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# THE HYDROGEN ATOM ACCORDING TO WAVE MECHANICS – III. ELLIPSOIDAL COORDINATES

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## Abstract

Schroedinger's temporally independent partial-differential equation is directly solvable in ellipsoidal coordinates to yield three ordinary-differential equations; with a common factor in equatorial angular coordinate $\phi$ as in spherical polar and paraboloidal coordinates, the product of their solutions contains confluent Heun functions in coordinates $\xi$ and $\eta$ that impede further calculations at present. To provide plots of these functions, we apply published solutions from Kereselidze et al. in series to illustrate the dependence of the shape of the amplitude functions on distance $d$ between the foci of the ellipsoids, between limiting cases of amplitude functions in spherical polar coordinates as $d \to 0$ and in paraboloidal coordinates as $d \to \infty$. These ellipsoidal coordinates are most appropriate for a treatment of a hydrogen atom in a diatomic-molecular context.

## Resumen

La ecuación parcial-diferencial independiente de la temporalidad de Schroedinger es solucionable en coordenadas elipsoidales para producir tres ecuaciones diferenciales ordinarias. Así como en las coordenadas esféricas polares y paraboloidales, ella tiene otro factor en la coordenada angular ecuatorial $\phi$, cuyo producto de su solución contiene funciones Heun confluentes en coordenadas $\xi$ y $\eta$ que impiden cálculos adicionales en la actualidad. Las soluciones publicadas de Kereselidze et al se aplican en serie para proporcionar gráficos de estas funciones e ilustrar la dependencia de la forma de las funciones de amplitud en la distancia d entre los focos de los elipsoides, entre casos limitantes de funciones de amplitud en coordenadas polares esféricas cuando $d \to 0$ y en coordenadas paraboloidales cuando $d \to \infty$. Estas coordenadas elipsoidales son las más apropiadas para un tratamiento de un átomo de hidrógeno en un contexto diatómico-molecular.

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

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

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## I. INTRODUCTION

In Schroedinger's four articles in a series of title *Quantisation as a Problem of Proper Values* [*1*,*2*,*3*,*4*] through which he introduced wave mechanics, he applied his partial-differential equation to the solution of the hydrogen atom in spherical polar and paraboloidal coordinates, and specified a method to calculate the frequencies and intensities of spectral lines. As the type of central field of force in the hydrogen atom is coulombic, the variables in the partial-differential equation are separable in not only spherical polar and paraboloidal coordinates but also ellipsoidal and spheroconical coordinates. In each case, the solution of Schroedinger's partial-differential equation independent of time yields three ordinary-differential equations, one for each spatial variable in the definition of a space of three dimensions. In this part III of a series of articles devoted to the hydrogen atom with its coordinates separable in these four systems, we state the temporally independent partial-differential equation and its solution in ellipsoidal coordinates, and provide plots of selected amplitude functions as surfaces corresponding to a chosen value of amplitude. 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 [*5*], and avoid that repetition. Although the equations governing the form of the amplitude functions are here, of necessity, defined in coordinates according to an ellipsoidal 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 of coordinates in which the algebra and calculus are performed to the system to which a human eye is accustomed.

## II. SCHROEDINGER'S TEMPORALLY INDEPENDENT EQUATION IN ELLIPSOIDAL COORDINATES

We first relate these three mutually orthogonal ellipsoidal coordinates $\xi$, $\eta$, $\phi$ to cartesian $x$, $y$, $z$ and spherical polar coordinate $r$ as algebraic formulae in direct relations. The system of ellipsoidal, or prolate spheroidal, coordinates, which Pauling and Wilson [*6*] called confocal elliptical coordinates, has two centres, corresponding to the foci of a respective ellipsoid; the distance between these two centres we denote $d$. For distances $r_a$ and $r_b$ of an electron from one or other centre, we define two coordinates $\xi$ and $\eta$, which are dimensionless.

