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THE HYDROGEN ATOM ACCORDING TO WAVE MECHANICS – IV. SPHEROCONICAL COORDINATES

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Abstract

In this fourth of five parts in a series, the Schroedinger equation is solved in spheroconical coordinates to yield amplitude functions that enable accurate plots of their surfaces to illustrate the variation of shapes and sizes with quantum numbers k, l, κ, for comparison with the corresponding plots of amplitude functions in coordinates of other systems. These amplitude functions directly derived have the unique feature of being prospectively only real, with no imaginary part.

Resumen

En este cuarto artículo de una serie de cinco, se resuelve la ecuación de Schrödinger en coordenadas esferocónicas para producer funciones de amplitude que facilitan gráficos exactos de sus superficies para ilustrar la variación de formas y tamaños con los números cuánticos k, l, κ, para comparación con los gráficos correspondientes de funciones de amplitus en coordenadas de otros sistemas. Estas funciones de amplitude derivadas directamente tiene la característica única de ser solo prospectivamente real, sin ninguna parte imaginaria.

Key words: hydrogen atom, wave mechanics, spheroconical coordinates, orbitals, atomic spectra

Palabras clave: átomo de hidrógeno, mecánica de onda, coordenadas esferocónicas, orbitales, espectro atómico.

I. INTRODUCTION

Schroedinger founded wave mechanics with four papers under a collective title in English translation [*1*] *Quantisation as a problem of proper values*, with auxiliary essays and lectures. In the first and third papers of that sequence, Schroedinger calculated the energies of the hydrogen atom in discrete states according to the solution of his partial-differential equation in coordinates in two systems -- spherical polar and paraboloidal, respectively. The former might be primarily appropriate to an isolated hydrogen atom subject to no external influence, so without breaking

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symmetry O_4 (also written as O(4)) of that atom, whereas the primary purpose of the latter coordinates was to facilitate the calculation of the influence of an externally applied electric field according to the linear Stark effect, which breaks that O_4 symmetry. Although a confirmation that a separation of coordinates in a molecular context is practicable also in ellipsoidal coordinates in an application to H_2^+ followed shortly [2] after Schroedinger's original work, a half century passed before the analogous recognition of spheroconical coodinates [3]. Of coordinates in those four systems in which Schroedinger's temporally independent equation is separable, the amplitude functions in ellipsoidal coordinates have as limiting cases the corresponding amplitude functions in either spherical polar coordinates, as distance d between the two centres of the ellipsoidal system tends to zero, or paraboloidal coordinates, as $d \to \infty$. In all three systems, one common coordinate ϕ is the equatorial angle between a half-plane containing polar axis z and the projection of a given point (x,y,z) and a reference half-plane also containing the polar axis, so as to define a half-plane extending from that polar axis; associated equatorial quantum number m is correspondingly common to these three systems. In the fourth system that we describe as spheroconical coordinates (called also spheroconal), that equatorial angular coordinate ϕ is, in contrast, no longer a member of the set; this system is hence distinct from the other three systems in that regard, but retains a radial distance r in common with spherical polar coordinates.

In this part IV of a series of articles devoted to the hydrogen atom with its coordinates separable in four systems, we state the temporally independent partial-differential equation in spheroconical coordinates and its direct solution, for the first time, and provide plots of selected amplitude functions as surfaces corresponding to an appropriately chosen value of amplitude; no plot of an explicit spheroconical amplitude function is previously reported. As the dependence on time occurs in the same manner in all systems of coordinates in which the Schroedinger equation is separable, we accept the results from part I [4] and avoid that repetition. Although the equations governing the form of the amplitude functions are here, of necessity, defined in coordinates according to a spheroconical system, we view the surfaces of these amplitude functions invariably in rectangular cartesian coordinates: a computer procedure (in *Maple*) translates effectively from the original system in which the algebra and calculus are performed to the system to which a human eye is accustomed.

II. SCHROEDINGER'S EQUATION IN SPHEROCONICAL COORDINATES

Among the three coordinates for three spatial dimensions, we define two right elliptical cones, each with two nappes, orientated about axes x and z that complement a radial distance r from the origin, as presented with surfaces of constant values of these coordinates in figure 1; each nappe must have an elliptical cross section perpendicular to its respective axis. Such elliptical cones might be considered to be limiting geometric cases of paraboloids that occur in the paraboloidal coordinates or the hyperboloid that occurs in the ellipsoidal coordinates. These spheroconical coordinates ξ,r,η are related to cartesian coordinates x,y,z as follows:

$$x = \frac{r\sqrt{(b^2+\xi^2)\,(b^2-\eta^2)}}{b},\ y = \frac{r\,\xi\,\eta}{a\,b},\ z = \frac{r\sqrt{(a^2-\xi^2)\,(a^2+\eta^2)}}{a}$$

the use here of ξ and η as symbols for dimensionless coordinates is not to be confused with those same symbols to denote coordinates in the ellipsoidal system. The domains of these coordinates are $-a \le \xi \le a$, $0 \le r < \infty$, $-b \le \eta \le b$. To conform to a requirement that $a^2 + b^2 = 1$ that enables the separation of coordinates in Schroedinger's partial-differential equation, we set $a = b = 1/\sqrt{2}$; the square root of the sum of the squares of the coordinates according to the above definitions, i.e. $(x^2 + y^2 + z^2)^{½} = r$, simplifies the form of the electrostatic potential energy. Required in integrals over volume, the jacobian of the transformation of coordinates is

$$\frac{4\, r^2\, (\eta^2 + \xi^2)}{\sqrt{(-4\, \xi^4 + 1)\,(-4\, \eta^4 + 1)}}\, .$$

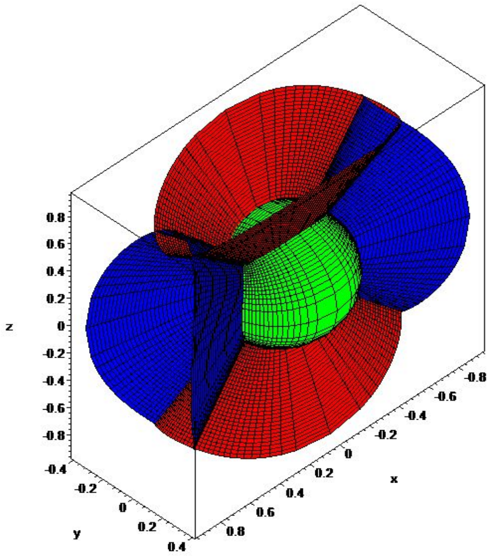

FIGURE 1. Definition of spheroconical coordinates ξ, *r*, η: a surface of a double elliptical cone (red), opening along positive and negative axis *z*, has ξ = ¼ and its apices at the origin; a surface of a sphere (green) has its centre at the origin and radius *r* = 2/5 units; a surface of another double elliptical cone (blue), opening along positive and negative axis *x*, has *η* = ¼ and its apices at the origin.

