_1) X_{00}(\xi_2) [C_{p1}(Y_{00}(\eta_1) Y_{00}(\eta_2) \\ &+ Y_{00}(-\eta_1) Y_{00}(-\eta_2)) \\ &+ C_{p2}(Y_{00}(\eta_1) Y_{00}(-\eta_2) + Y_{00}(\eta_2) Y_{00}(-\eta_1))], \\ p &= 1,2 \end{split}$$

in which  $C_{p1} = C_{p11} + C_{p22}$ ,  $C_{p2} = C_{p11} - C_{p22}$  and two antisymmetric amplitude functions with total spin S = 0 and 1

$$\Psi_{10}^{(-)} = C_{112}X_{00}(\xi_1)X_{00}(\xi_2)(Y_{00}(\eta_1)Y_{00}(\eta_2) -Y_{00}(-\eta_1)Y_{00}(-\eta_2)), \quad S = 0,$$
  
$$\Psi_{10}^{(-)} = C_{112}X_{00}(\xi_1)X_{00}(\xi_2)(Y_{00}(\eta_1)Y_{00}(-\eta_2) -Y_{00}(\eta_2)Y_{00}(-\eta_1)), \quad S = 1.$$
(23)

When  $R \rightarrow \infty$   $C_{111} = C_{122} = 1/2$  and  $C_{211} = -C_{222} = 1/2$ ; therefore  $C_{11} = 1$ ,  $C_{12} = 0$  and  $C_{21} = 0$ ,  $C_{22} = 1$  in (22); in the limit of separate atoms, amplitude functions  $\Psi_{10}^{(+)}$  and  $\Psi_{20}^{(+)}$  correspond to the location of electrons at the same or different nucleus, respectively. In (23) the first amplitude function corresponds to the location of electrons at the same nucleus, whereas the second one corresponds to location of electrons at different nuclei.

The diagonalisation of the diatomic molecular Hamiltonian with amplitude functions (21) produces a secular equation for the energy terms. Retaining terms of finite number in the secular equation and solving this equation, we find thereby the energy terms at all separations in the appropriate approximation. With many configurations we become able to calculate the one- and twoelectron highly excited states of diatomic molecules.



**Figure 5.** As in Figure 4 but for Coulomb spheroidal Sturmian  $\psi_{110}$ .

In this calculation the main problem is the accurate calculation of the matrix element for the Coulomb repulsion between the electrons

$$\langle ij | r_{12}^{-1} | lq \rangle = \int \int \psi_{im_i}^*(\vec{r}_1) \psi_{jm_j}^*(\vec{r}_2) | \vec{r}_1 - \vec{r}_2 |^{-1} \\ \times \psi_{lm_l}(\vec{r}_1) \psi_{qm_q}(\vec{r}_2) d\vec{r}_1 d\vec{r}_2.$$
 (24)

For this purpose a method [33,34] is based on an expansion of  $|\vec{r} - \vec{r}|^{-1}$  over Legendre polynomials defined in spheroidal coordinates [35] and a calculation of appropriate integrals. An explicit expression for repulsion matrix element (24) derived in the spheroidal Sturmian basis is presented in Appendix D.

#### 6. Conclusion

The Coulomb Sturmian amplitude functions defined in spherical coordinates have been long used for molecular calculations. Application of Coulomb Sturmians defined in spheroidal coordinates for calculations on one-electron diatomic molecules is explored in [29]; we show therein that the application of a spheroidal Sturmian basis for calculations substantially improves the results. We attribute this improvement to the fact that spheroidal Sturmian amplitude functions reproduce diatomic molecular orbitals better that other functions of exponential type.