$$\xi = \frac{r_a + r_b}{d} \quad \eta = \frac{r_a - r_b}{d}$$

The relations between these dimensionless distance coordinates $\xi$ and $\eta$, with equatorial angle $\phi$, and cartesian and polar coordinates follow.

$$x = \frac{d\sqrt{(\xi^2 - 1)(1 - \eta^2)}\cos(\phi)}{2}, \quad y = \frac{d\sqrt{(\xi^2 - 1)(1 - \eta^2)}\sin(\phi)}{2},$$

$$z = \frac{d(\eta\,\xi + 1)}{2}, \quad r = \frac{d(\eta + \xi)}{2}, \quad \phi = \arctan\left(\frac{y}{x}\right)$$

The domains of these variables are $1 \leq \xi < \infty$, $-1 \leq \eta \leq +1$, $0 \leq \phi < 2\,\pi$. We take an atomic nucleus of electric charge $+Z > 0$ as being located at a centre of coordinates with $\xi = 1$ and $\eta = -1$; the other focus at distance $d$ has coordinates $\xi = 1$ and $\eta = 1$ and is a dummy centre with $Z = 0$, which might, however, become the location of another atomic nucleus in the case of a diatomic molecule, such as

$H_2^+$. Surfaces of constant values of these coordinates are for ξ an ellipsoid, for η an hyperboloid of one sheet, and for equatorial angle ϕ a half-plane extending from polar axis *z*, the latter as in both spherical polar and paraboloidal coordinates. Although coordinates ξ and η are both dimensionless, one might consider ξ to be quasi-radial and η to be quasi-angular. For use within the volume element in subsequent integrals, the jacobian of the transformation between cartesian and ellipsoidal coordinates, as defined above, is $\frac{(\eta^2-\xi^2)\,d^3}{8}$. Whereas these coordinates have been described as prolate spheroidal, the presence of a characteristic ellipsoid with its two foci makes preferable a description as ellipsoidal coordinates. These coordinates are illustrated in figure 1.

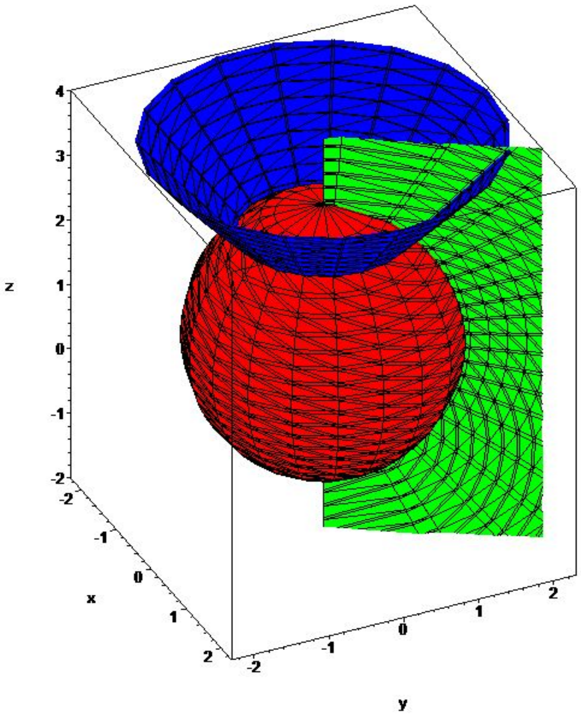


**FIGURE 1.** Surfaces of constant ellipsoidal coordinates: for the ellipsoid, ξ = 1.2 units, red; for the hyperboloid, η = π/4 units, blue; for the half-plane, equatorial angle ϕ = π/3 rad green.