After separation of the coordinates of the centre of mass of the H atom, Schroedinger's temporally independent equation in explicit SI units contains within terms on the left side an electrostatic potential energy, proportional to r^{-1}, and first and second partial derivatives of an assumed amplitude function $\psi(\xi,r,\eta)$ with respect to spatial coordinates ξ, *r*, η within hamiltonian operator $H(\xi,r,\eta)$; the right side comprises a product of energy as parameter *E* independent of ccordinates with the same amplitude function, so that the entire equation resembles an eigenvalue relation expressed as $H(\xi,r,\eta)\ \psi(\xi,r,\eta) = E\ \psi(\xi,r,\eta)$.

$$- h^2 \left(- \frac{\xi^4 \left(\frac{\partial^2}{\partial \xi^2} \psi(\xi, r, \eta) \right)}{r^2\, (\eta^2 + \xi^2)} + \frac{\eta^2 \left(\frac{\partial^2}{\partial r^2} \psi(\xi, r, \eta) \right)}{\eta^2 + \xi^2} + \frac{\xi^2 \left(\frac{\partial^2}{\partial r^2} \psi(\xi, r, \eta) \right)}{\eta^2 + \xi^2} \right.$$
$$\left. - \frac{\eta^4 \left(\frac{\partial^2}{\partial \eta^2} \psi(\xi, r, \eta) \right)}{r^2\, (\eta^2 + \xi^2)} - \frac{2 \left(\frac{\partial}{\partial \xi} \psi(\xi, r, \eta) \right) \xi^3}{r^2\, (\eta^2 + \xi^2)} + \frac{2 \left(\frac{\partial}{\partial r} \psi(\xi, r, \eta) \right) \eta^2}{r\, (\eta^2 + \xi^2)} \right.$$

$$+\frac{2\left(\frac{\partial}{\partial r}\psi(\xi,r,\eta)\right)\xi^2}{r\,(\eta^2+\xi^2)}-\frac{2\left(\frac{\partial}{\partial \eta}\psi(\xi,r,\eta)\right)\eta^3}{r^2\,(\eta^2+\xi^2)}+\frac{\frac{\partial^2}{\partial \xi^2}\psi(\xi,r,\eta)}{4\,r^2\,(\eta^2+\xi^2)}+\frac{\frac{\partial^2}{\partial \eta^2}\psi(\xi,r,\eta)}{4\,r^2\,(\eta^2+\xi^2)}\Bigg)$$

$$\Big/\,(8\,\pi^2\,\mu)-\frac{Z\,e^2\,\psi(\xi,r,\eta)}{4\,\pi\,\varepsilon_0\,r}=E\,\psi(\xi,r,\eta)$$

Apart from fundamental physical constants electric permittivity of free space ε_0, Planck constant h and protonic charge e, there appear parameters Z for atomic number – $Z = 1$ for H – and μ for the reduced mass of the atomic system, practically equal to the electronic rest mass m_e, apart from energy E that is absent from the temporally dependent Schroedinger equation in these same coordinates. After separation of the variables in the partial-differential equation to produce a product of functions of each a single variable,

$$\psi(\xi,r,\eta) = \Xi(\xi)\,\mathrm{R}(r)\,\mathrm{H}(\eta)$$

and solution of the three consequent ordinary-differential equations including definition of the integration constants, the full solution of the above equation has this form [5],

$$\psi(\xi,r,\eta)=c\,N\sqrt{\frac{Z\,k!}{(1+2\,l+k)!\,a_0}}\left(\frac{2\,Z}{a_0\,(k+l+1)}\right)^{(l+1)} r^l\,\mathbf{e}^{\left(-\frac{Z\,r}{a_0\,(k+l+1)}\right)}$$

$$\mathrm{LaguerreL}\left(k,2\,l+1,\frac{2\,Z\,r}{a_0\,(k+l+1)}\right)\sqrt{1-2\,\xi^2}$$

$$\mathrm{HeunG}\left(-1,\kappa+\frac{1}{4},1+\frac{l}{2},-\frac{l}{2}+\frac{1}{2},\frac{1}{2},\frac{1}{2},-2\,\xi^2\right)\sqrt{1-2\,\eta^2}$$

$$\mathrm{HeunG}\left(-1,-\kappa+\frac{1}{4},1+\frac{l}{2},-\frac{l}{2}+\frac{1}{2},\frac{1}{2},\frac{1}{2},-2\,\eta^2\right)\Big/(k+l+1)$$

that has become simplified on incorporating Bohr radius a_0,

$$a_0=\frac{\varepsilon_0\,h^2}{\pi\,m_e\,e^2},$$

to contain other constants and parameters in a compact manner. That solution is formally normalized such that