In this work we present, in a closed algebraic form, Coulomb spheroidal Sturmians; we demonstrate that the



**Figure 6.** Moduli of Coulomb spheroidal Sturmian  $|\psi_{101}|$  at distance *R* from a nucleus to the dummy centre: (a) R = 0, (b) R = 5, (c) R = 20 and (d) R = 50. Parameter *k* is taken to have value unity.

introduced functions are related to the polynomial solutions of Heun's confluent equation. We explore the properties of spheroidal Sturmians, and show that they are hybrid orbitals with shapes that substantially alter as Rvaries. The dependence of Coulomb spheroidal Sturmians on R naturally follows from the Schrödinger equation (4), which is written for the hydrogen atom in spheroidal coordinates and contains R as a parameter. At two limiting cases R = 0 and  $R \rightarrow \infty$ , spheroidal orbitals are purely atomic spherical and paraboloidal orbitals, respectively; at intermediate R they contain many features intrinsic to diatomic molecular orbitals. This nature enables us to assert that Coulomb spheroidal Sturmians are the most appropriate basis functions for calculations on diatomic molecules. The additional advantages of the spheroidal basis that we emphasise are that all relevant integrals that arise in molecular calculations are functions of purely parameter kR, in which k is the exponent common to the basic functions; the integrals can be calculated algebraically once and for all, with kR and nuclear charges as parameters.

The spheroidal Sturmian basis thus seems promising; we seek to apply this basis to calculate various characteristic properties – energy terms, amplitude functions, dipole moments, etc. – of diatomic molecules involving two or more electrons. Particular attention will be devoted to the study of one- and two-electron Rydberg states of diatomic molecules.

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### **Disclosure statement**

No potential conflict of interest was reported by the authors.

#### References

- [1] H. Shull and P.O. Löwdin, J. Chem. Phys. 30, 617 (1959).
- [2] M. Rotenberg, Ann. Phys. 19, 262 (1962).
- [3] M. Rotenberg, Adv. At. Mol. Phys. 6, 233 (1970).
- [4] J. Avery and J. Avery, *Generalized Sturmians and Atomic Spectra* (World Scientific, New Jersey, London, Singapore, Beijing, Shanghai, Hong Kong, Taipei, Chennai, 2006).
- [5] T. Shibuya and C. Wulfman, Proc. R. Soc. A 286, 376 (1965).
- [6] V. Aquilanti, S. Cavalli, D. de Fazio, and G. Grossi, in *New Methods in Quantum Theory*, edited by C.A. Tsipis, V.S. Popov, D.R. Herschbach, and J.S. Avery (Springer, Berlin, 1996).
- [7] V. Aquilanti, S. Cavalli, C. Coletti, and G. Grossi, Chem. Phys. 209, 405 (1996).
- [8] V. Aquilanti and C. Coletti, Chem. Phys. 214, 1 (1997).
- [9] V. Aquilanti and A. Caligiana, Chem. Phys. Lett. 366, 157 (2002).
- [10] T. Koga and T. Matsuhashi, J. Chem. Phys. 87, 4696 (1987).
- [11] T. Koga and T. Matsuhashi, J. Chem. Phys. 89, 983 (1988).
- [12] J. Avery and J. Avery, J. Phys. Chem. A 113, 14565 (2009).
- [13] J. Avery and J. Avery, Mol. Phys. 110, 1593 (2012).
- [14] J. Avery, Hyperspherical Harmonics and Generalized Sturmians (Kluwer Academic Publishers, Dordrecht, 2000).
- [15] L.D. Landau and E.M. Lifshitz, Quantum Mechanics: Non-relativistic Theory (Pergamon, New York, 1977).
- [16] I.V. Komarov, L.I. Ponomarev, and S.Yu. Slavyanov, Spheroidal and Coulomb Spheroidal Functions (Nauka, Moscow, 1976). (in Russian).
- [17] V. Aquilanti, A. Caligiana, and S. Cavalli, Int. J. Quantum Chem. 92, 99 (2003).
- [18] C. Coletti, D. Calderini, and V. Aquilanti, Adv. Quantum Chem., 67, 73 (2013).
- [19] C.A. Coulson and P.D. Robinson, Proc. Phys. Soc. 71, 815 (1958).
- [20] P.D. Robinson, Proc. Phys. Soc. 71, 828 (1958).
- [21] C.A. Coulson and A. Joseph, Proc. Phys. Soc. London 90, 887 (1967).
- [22] S.M. Sung and D.R. Herschbach, J. Chem. Phys. 95, 7437 (1991).
- [23] L.G. Mardoyan, G.S. Pogosyan, A.N. Sissakyan, and V.M. Ter-Antonyan, J. Phys. A 16, 711 (1983).