A separation of the coordinates of the centre of mass of the H atom produces reduced mass μ of the system that is distant *r* from the origin, to supplant distance *r* between the electron and the atomic nucleus at one centre of the ellipsoid in the limit of infinite nuclear mass. Schroedinger's temporally independent equation in explicit SI units then contains within terms on the left side of the equality an electrostatic potential energy and first and second partial derivatives of an assumed amplitude function ψ(ξ,η,ϕ) with respect to spatial coordinates ξ, η, ϕ within an hamiltonian operator *H* ψ; the right side of the equality comprises a product of parameter energy, *E*, which is independent of coordinates, with the same amplitude function. The resultant form, as *H*(ξ,η,ϕ) ψ(ξ,η,ϕ) = *E* ψ(ξ,η,ϕ), resembles an eigenvalue relation:

$$
\begin{aligned}
\frac{1}{2} h^2 \Bigg( & \left(\frac{\partial^2}{\partial \xi^2} \psi(\xi, \eta, \phi)\right) \eta^2 \xi^4 - \left(\frac{\partial^2}{\partial \eta^2} \psi(\xi, \eta, \phi)\right) \eta^4 \xi^2 + 2 \left(\frac{\partial}{\partial \xi} \psi(\xi, \eta, \phi)\right) \eta^2 \xi^3 \\
& - 2 \left(\frac{\partial}{\partial \eta} \psi(\xi, \eta, \phi)\right) \eta^3 \xi^2 - 2 \left(\frac{\partial^2}{\partial \xi^2} \psi(\xi, \eta, \phi)\right) \eta^2 \xi^2 - \left(\frac{\partial^2}{\partial \xi^2} \psi(\xi, \eta, \phi)\right) \xi^4 \\
& + \left(\frac{\partial^2}{\partial \eta^2} \psi(\xi, \eta, \phi)\right) \eta^4 + 2 \left(\frac{\partial^2}{\partial \eta^2} \psi(\xi, \eta, \phi)\right) \eta^2 \xi^2 - 2 \left(\frac{\partial}{\partial \xi} \psi(\xi, \eta, \phi)\right) \eta^2 \xi \\
& - 2 \left(\frac{\partial}{\partial \xi} \psi(\xi, \eta, \phi)\right) \xi^3 + 2 \left(\frac{\partial}{\partial \eta} \psi(\xi, \eta, \phi)\right) \eta^3 + 2 \left(\frac{\partial}{\partial \eta} \psi(\xi, \eta, \phi)\right) \eta \xi^2 \\
& + \left(\frac{\partial^2}{\partial \xi^2} \psi(\xi, \eta, \phi)\right) \eta^2 + 2 \left(\frac{\partial^2}{\partial \xi^2} \psi(\xi, \eta, \phi)\right) \xi^2 - 2 \left(\frac{\partial^2}{\partial \eta^2} \psi(\xi, \eta, \phi)\right) \eta^2 \\
& - \left(\frac{\partial^2}{\partial \eta^2} \psi(\xi, \eta, \phi)\right) \xi^2 + \left(\frac{\partial^2}{\partial \phi^2} \psi(\xi, \eta, \phi)\right) \eta^2 - \left(\frac{\partial^2}{\partial \phi^2} \psi(\xi, \eta, \phi)\right) \xi^2 \\
& + 2 \left(\frac{\partial}{\partial \xi} \psi(\xi, \eta, \phi)\right) \xi - 2 \left(\frac{\partial}{\partial \eta} \psi(\xi, \eta, \phi)\right) \eta - \left(\frac{\partial^2}{\partial \xi^2} \psi(\xi, \eta, \phi)\right) + \left(\frac{\partial^2}{\partial \eta^2} \psi(\xi, \eta, \phi)\right) \\
\Bigg) & \Big/ (\pi^2 \mu (\eta^4 \xi^2 - \eta^2 \xi^4 - \eta^4 + \xi^4 + \eta^2 - \xi^2) d^2) - \frac{1}{2} \frac{Z e^2 \psi(\xi, \eta, \phi)}{\pi \varepsilon_0 d (\eta + \xi)} = E \psi(\xi, \eta, \phi)
\end{aligned}
$$