$$\int \psi(\xi,r,\eta)^*\,\psi(\xi,r,\eta)\,\mathrm{d}vol = 1,$$

in which d*vol* is a volume element incorporating the jacobian specified above. Coefficient N is a normalizing factor, to be evaluated, to take into account that factors $\Xi(\xi)$ and $\mathrm{H}(\eta)$ of $\psi(\xi,r,\eta)$ are not separately normalized, unlike factor $\mathrm{R}(r)$. Coefficient c that equals a complex number of modulus unity such as a fourth root of unity – $c = \pm 1, \pm\sqrt{-1}$, appears because Schroedinger's equation is linear and homogeneous, or equally because that temporally independent equation has the form of an eigenvalue relation, as shown above. The conventional choice $c = 1$ – a choice that is arbitrary and lacks physical justification – imposes that solutions $\psi(\xi,r,\eta)$ as amplitude functions from Schroedinger's temporally independent equation appear in an entirely real form because a general Heun function, denoted HeunG, includes here no imaginary part; with a mathematically valid alternative choice $c = \pm\,\mathbf{i}$, amplitude functions would be entirely imaginary, thus alien to physical space, or $c = -1$ would merely reverse the phase of the amplitude function. This direct solution of the differential equations hence contains general Heun functions of coordinates both ξ and η appearing as their squares, not previously suggested to be applicable in this context; Lamé polynomials, of which products form ellipsoidal harmonics, have been instead mentioned [*3*], although no explicit formula was ever provided. The ellipsoidal harmonics in these spheroconical coordinates replace the spherical harmonics of spherical polar coordinates. Lamé's differential equation corresponds to a special case of the Heun differential equation with particular relations between the parameters; in the solution of the Heun differential equation, the fifth and sixth arguments in the general, or non-confluent, Heun function equal ½ for this particular Lamé case, as exhibited above. Parameters that appear in the solution but not the partial-differential equation take discrete variables, imposed by boundary conditions, as follows: radial quantum number k and azimuthal quantum number l appear in generalized Laguerre function $R(r)$ in exactly the same form as in spherical polar coordinates because, after the separation of variables, the ordinary-differential equation that governs $R(r)$ is exactly the same in both spherical polar and spheroconical coordinates. There is no constraint on the relative values of quantum numbers k and l, each of which assumes values of non-negative integers. Another quantity κ occurs in one of seven arguments of the general Heun function of each coordinate ξ and η; although these two coordinates have, by design, the same domain, specifically $-1/\sqrt{2}$ ... $1/\sqrt{2}$, κ occurs in distinct forms in those two arguments: $\kappa + 1/4$ for coordinate ξ, and $\kappa - 1/4$ for coordinate η. The energy depends on only k and l, hence $n = k + l + 1$ as for spherical polar coordinates; in the absence of an external field imposed on a hydrogen atom, the energy is thus independent of κ in spheroconical coordinates, as proved by calculations with varied κ, similarly to a lack of dependence on m in spherical polar coordinates [*4*].

III. GRAPHICAL REPRESENTATIONS OF AMPLITUDE FUNCTION $\psi(\xi,r,\eta)$

As these amplitude functions $\psi(\xi,r,\eta)$ in spheroconical coordinates were entirely unknown in an explicit algebraic form before this work, we here provide several instances of their nature and form, represented as surfaces in three spatial dimensions for ψ set equal to a particular value, analogously to the presentation of amplitude functions in other systems of coordinates in three preceding parts of this series of papers. All these functions contain general Heun functions that fail to simplify to an explicit algebraic structure when particular values of parameters are specified, but they might be converted approximately to polynomials through formation of Taylor series. The latter practice is useful primarily because the domain of each of ξ and η is finite; calculations, such as plots or integrations, involving these functions are thus implemented with such expansions within *Maple* to attain a satisfactory accuracy.

The formula for $\psi(\xi,r,\eta)$ for the state of least energy specified with quantum numbers $k = l = \kappa = 0$, with $Z = 1$ assumed here and in each following formula, is thereby expressed as

$$\psi_{0,0,0} = \frac{58720}{70219}\, \mathbf{e}^{\left(-\frac{r}{a_0}\right)} \sqrt{1-2\,\xi^2}\,\sqrt{1-2\,\eta^2}\;\mathrm{HeunG}\left(-1, \frac{1}{4}, \frac{1}{2}, 1, \frac{1}{2}, \frac{1}{2}, -2\,\xi^2\right)$$
$$\mathrm{HeunG}\left(-1, \frac{1}{4}, \frac{1}{2}, 1, \frac{1}{2}, \frac{1}{2}, -2\,\eta^2\right) \Big/ a_0^{(3/2)}$$

of which a surface for a particular value, $\psi_{0,0,0} = 0.008\ a_0^{-3/2}$, yields a shape shown in figure 2. In generating that formula for arguments in a particular set, a simplification is automatically incorporated involving the third and fourth arguments; there is hence no inconsistency between the general formula above and its particular representation here. In the absence of an explicit algebraic formula for the normalizing factor, we apply a numerical method that yields the numerical coefficient specified within this, and other, formula in rational form. In all plots of these surfaces of amplitude functions formed in spheroconical coordinates, the distance scale has unit a_0 = 5.2917721067x10^{-11} m; the value of the surface of $\psi(\xi,r,\eta)$ in each figure is 1/100 of the maximum value of $\psi(\xi,r,\eta)/a_0^{3/2}$ so that the corresponding volume of $\psi(\xi,r,\eta)^2$ encloses about 0.995 of the total electronic charge density. Because of the presence of factors $(1 - 2\,\xi^2)^{½}$ and $(1 - 2\,\eta^2)^{½}$ in each amplitude function, each such square root must be accommodated in both its positive and negative signs. The symmetric patterns observable in the plots reflect also the presence of ξ and η in the seventh arguments of the Heun functions appearing as squares. The surface of each spheroconical amplitude function $\psi(k,l,\kappa)$ must hence be plotted as four separate segments; a gap between each two segments results from the fact that calculation of the general Heun functions becomes slow when ξ or η is near either bound at ±1/√2, necessitating making the magnitudes of the bounds of these variables in the plot slightly less than 1/√2. Despite the presence of Bohr radius a_0 that is an atomic unit, the use of SI units is maintained throughout: a_0 serves as merely a scaling factor.