- [24] L.G. Mardoyan, G.S. Pogosyan, A.N. Sissakyan, and V.M. Ter-Antonyan, Teor. Mat. Fiz. 64, 171 (1985).
- [25] T.M. Kereselidze, Bull. Acad. Sci. Georgian SSR 139, 481 (1990).
- [26] T.M. Kereselidze, Z.S. Machavariani, and I.L. Noselidze, J. Phys. B At. Mol. Opt. Phys. 29, 257 (1996).
- [27] T.M. Kereselidze, Z.S. Machavariani, and I.L. Noselidze, J. Phys. B At. Mol. Opt. Phys. 31, 15 (1998).
- [28] T. Kereselidze, Z.S. Machavariani, and G. Chkadua, Eur. Phys. J. D **63**, 81 (2011).
- [29] T. Kereselidze, G. Chkadua, and P. Defrance, Mol. Phys. (2015). (accepted for publication).
- [30] K. Heun, Math. Ann. 33, 161 (1889).
- [31] S.Yu. Slavyanov, W. Lay, and A. Seeger, in *Heun's Differential Equations*, edited by A. Ronveaux (Oxford University Press, Oxford, 1995).
- [32] S.Yu. Slavyanov and W. Lay, Special Functions: A United Theory Based on Singularities (Oxford University Press, Oxford, 2000).
- [33] F.R. Vukailovic and O.A. Mogilevsky, JINR, Dubna Preprint P4-12710 (1979).
- [34] F.R. Vukailovic and O.A. Mogilevsky, J. Phys. B At. Mol. Phys. 13, 1947 (1980).
- [35] P.M. Morse and H. Feshbach, *Methods of Theoretical Physics* (McGraw-Hill Book Company, New York, 1953).
- [36] G.A. Korn and T.M. Korn, Mathematical Handbook for Scientists and Engineers (McGraw-Hill Book Company, New York, 1961).
- [37] G.M. Fikhtengoltz, *Course of Differential and Integral Calculus* v. 3 (Nauka, Moscow, 1966). (in Russian).
- [38] H. Bateman and A. Erdelyi, *Higher Transcendental Functions* (McGraw-Hill Book Company, New York, 1973).

#### **Appendix A**

We fix *m* and find the roots of algebraic equations (11). When s = 1, separation parameter *h* is a solution of quadratic equation (11.b) that has two real and distinct roots

$$h_{1,2} = m + 1 \mp \sqrt{(m+1)^2 + k^2 R^2}.$$
 (A.1)

When s = 2, h is a solution of cubic equation (11.c) that has three real and distinct roots that are represented in this trigonometric form [36]

$$h_{1,2} = -2\sqrt{-p/3}\cos\left((\omega \mp \pi)/3\right) + 2(3m+5)/3,$$
  

$$h_3 = 2\sqrt{-p/3}\cos(\omega/3) + 2(3m+5)/3,$$
  
(A.2)

in which

$$p = -4(m^{2} + 3m + 7/3 + k^{2}R^{2}),$$
  

$$q = 8(m^{2} + 3m + 20/9 - 2k^{2}R^{2})/3,$$
  

$$\cos \omega = -(q/2)/\sqrt{-(p/3)^{3}}.$$

When s = 3, *h* is a solution of Equation (11.c) of fourth degree; this equation has four real and distinct roots that can be found by means of the Ferrari method [36].

$$h_{1,2} = -\sqrt{y/2} \mp \sqrt{\left(y - p + q/\sqrt{2y}\right)/2} - y + 3m + 7,$$
  

$$h_{3,4} = \sqrt{y/2} \mp \sqrt{\left(y - p - q/\sqrt{2y}\right)/2} - y + 3m + 7.$$
(A.3)