Apart from fundamental physical constants electric permittivity of free space $\varepsilon_0$, Planck constant $h$ and protonic charge $e$, there appear parameters $Z$ for atomic number – $Z = 1$ for H – and $\mu$ for the reduced mass of the atomic system, practically equal to the electronic rest mass $m_e$. After separation of the variables and solution of the three consequent ordinary-differential equations including definition of the separation parameters or integration constants, the eventual full solution of the above equation has exactly this form [7].

$$
\begin{aligned}
\psi(\xi, \eta, \phi) = c\, N (\xi^2 - 1)^{\left(\frac{|m|}{2}\right)} & (\eta^2 - 1)^{\left(\frac{|m|}{2} + \frac{1}{2}\right)} \mathbf{e}^{\left(-\frac{d Z (\xi + \eta + 1)}{2 a_0 n} + i m \phi\right)} \\
& \mathrm{HeunC}\left(\frac{2 d Z}{a_0 n}, |m|, |m|, \frac{2 d}{a_0}, -\frac{Z^2 d^2}{4 a_0^2 n^2} + \frac{m^2}{2} + \lambda - \frac{d}{a_0}, \frac{\xi}{2} + \frac{1}{2}\right) \\
& \mathrm{HeunC}\left(\frac{2 d Z}{a_0 n}, |m|, |m|, \frac{2 d}{a_0}, -\frac{Z^2 d^2}{4 a_0^2 n^2} + \frac{m^2}{2} + \lambda - \frac{d}{a_0}, \frac{\eta}{2} + \frac{1}{2}\right) \Big/ \sqrt{2 \pi}
\end{aligned}
$$

In this formula some clusters of fundamental constants have been replaced with Bohr radius $a_0$,

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

that invariably appears as a ratio with distance $d$ to maintain the correct dimensions; normalizing factor $N$ ensures that

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

in which d*vol* is a volume element containing the jacobian specified above; the implied triple integration is over all space. An asterisk as raised suffix of an amplitude function, so $\psi^*$, implies a complex conjugate of $\psi$ such that, wherever $\mathbf{i} = \sqrt{-1}$ appears in $\psi$, $-\mathbf{i}$ appears in $\psi^*$. The presence of

**i** in an exponential factor as product with equatorial angle $\phi$ signifies that this formula is complex, thus containing real and imaginary parts. Coefficient $c$ that equals any complex number of magnitude unity, such as a fourth root of unity – i.e. $\pm 1$, $\pm\sqrt{-1}$, occurs because the Schroedinger equation independent of time is a linear homogeneous partial-differential equation, or equally because the temporally independent Schroedinger equation has the form of an eigenvalue relation, as shown above. The conventional choice $c = 1$, which is arbitrary and lacks physical justification, signifies that some solutions $\psi(\xi,\eta,\phi)$ as amplitude functions from the temporally independent Schroedinger equation might appear in a purely real form; with a mathematically valid alternative choice $c = \mathbf{i}$, some amplitude functions might be entirely imaginary, but most would still be complex and thus alien to physical space. Choosing $c = -1$ or $-\mathbf{i}$ merely reverses the phase of an amplitude function or its constituent parts. Parameters that appear in the solution but not the partial-differential equation take discrete values, imposed by boundary conditions, as follows: $m$ is called the equatorial, or magnetic, quantum number that assumes values of only negative and positive integers and zero, and that arises in the solution of the equatorial angular equation to define $\Phi(\phi)$; $n$ denotes the energy quantum number, which is incorporated in the formula at several locations on comparison with the corresponding solutions in spherical polar coordinates. The third quantum parameter $\lambda$ that arises in this solution is unique to these ellipsoidal coordinates; it occurs only in the fifth argument of each confluent Heun function, so for these functions of $\xi$ and $\eta$ separately but in the same form. Apart from factor $(\eta^2 - 1)^{\left(\frac{|m|}{2} + \frac{1}{2}\right)}$ that also generally contributes a complex character to $H(\eta)$, the confluent Heun function containing variable $\eta$ might assume only real values, whereas the Heun function containing variable $\xi$ definitely assumes complex values, so having real and imaginary parts, in addition to the real and imaginary parts resulting from $i\, m\, \phi$ in the exponential term.