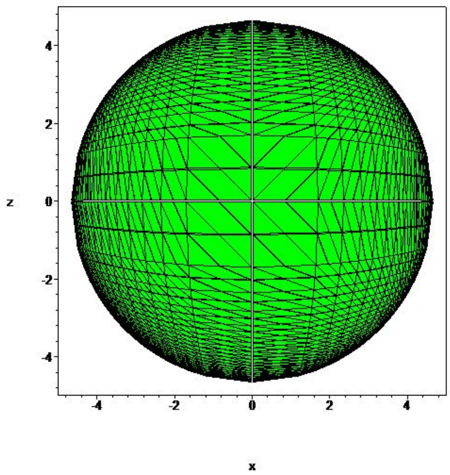

FIGURE 2. Surface of real spheroconical amplitude function $\psi_{0,0,0}$ = 0.008 $a_0^{-3/2}$; the distance scale here and in succeeding plots has unit a_0 = 5.2917721067x10^{-10} m.

The surface of $\psi_{0,0,0}$ = 0.008 $a_0^{-3/2}$ has hence a rigorously spherical shape; its radius is 4.72 a_0 = 2.47x10^{-10} m, exactly the same as for the surface of spherical polar amplitude function $\psi_{0,0,0}(r,\theta,\phi)$ or paraboloidal amplitude function $\psi_{0,0,0}(u,v,\phi)$ according to a corresponding criterion.

The variation of the shape of the surface of $\psi(k,l,\kappa)$ with κ is of particular interest because of the novelty of the present solution of the Schroedinger equation in spheroconical coordinates that uniquely contains this particular quantum parameter. For these amplitude functions with varied κ, the numerical normalizing factor for $\psi_{k,l,-\kappa}$ is the same as that of $\psi_{k,l,+\kappa}$ and is independent of the value of k. This formula for $\psi_{0,0,1}$,

$$\psi_{0,\,0,\,1} = \frac{12441}{30725}\,\mathbf{e}^{\left(-\frac{r}{a_0}\right)}\sqrt{1-2\,\xi^2}\,\sqrt{1-2\,\eta^2}\;\mathrm{HeunG}\left(-1,\frac{5}{4},\frac{1}{2},1,\frac{1}{2},\frac{1}{2},-2\,\xi^2\right)$$
$$\mathrm{HeunG}\left(-1,\frac{-3}{4},\frac{1}{2},1,\frac{1}{2},\frac{1}{2},-2\,\eta^2\right)\Big/\,a_0^{(3/2)}$$

yields a surface presented in figure 3; this surface is symmetric across planes $x = 0$, $y = 0$ and $z = 0$, and has planar nodal surfaces containing axis z. The positive lobes along axis x have the shapes of two spheroids that become pointed at the origin. The negative lobe resembles an elliptical torus around axis x, extending almost to the origin to separate the two positive lobes. The extent of the lobes parallel to axes x and y is about 13 a_0, but only 9 a_0 along axis z. The surface of the square of this amplitude function, which has accordingly only a positive phase, has a similar shape and size. The corresponding surface of $\psi_{0,0,-1}$ has a form similar to that of $\psi_{0,0,1}$, but its extent perpendicular to plane $x = 0$ is less than across planes $y = 0$ and $z = 0$; its positive lobes lie along axis z and its negative lobe resembles an elliptical torus around z.

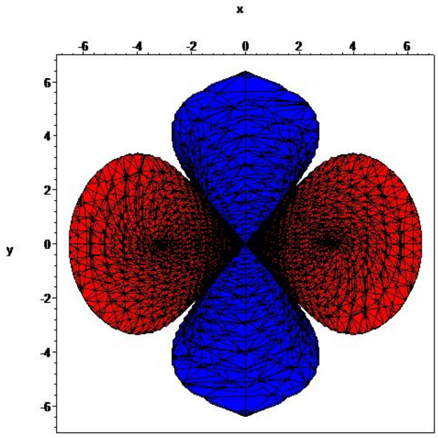

FIGURE 3. Surface of real spheroconical amplitude function $\psi(0,0,1) = 0.0041\ a_0^{-3/2}$, cut open to reveal the diagonal nodal surfaces; the positive lobes (red) extend along axis y and the negative lobe like an elliptical torus (blue) is perpendicular to axis y.

Spheroconical amplitude function $\psi_{0,0,2}$ conforms to this formula,

$$\psi_{0,0,2} = \frac{2783}{21438}\, \mathbf{e}^{\left(-\frac{r}{a_0}\right)} \sqrt{1-2\,\xi^2}\,\sqrt{1-2\,\eta^2}\ \mathrm{HeunG}\left(-1, \frac{9}{4}, \frac{1}{2}, 1, \frac{1}{2}, \frac{1}{2}, -2\,\xi^2\right)$$
$$\mathrm{HeunG}\left(-1, \frac{-7}{4}, \frac{1}{2}, 1, \frac{1}{2}, \frac{1}{2}, -2\,\eta^2\right) \Big/ a_0^{(3/2)}$$

and presents a surface in figure 4 in which there are again planar nodal surfaces through the origin that separate the positive and negative lobes; these lobes are symmetric across that origin, but the negative lobe is an elliptical torus around axis y; its cross section in plane $z = 0$ is larger than the cross section of the positive lobes, in contrast with the respective lobes of $\psi_{0,0,1}$. The corresponding surface of $\psi_{0,0,-2}$ has a similar form but with its positive lobes along axis z; the negative lobe resembles a flattened torus also about axis y, separating the positive lobes along axis z; its thickness parallel to axis x is thus less than that parallel to axes y and z.

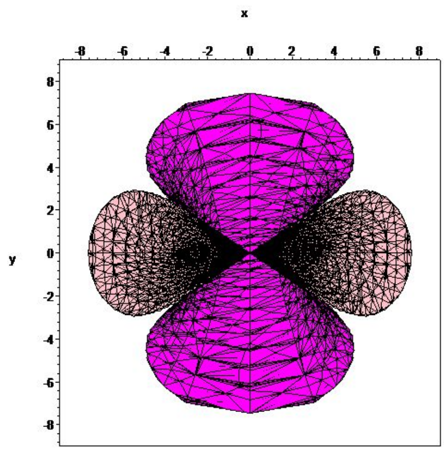

FIGURE 4. Surface of real spheroconical amplitude function $\psi_{0,0,2}$ = 0.0013 $a_0^{-3/2}$, cut open to reveal the diagonal nodal surfaces; the positive lobes (pink) extend along axis x and the negative lobe (magenta) is a torus about axis y.