Here  $y = \sqrt{p^2/9 + 4r/3}\cos(\omega/3) - p/3$  is one positive root of the relevant cubic resolvent and

$$p = -2(5m^{2} + 20m + 21 + 5k^{2}R^{2}),$$
$$q = 16(m^{2} + 4m + 4 - 2k^{2}R^{2}),$$

 $r = 9m^{2} + 72m^{3} + 206m^{2} + 248m + 105 + k^{2}R^{2}(18m^{2} + 72m + 50 + 9k^{2}R^{2}),$ 

$$\cos\omega = (p^3 - 36pr + 27q^2/2)/(p^2 + 12r)^{3/2}$$

When s = 4, 5, ..., we arrive at equations of fifth, sixth, ... degree that can be solved only numerically.

### **Appendix B**

Coulomb Sturmians defined in spherical coordinates are normalised by the condition [4]

$$\int \Psi_{nlm}^*(\vec{r}) \frac{1}{r} \Psi_{nlm}(\vec{r}) d\vec{r} = \frac{k}{n}.$$
 (B.1)

For spheroidal Sturmians  $\psi_{n_{\xi}n_{\eta}m} = C_{n_{\xi}n_{\eta}m}X_{n_{\xi}}(\xi)Y_{n_{\eta}}(\eta)e^{\pm im\varphi}$  the condition for normalisation is expressible as

$$\frac{\pi R^2}{2} C_{n_{\xi}n_{\eta}m}^2 \int_1^{\infty} \int_{-1}^1 X_{n_{\xi}}^2(\xi) Y_{n_{\eta}}^2(\eta) (\xi - \eta) d\xi d\eta = \frac{k}{n}.$$
(B.2)

Using Equation (B.2), we have calculated the normalising factors for some amplitude functions:

$$C_{000} = \frac{k^{3/2}}{\pi^{1/2}},\tag{B.3}$$

$$C_{010} = \frac{k^{5/2}R}{2\pi^{1/2}} \left[ 1 + \frac{k^2R^2}{2} + \frac{1}{k^2R^2} \left( 1 - \sqrt{1 + k^2R^2} \right)^2 \right]^{-1/2},$$
  

$$C_{100} = \frac{k^{5/2}R}{2\pi^{1/2}} \left[ 1 + \frac{k^2R^2}{2} + \frac{1}{k^2R^2} \left( 1 + \sqrt{1 + k^2R^2} \right)^2 \right]^{-1/2},$$
  
(B.4)

$$C_{001} = \frac{k^{5/2}R}{2^{3/2}\pi^{1/2}}$$

$$C_{n_{\xi}n_{\eta}0} = \frac{k^{2/2}R^{2}}{2^{5/2}\pi^{1/2}} \left[1 + \frac{3}{4} \left(k^{2}R^{2} + \frac{h^{2}}{k^{2}R^{2}}\right) + h^{2} \left(\frac{3}{16} + \frac{2}{(h-6)^{2}}\right) + 3g^{2}\right]^{-1/2},$$

$$C_{011} = \frac{k^{7/2}R}{2^{2}3^{1/2}\pi^{1/2}} \times \left[1 + \frac{k^{2}R^{2}}{4} + \frac{1}{k^{2}R^{2}} \left(2 - \sqrt{4 + k^{2}R^{2}}\right)^{2}\right]^{-1/2},$$
(B.5)

$$C_{101} = \frac{k^{7/2}R}{2^2 3^{1/2} \pi^{1/2}} \times \left[1 + \frac{k^2 R^2}{4} + \frac{1}{k^2 R^2} \left(2 + \sqrt{4 + k^2 R^2}\right)^2\right]^{-1/2},$$
$$C_{002} = \frac{k^{7/2} R^2}{2^3 3^{1/2} \pi^{1/2}}.$$

In (B.5)  $C_{n_{\xi}n_{\eta}0} = C_{020}$  if  $h = h_1$ ,  $C_{n_{\xi}n_{\eta}0} = C_{110}$  if  $h = h_2$ and  $C_{n_{\xi}n_{\eta}0} = C_{200}$  if  $h = h_3$ .