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

Not only for comparison with graphical representations of amplitude functions calculated in coordinates of other systems but also to present quantitatively accurate shapes and sizes of these functions, we display here some selected examples. As a plot involving three independent variables – spatial coordinates $\xi, \eta, \phi$ – and dependent variable $\psi(\xi,\eta,\phi)$ would require four dimensions, the best way to proceed with two dimensions, or three pseudo-dimensions, is to exhibit a surface of constant $\psi$ at a value selected to display the overall spatial properties of a particular amplitude function in a satisfactory manner. As our following figures demonstrate plainly, the shapes of these ellipsoidal amplitude functions depend markedly on distance $d$ between the centres of the ellipsoids. In the two limiting cases, as $d \to 0$, the shape of an amplitude function tends to a shape of a corresponding function in spherical polar coordinates, whereas, as $d \to \infty$, the shape tends to a shape of a respective function in paraboloidal coordinates. With the direct confluent Heun functions as specified above, these features are depicted with difficulty because the confluent Heun function of at least $\xi$, in the general formula above, has complex values, in addition to the complex character dictated in relation to equatorial angular coordinate $\phi$. Working with these confluent Heun functions is hence at present difficult; for this reason we present figures prepared with ellipsoidal amplitude functions indirectly obtained through solution of Schroedinger's equation in series [*8*], rather than our direct solution stated above. These functions $\psi_{n_\xi,n_\eta,m}$ are characterised with three quantum numbers -- $n_\xi$, $n_\eta$, $m$, of which equatorial quantum number $m$ has the same significance as for amplitude functions in spherical polar and paraboloidal coordinates; the values of $n_\xi$ and $n_\eta$ take non-negative integers, and $m$ positive and negative integers and zero, as before. The relation for energy quantum number is $n = n_\xi + n_\eta + |m| + 1$. When $d \to 0$, $n_\xi \to$ radial quantum number $k$ for spherical polar coordinates, $n_\eta \to l - |m|$; when $d \to \infty$, $n_\xi \to$ paraboloidal quantum number $n_1$ and $n_\eta \to n_2$ [8]. According to the nature of the preparation of these amplitude functions, their algebraic form contains long expressions in their algebraic normalizing factors involving polynomials in $d$ to inverse powers, except $\psi_{0,0,0}(\xi,\eta,\phi)$. In this formula and all succeeding formulae and plots, atomic number is set to $Z = 1$, so appropriate directly to the hydrogen atom.

$$\psi_{0,\,0,\,0} := \frac{\mathbf{e}^{\left(-\frac{d\,(\xi+\eta)}{2\,a_0}\right)}}{\sqrt{\pi}}$$

The plot of this surface, in figure 2, has the form of a perfect sphere.