Figure 5 shows a surface of real spheroconical amplitude function $\psi_{0,0,3}$ that conforms to this formula.

$$\psi_{0,\,0,\,3} = \frac{36998}{561969}\,\mathbf{e}^{\left(-\frac{r}{a_0}\right)}\sqrt{1-2\,\xi^2}\,\sqrt{1-2\,\eta^2}\,\mathrm{HeunG}\left(-1, \frac{13}{4}, \frac{1}{2}, 1, \frac{1}{2}, \frac{1}{2}, -2\,\xi^2\right)$$
$$\mathrm{HeunG}\left(-1, \frac{-11}{4}, \frac{1}{2}, 1, \frac{1}{2}, \frac{1}{2}, -2\,\eta^2\right) \Big/ a_0^{(3/2)}$$

This surface exhibits three nodal surfaces: two such surfaces resemble hyperboloids oriented separating the spheroidal positive lobes, and plane x = 0 constitutes a third nodal surface. The single torus of $\psi(0,0,1)$ or $\psi(0,0,2)$ here is split into positive and negative lobes with the planar nodal surface between them. The surface of $\psi_{0,0,3}^2$ has a similar shape and size. The corresponding surface of real spheroconical amplitude function $\psi_{0,0,-3}$ has three analogous nodal surfaces and each lobe is symmetric across plane x = 0.

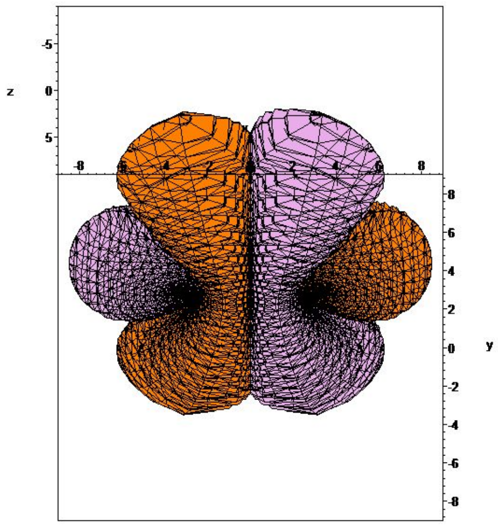

FIGURE 5. Surface of real spheroconical amplitude function $\psi_{0,0,3}$ = 0.00065 $a_0^{-3/2}$; the positive lobes (coral) are symmetrically related to the negative lobes (plum) across plane x=0 with reversed phase.

Figure 6 presents a surface of real spheroconical amplitude function $\psi_{0,0,4}$ that conforms to this formula.

$$\psi_{0,0,4} = \frac{2249}{57376} \mathbf{e}^{\left(-\frac{r}{a_0}\right)} \sqrt{1-2\,\xi^2}\,\sqrt{1-2\,\eta^2}\,\mathrm{HeunG}\left(-1, \frac{17}{4}, \frac{1}{2}, 1, \frac{1}{2}, \frac{1}{2}, -2\,\xi^2\right)$$
$$\mathrm{HeunG}\left(-1, \frac{-15}{4}, \frac{1}{2}, 1, \frac{1}{2}, \frac{1}{2}, -2\,\eta^2\right) \Big/ a_0^{(3/2)}$$

There are two positive lobes that extend along axis x from a point at the origin, and three lobes resembling tori about axis y, of which a positive toroidal lobe separates two negative toroidal lobes; all lobes are symmetric with respect to plane $z = 0$. The surface has an extent greater parallel to axes x and y than parallel to axis z. Real spheroconical amplitude function $\psi_{0,0,-4}$ has a similar shape and size; its toroidal lobes are also perpendicular to axis y, but its extension parallel to axis x is less than in the other two directions.

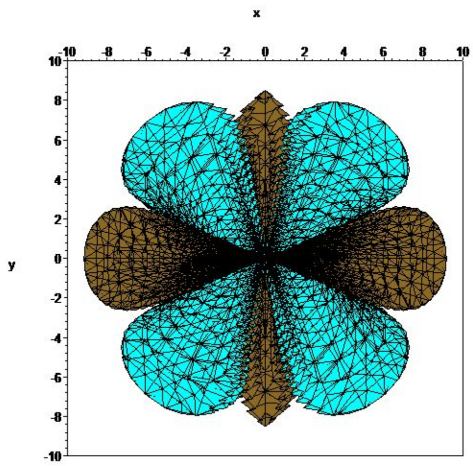

FIGURE 6. Surface of real spheroconical amplitude function $\psi_{0,0,4} = 0.00039\ a_0^{-3/2}$, cut open to reveal the four nodal surfaces that all cross the origin; the positive lobes (sienna) extend along axis x; two negative tori (cyan) with one positive torus (sienna) between them surround axis y.

As a first exhibit of the shape of a surface of a spheroconical amplitude function with quantum number $l > 0$, figure 7 shows first a surface of $\psi_{0,1,0}$, which conforms to this formula.

$$\psi_{0,1,0} = \frac{112337}{2139648} \sqrt{6}\, r\, \mathbf{e}^{\left(-\frac{r}{2\,a_0}\right)} \sqrt{1-2\,\xi^2}\,\sqrt{1-2\,\eta^2}\,\mathrm{HeunG}\left(-1, \frac{1}{4}, 0, \frac{3}{2}, \frac{1}{2}, \frac{1}{2}, -2\,\xi^2\right)$$
$$\mathrm{HeunG}\left(-1, \frac{1}{4}, 0, \frac{3}{2}, \frac{1}{2}, \frac{1}{2}, -2\,\eta^2\right) \Big/ a_0^{(5/2)}$$

For the particular surface of spheroconical amplitude function $\psi_{0,1,0}$ depicted in figure 7, the shape is roughly an oblate spheroid; the maximum extent in direction x or z is about 10.8 a_0, but only 9.4 a_0 in direction y. Only one lobe is discernible, corresponding to a positive phase of $\psi_{0,1,0}$; there is no nodal plane. As the amplitude function contains a factor r, the function has zero amplitude at the origin of the coordinate system and hence formally an inner surface at which $\psi_{0,1,0} = 0.00093\ a_0^{-3/2}$, but its radius is too small to appear even when the surface is cut open. The surface of $\psi_{0,1,0}^2$ resembles that of $\psi_{0,1,0}$ in figure 7, also having an oblate spheroidal shape with minor axis y.