#### **Appendix C**

Here we represent spheroidal Sturmian amplitude functions  $\psi_{n_{\xi}n_{\eta}m}(\xi, \eta, \varphi)$   $(n_{\xi} + n_{\eta} + m \le 2)$  through Coulomb spherical Sturmians  $\Psi_{nlm}(r_a, \vartheta_a, \varphi)$ 

$$\psi_{000} = \frac{\pi^{1/2} C_{000}}{k^{3/2}} \Psi_{1s0}, \qquad (C.1)$$

$$\begin{split} \psi_{010} &= \frac{2\pi^{1/2}C_{010}}{k^{5/2}R} \\ &\times \left[ \Psi_{2p0} + \frac{1}{kR} \left( 1 - \sqrt{1 + k^2 R^2} \right) \Psi_{2s0} + \frac{kR}{2} \Psi_{1s0} \right], \\ \psi_{100} &= \frac{2\pi^{1/2}C_{100}}{k^{5/2}R} \\ &\times \left[ \Psi_{2p0} + \frac{1}{kR} \left( 1 + \sqrt{1 + k^2 R^2} \right) \Psi_{2s0} + \frac{kR}{2} \Psi_{1s0} \right], \end{split}$$
(C.2)

$$\begin{split} \psi_{001} &= \frac{2^{3/2} \pi^{1/2} C_{001}}{k^{5/2} R} \Psi_{2p1}, \\ \psi_{n_{\xi} n_{\eta} 0} &= \frac{2^{5/2} \pi^{1/2} C_{n_{\xi} n_{\eta} 0}}{k^{7/2} R^2} \\ & \times \left[ \Psi_{3d0} + \frac{\sqrt{3}h}{2kR} \Psi_{3p0} + \frac{\sqrt{2}h}{h-6} \Psi_{3s0} + \frac{kR}{\sqrt{2}} \Psi_{2p0} \right. \\ & \left. + \frac{h}{2\sqrt{2}} \Psi_{2s0} + g \Psi_{1s0} \right], \\ \psi_{011} &= \frac{2^{2} 3^{1/2} \pi^{1/2} C_{011}}{Rk^{7/2}} \\ & \times \left[ \Psi_{3d1} + \frac{1}{kR} \left( 2 - \sqrt{4 + k^2 R^2} \right) \Psi_{3p1} + \frac{kR}{\sqrt{6}} \Psi_{2p1} \right], \end{split}$$
(C.3)

$$\begin{split} \psi_{101} &= \frac{2^2 3^{1/2} \pi^{1/2} C_{101}}{R k^{7/2}} \\ &\times \left[ \Psi_{3d1} + \frac{1}{kR} \left( 2 + \sqrt{4 + k^2 R^2} \right) \Psi_{3p1} + \frac{kR}{\sqrt{6}} \Psi_{2p1} \right], \\ \psi_{002} &= \frac{2^3 3^{1/2} \pi^{1/2} C_{002}}{k^{7/2} R^2} \Psi_{3d2}. \end{split}$$

In (C.3)  $\psi_{n_{\xi}n_{\eta}0} = \psi_{020}$  if  $h = h_1$ ,  $\psi_{n_{\xi}n_{\eta}0} = \psi_{110}$  if  $h = h_2$  and  $\psi_{n_{\xi}n_{\eta}0} = \psi_{200}$  if  $h = h_3$ .