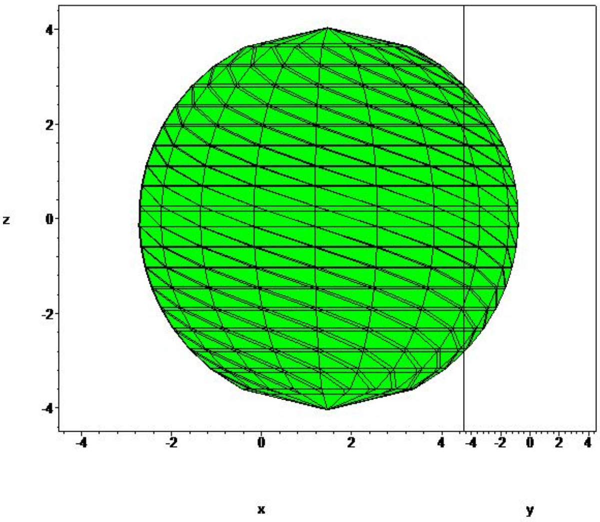


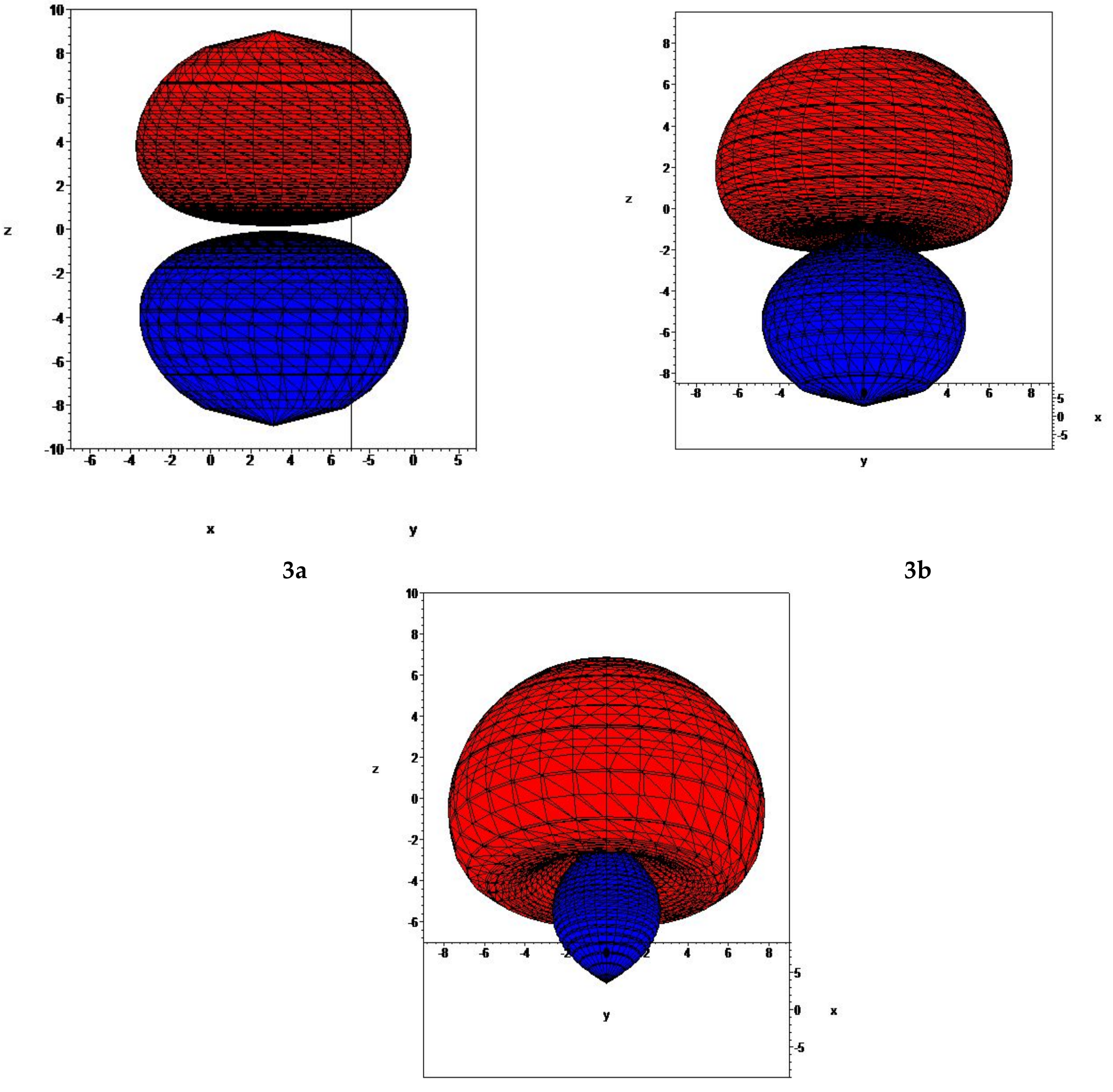
**FIGURE 2.** Surface of $\psi_{0,0,0} = 1/100\ a_0^{-3/2}$; as parameter $d$ is taken in unit $a_0$, the distance along each axis is expressed also in this unit, in this and succeeding plots of surfaces.