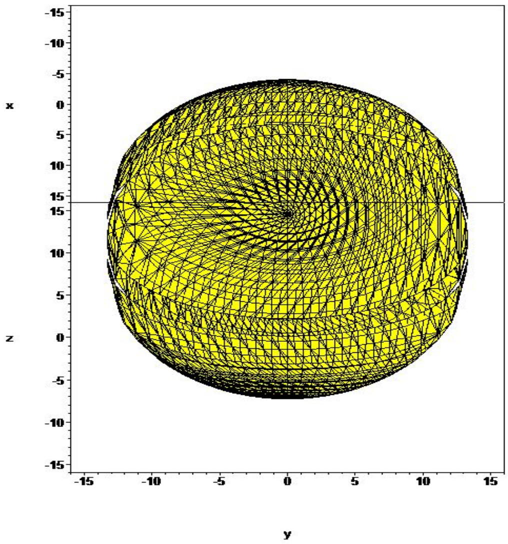

FIGURE 7. Surface of real spheroconical amplitude function $\psi_{0,1,0} = 0.00093\ a_0^{-3/2}$

Figure 8 shows the surface of $\psi_{0,2,0}$, which has this algebraic form.

$$\psi_{0,2,0} = \frac{8393}{6598665}\sqrt{30}\, r^2\, \mathbf{e}^{\left(-\frac{r}{3\,a_0}\right)}\sqrt{1-2\,\xi^2}\,\sqrt{1-2\,\eta^2}\ \mathrm{HeunG}\left(-1, \frac{1}{4}, \frac{-1}{2}, 2, \frac{1}{2}, \frac{1}{2}, -2\,\xi^2\right)$$
$$\mathrm{HeunG}\left(-1, \frac{1}{4}, \frac{-1}{2}, 2, \frac{1}{2}, \frac{1}{2}, -2\,\eta^2\right) \Big/ a_0^{(7/2)}$$

This surface shows four lobes, of alternating positive and negative phase around axis y, directed parallel to axis y between nodal planes $x = 0$ and $z = 0$. Its maximum extent parallel to axes x and z is about 14.3 a_0 but parallel to axis y only 11.1 a_0, so exhibiting an overall roughly oblate spheroidal shape. The shape of this surface strongly resembles the corresponding surface of the imaginary part of $\psi_{0,2,1}(r,\theta,\phi)$ in spherical polar coordinates.

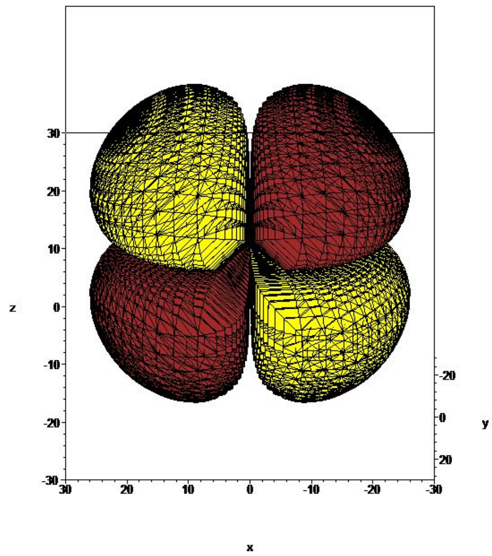

FIGURE 8. Surface of real spheroconical amplitude function $\psi_{0,2,0} = 0.00034\ a_0^{-3/2}$ with two positive lobes (yellow) and two negative lobes (brown)

Figure 9 shows the surface of amplitude function $\psi_{0,3,0}$, which has this algebraic form.

$$\psi_{0,3,0} = \frac{7135}{186267648}\sqrt{35}\, r^3\, \mathbf{e}^{\left(-\frac{r}{4 a_0}\right)} \sqrt{-2\,\xi^2+1}\,\sqrt{-2\,\eta^2+1}$$
$$\mathrm{HeunG}\left(-1, \frac{1}{4}, -1, \frac{5}{2}, \frac{1}{2}, \frac{1}{2}, -2\,\xi^2\right)\mathrm{HeunG}\left(-1, \frac{1}{4}, -1, \frac{5}{2}, \frac{1}{2}, \frac{1}{2}, -2\,\eta^2\right) \Big/ a_0^{(9/2)}$$

Whereas the surfaces of spheroconical amplitude functions $\psi_{0,0,0}$ and $\psi_{0,1,0}$ both have only one lobe and the surface of $\psi_{0,2,0}$ has four lobes, two of positive phase and two of negative phase, according to a phase convention with coefficient $c = 1$, amplitude function $\psi_{0,3,0}$ has ten lobes, four of negative phase along axes x and z; of six lobes of positive phase, four lie between planes xy and yz but two are located along axis y on either side of, and remote from, the origin.

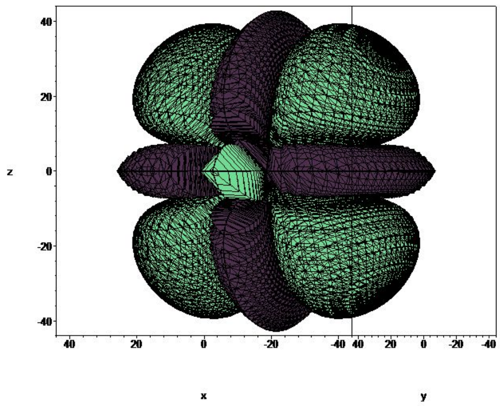

FIGURE 9. Surface of real spheroconical amplitude function $\psi_{0,3,0} = 0.00020\ a_0^{-3/2}$. The negative lobes (aquamarine) are directed along axes x and z; the positive lobes (violet) lie between those axes with additional small lobes located along axis y on either side of the origin.