### **Appendix D**

For  $r_{12}^{-1} \equiv |\vec{r} - \vec{r}|^{-1}$  we employ Neumann's expansion [35]

$$\frac{1}{r_{12}} = \frac{2}{R} \sum_{n=0}^{\infty} \sum_{m=0}^{n} (-1)^{m} \varepsilon_{m} (2n+1) \left[ \frac{(n-m)!}{(n+m)!} \right]^{2} P_{n}^{m}(\eta_{1}) P_{n}^{m}(\eta_{2})$$
$$\cdot P_{n}^{m}(\xi_{<}) Q_{n}^{m}(\xi_{>}) \cos\left(m(\varphi_{1}-\varphi_{2})\right)$$
(D.1)

in which  $\varepsilon_m = 2 - \delta_{m0}$  and  $P_n^m$ ,  $Q_n^m$  are Legendre polynomials of first and second kinds, respectively;  $\xi_>$ ,  $\xi_<$  denote the larger or the smaller of  $\xi_1$  and  $\xi_2$ .

Substituting (D.1) into (26) and integrating over  $\varphi_1$  and  $\varphi_2$ , we arrive at the following expression for the matrix element:

$$\langle ij | r_{12}^{-1} | lp \rangle = (-1)^m \frac{CR^5}{32} \sum_{n=0}^{\infty} (2n+1) \left[ \frac{(n-m)!}{(n+m)!} \right]^2$$

$$\int_1^{\infty} X_i(\xi_1) X_l(\xi_1) I_{il}(\xi_1)$$

$$\cdot \left[ Q_n^m(\xi_1) \int_1^{\xi_1} X_j(\xi_2) P_n^m(\xi_2) X_p(\xi_2) I_{jp}(\xi_2) d\xi_2 \right]$$

$$+ P_n^m(\xi_1) \int_{\xi_1}^{\infty} X_j(\xi_2) Q_n^m(\xi_1) X_p(\xi_2) I_{jp}(\xi_2) d\xi_2 \right] d\xi_1$$
(D.2)
in which  $C = CCCCC$   $m = |m_1 - m_1| = |m_2 - m_1| = |m_1 - m_1| = |m_1| = |m_1 - m_1| = |m_1| =$ 

in which  $C = C_i C_j C_l C_p$ ,  $m = |m_i - m_l| = |m_j - m_p|$ 

and

$$I_{il}(\xi) = \int_{-1}^{1} Y_i(\eta) P_n^m(\eta) Y_l(\eta) (\xi^2 - \eta^2) d\eta.$$
 (D.3)

Note that, here and below, we omit m in the subscript of the amplitude functions.

Now using Dirichlet equation [37] and carrying out some transformations, we obtain

$$\begin{aligned} \left\langle ij \right| r_{12}^{-1} \left| lp \right\rangle &= (-1)^{m+1} \frac{CR^5}{32} \sum_{n=0}^{\infty} (2n+1) \left[ \frac{(n-m)!}{(n+m)!} \right]^2 \\ \left\{ \int_1^\infty \frac{d}{d\xi} \left[ \frac{Q_n^m(\xi)}{P_n^m(\xi)} \right] \int_1^{\xi} X_i(\xi_1) P_n^m(\xi_2) X_l(\xi_1) I_{il}(\xi_1) d\xi_1 \\ \cdot \int_1^{\xi} X_j(\xi_2) P_n^m(\xi_2) X_p(\xi_2) I_{jp}(\xi_2) d\xi_2 d\xi \right\}. \end{aligned}$$
(D.4)

The integrand in the first integral in (D.4) can be expressed as Wronskian  $W\{P_n^m(\xi)Q_n^m(\xi)\}$  [38]. As a result we derived for the repulsion matrix element

$$\langle ij | r_{12}^{-1} | lp \rangle = \frac{CR^5}{32} \sum_{n=0}^{\infty} (2n+1) \frac{(n-m)!}{(n+m)!}$$
$$\times \int_1^\infty \frac{F_{il}^{(n,m)}(\xi) F_{jp}^{(n,m)}(\xi) d\xi}{(\xi^2 - 1) [P_n^m(\xi)]^2}, (D.5)$$

in which

$$F_{il}^{(n,m)}(\xi) = \int_{1}^{\xi} X_{i}(\xi_{1}) P_{n}^{m}(\xi_{1}) X_{l}(\xi_{1}) I_{il}(\xi_{1}) d\xi_{1} \quad (D.6)$$

and  $I_{il}(\xi)$  is defined by Equation (D.3).