As in figures of surfaces of amplitude functions in spherical polar and paraboloidal coordinates in preceding parts of this series [5,9], this surface of an amplitude function at a stated value of that function is chosen such that the square of the amplitude function contains about 0.995 of the total electronic charge; this criterion is applicable to all further plots of surfaces presented in this article. The plot in figure 2 is actually formed with $d = 1/10\ a_0$, because a numerical value of $d$ must be provided to make such a plot. The shape, spherical, of this surface of constant $\psi$ is invariant with $d$; the size decreases only slightly, in unit $a_0$, as $d$ increases to 200 $a_0$; the reason is that, although variable $\eta$ has a fixed domain -1..1, the same for each plot, the extent of variable $\xi$ to make the plot varies greatly. For instance, for $d = a_0/10$, the necessary extent of $\xi$ is 1..90, whereas for $d = 200\ a_0$, the domain is only 1..1.041. Although all surfaces appear to have apparently pointed extremities along polar axis $z$, this effect is likely a distortion, due to a numerical artifact of the plotting routine with finite numerical accuracy for poorly behaved functions in terms of awkward arguments and of the conversion between ellipsoidal and cartesian coordinates. This amplitude function $\psi_{0,0,0}$ is the only one corresponding to energy quantum number $n = 1$.

For further amplitude functions of which the shape varies markedly with distance $d$, we exhibit a few surfaces at varied values of $d$, to illustrate the limiting and intermediate cases. As noted above, the limiting case as $d \to 0$ is a respective surface of an amplitude function in spherical polar coordinates; as $d \to \infty$, the respective surface is that in paraboloidal coordinates.

For the first instance, at distances $d/a_0$ = 1/10, 1.55 and 20 between the foci of the ellipsoids, in figures 3a, 3b and 3c respectively we exhibit $\psi_{0,1,0}$; this formula is expressed with symbolic normalizing factor $N_{0,1,0}$ because its explicit algebraic formula [8], which was used in the calculations to form the plot, is too long for practical presentation here.

$$\psi_{0,\,1,\,0} = N_{0,\,1,\,0}\, \mathbf{e}^{\left(-\frac{d\,(\xi+\eta)}{4\,a_0}\right)} \left(\xi - \frac{2\,a_0\left(1-\sqrt{1+\frac{d^2}{4\,a_0^{\,2}}}\right)}{d}\right)\left(\eta - \frac{2\,a_0\left(1-\sqrt{1+\frac{d^2}{4\,a_0^{\,2}}}\right)}{d}\right)$$



3a

3b

3c

**FIGURE 3**. Surfaces of $\psi_{0,1,0}$ = 1/100 $a_0^{-3/2}$ at, from top down, a) $d$ = 1/10 $a_0$, b) $d$ = 1.55 $a_0$ and c) $d$ = 20 $a_0$; the positive lobe is red and the negative lobe is blue.