Figure 10 shows the surface of amplitude function $\psi_{0,4,0}$, which has this algebraic form.

$$\psi_{0,4,0} = \frac{1226}{2877459375}\sqrt{70}\, r^4\, \mathbf{e}^{\left(-\frac{r}{5 a_0}\right)} \sqrt{1-2\,\xi^2}\,\sqrt{1-2\,\eta^2}$$
$$\mathrm{HeunG}\left(-1, \frac{1}{4}, \frac{-3}{2}, 3, \frac{1}{2}, \frac{1}{2}, -2\,\xi^2\right)\mathrm{HeunG}\left(-1, \frac{1}{4}, \frac{-3}{2}, 3, \frac{1}{2}, \frac{1}{2}, -2\,\eta^2\right) \Big/ a_0^{(11/2)}$$

Like spheroconical amplitude function $\psi_{0,3,0}$ and unlike function $\psi_{0,2,0}$ that exhibits only four lobes, of its ten lobes function $\psi_{0,4,0}$ has four lobes of positive phase between planes xy and yz, and two further and smaller lobes along axis y remote from the origin, but the positive lobes along axis y are larger than the corresponding features of function $\psi_{0,3,0}$; four negative lobes lie along axes x and z. The four positive lobes between the axes might appear to be connected across the origin, so separating the negative lobes, but factor r^4 in the formula for the amplitude function above imposes zero amplitude at the origin, independent of direction. For amplitude function $\psi_{0,5,0}$ that has no chemical or physical interest and is hence not shown here, the positive lobes along axis y become still larger relative to the other lobes.

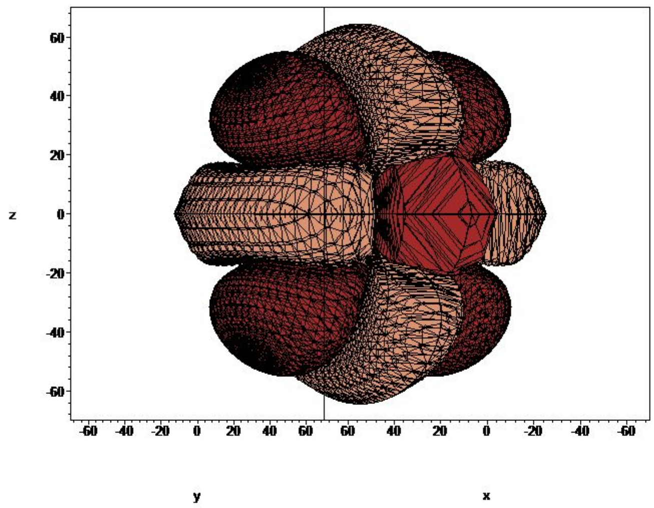

FIGURE 10. Surface of real spheroconical amplitude function $\psi_{0,4,0} = 0.000105\ a_0^{-3/2}$. The positive lobes (brown) are directed between axes x and z and the negative lobes (tan) lie along those axes, with additional positive lobes (brown) located along axis y farther from the origin.

Spheroconical amplitude function $\psi_{1,0,0}$ has this formula;

$$\psi_{1,0,0} = \frac{7340}{70219}\sqrt{2}\,\mathbf{e}^{\left(-\frac{r}{2\,a_0}\right)}\sqrt{1-2\,\xi^2}\,\sqrt{1-2\,\eta^2}\,(2\,a_0 - r)\,\mathrm{HeunG}\left(-1, \frac{1}{4}, \frac{1}{2}, 1, \frac{1}{2}, \frac{1}{2}, -2\,\xi^2\right)\mathrm{HeunG}\left(-1, \frac{1}{4}, \frac{1}{2}, 1, \frac{1}{2}, \frac{1}{2}, -2\,\eta^2\right) \Big/ a_0^{(5/2)}$$

its surfaces have the shape shown in figure 11. Three concentric spheres display their centres at the origin: one innermost sphere has a positive phase, and an only slightly larger sphere has a negative phase; the latter sphere and the outer sphere demarcate a spherical shell of negative phase. These surfaces strongly resemble those of $\psi_{1,0,0}(r,\theta,\phi)$ in spherical polar coordinates.

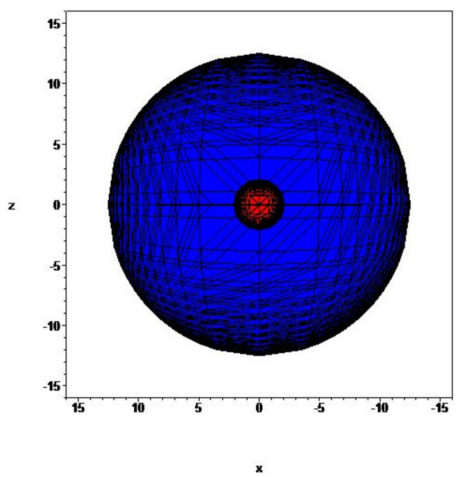

FIGURE 11. Surface of real spheroconical amplitude function $\psi_{1,0,0} = 0.0014\ a_0^{-3/2}$ cut open to reveal the interior structure; a small inner positive spherical lobe (red) is surrounded with a thick negative spherical shell (blue).

Spheroconical amplitude function $\psi_{1,1,0}$ has this formula;

$$\psi_{1,1,0} = \frac{112337}{21663936}\sqrt{6}\, r\, \mathbf{e}^{\left(-\frac{r}{3 a_0}\right)} \sqrt{1-2\xi^2}\sqrt{1-2\eta^2}\,(6 a_0 - r)$$
$$\mathrm{HeunG}\left(-1, \frac{1}{4}, 0, \frac{3}{2}, \frac{1}{2}, \frac{1}{2}, -2\xi^2\right) \mathrm{HeunG}\left(-1, \frac{1}{4}, 0, \frac{3}{2}, \frac{1}{2}, \frac{1}{2}, -2\eta^2\right) \Big/ a_0^{(7/2)}$$

its surfaces of constant $\psi_{1,1,0}$ have the shape exhibited in figure 12. Like the surfaces of amplitude function $\psi_{1,0,0}$ in figure 11, there is a small inner spheroidal surface, nearly spherical and of positive phase, surrounded closely with a surface of negative phase and an outer spheroidal surface, oblate like that of amplitude function $\psi_{0,1,0}$ presented in figure 7, that marks the distance at which the amplitude function decays to the stated value on its way asymptotically to zero.

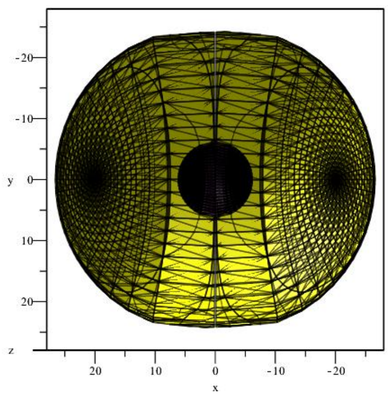

FIGURE 12. Surface of real spheroconical amplitude function $\psi_{1,1,0}$ = 0.00053 $a_0^{-3/2}$, cut open to reveal the interior structure; an inner positive spherical lobe (violet) is surrounded with a thick negative oblate spheroidal shell (yellow).

Surfaces of further real spheroconical amplitude functions $\psi_{k,l,\kappa}$ exhibit features that are predictable on the basis of the figures presented above, specifically that inner spheres numbering k appear within an outer surface resembling that of $\psi_{0,l,\kappa}$.

IV. DISCUSSION

Like coordinates in three other systems, as specified in three preceding papers in this series, the spheroconical coordinates enable a separation of the variables in the temporally independent Schroedinger equation, with a restriction on variables ξ and η that limits each domain to the same interval −1/√2 to +1/√2 in a unit with no physical dimension. Only radial distance r from the origin is common to another system of coordinates. In conjunction with these three distinct variables, three quantum parameters k, l and κ characterize these spheroconical amplitude functions and the shapes of their surfaces of $\psi_{k,l,\kappa}$ set at a selected value. Although the amplitude functions in this spheroconical system have uniquely defined algebraic formulae and shapes of their surfaces according to the specified criterion, a transformation of coordinates converts an amplitude function of this system into amplitude functions of a selected other system in an appropriate linear combination, just as illustrated between spherical polar and paraboloidal coordinates in part II of this series [7]. The existence of such a general transformation in no way makes one system, and the amplitude functions expressed therein, objectively superior or preferable to another system and its particular functions. The great advantage of amplitude functions in this spheroconical system is that, with coefficient $c = 1$, all formulae are *real* – i.e. have no imaginary part, so that their full surfaces can be presented directly in real space, as figures 2 – 12 demonstrate emphatically. Amplitude functions $\psi_{k,l,\kappa}(\xi,r,\eta)$ beyond those depicted in the eleven specified figures show inner spheroidal surfaces directly analogous to those of surfaces of $\psi_{k,l,m}(r,\theta,\phi)$ or amplitude functions in the two other systems of coordinates, just as the surfaces in figures 11 and 12 transcend those of figures 2 and 7.

Regarding spheroconical amplitude functions $\psi_{0,0,\kappa}$, their size increases slightly with increasing κ, and the number of nodal surfaces tends also to increase, although not from $\psi_{0,0,1}$ to $\psi_{0,0,2}$. In all cases there exist axes of symmetry two fold along the coordinate axes, which reflects the dual axes about which the double cones of coordinates ξ and η locate; for the same reason, the planes of symmetry for the thinner extents are $z = 0$ for $\psi_{0,0,+\kappa}$ and $x = 0$ for $\psi_{0,0,-\kappa}$. Other planes of symmetry are generally also present. All lobes of $\psi_{0,0,\kappa}$ with $\kappa > 0$ begin at one of these two axes and have zero magnitude at that axis.

For spheroconical amplitude functions $\psi_{0,l,0}$, in contrast their size increases rapidly with increasing quantum number l, like the size of functions $\psi_{k,0,0}$, and according to the same property: the energy of such an amplitude function increases proportionally to $-1/(k + l + 1)^2$, in which quantum numbers k and l appear on an equivalent basis.

Because quantum numbers k for radial and l for angular momentum are precisely defined for amplitude functions in spheroconical coordinates, the spectrometric states conventionally expressed in terms of these quantum numbers are defined with respect to these coordinates equally as well as in spherical polar coordinates. Explicitly, the designation of a spectrometric state of the hydrogen atom not subject to an externally applied field is conventionally based on such a value of the quantum number for angular momentum – S states for $l = 0$, P states for $l = 1$, D states for $l = 2$ et cetera; energy quantum number n is directly included in such a designation as $n\ l$ and all states of the hydrogen atom are doublet states when the intrinsic angular momentum of the electron is taken into account, to yield a term symbol such as 1 ^{2}S, 2 ^{2}S, 2 ^{2}P et cetera. The presence of κ for spheroconical coordinates instead of equatorial quantum number m for spherical polar coordinates has no implication for this nomenclature.

Cook and Fowler [6] sought to explore solutions of the temporally independent Schroedinger equation for the hydrogen atom in spheroconical coordinates in terms of Lamé functions of the first and second kind, but produced neither an explicit formula for a spheroconical amplitude function nor a plot thereof.

V CONCLUSION

Amplitude functions in spheroconical coordinates have several attractive features: they are entirely real and hence lend themselves directly to a physical depiction in cartesian coordinate space, they are associated with integer values of quantum numbers k and l that define, in a sum with unity, the energy, and spectral states are readily associated with those quantum numbers. Like their real counterparts in spherical polar coordinates, they lack a particular directional character, having mostly an overall oblate spheroidal shape. Further assessment of their character and a comparison with the amplitude functions in other systems of coordinates appears in part V of this series of articles.

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