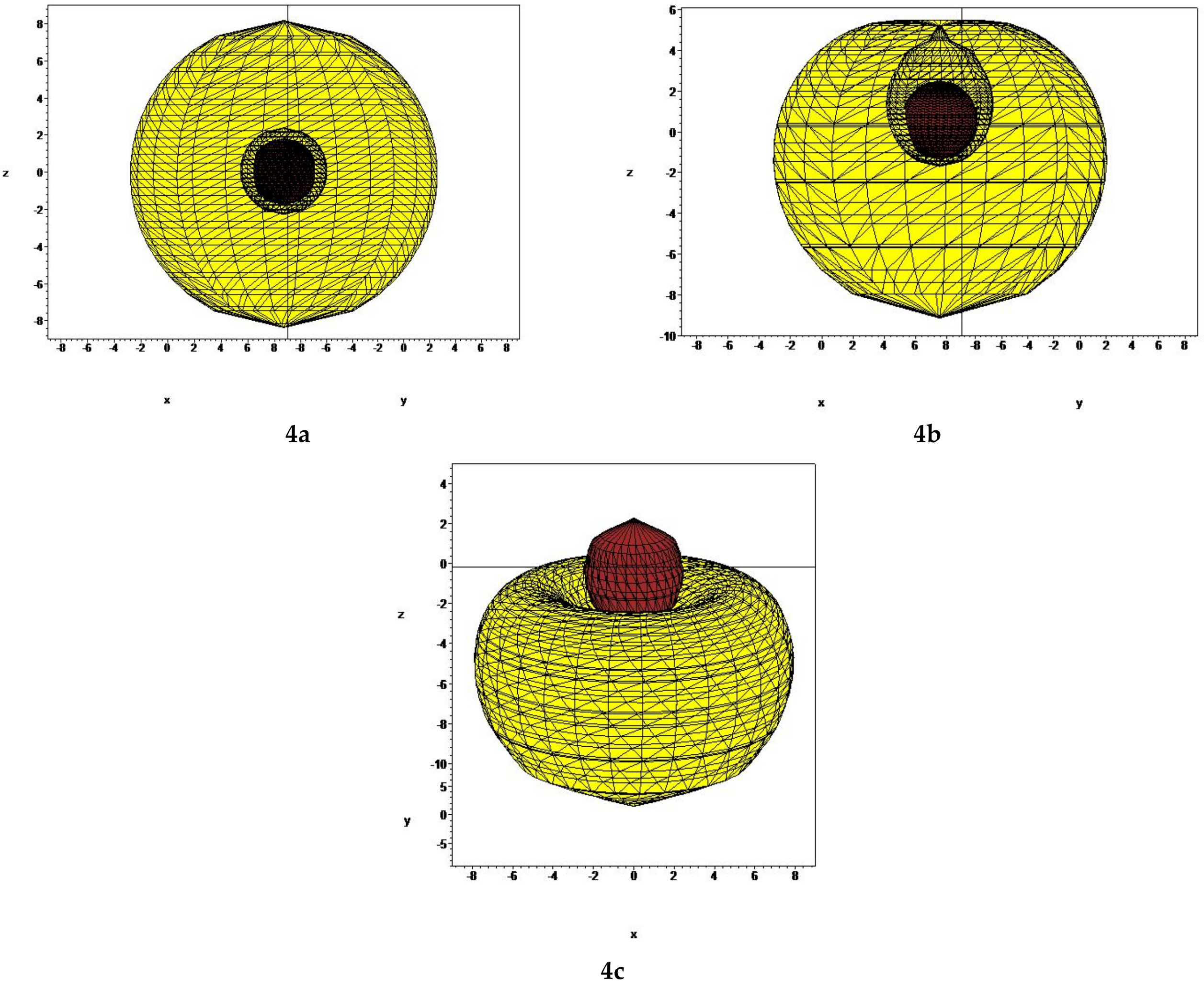
The shape of $\psi_{0,1,0}$ at $d$ = 1/10 $a_0$ is practically indistinguishable from that of $\psi_{0,1,0}(r,\theta,\phi)$ in spherical polar coordinates as shown in figure 8 of part I [*5*]: the two lobes are nearly hemispherical with rounded edges, and have nearly the same size with a nodal plane of zero amplitude between them. At $d$ = 20 $a_0$ the shape is nearly that of $\psi_{1,0,0}(u,v,\phi)$, as shown in figure 3 of part II [*9*]. The intermediate case at $d$ = 1.55 $a_0$ simply shows that the negative lobe contracts gradually and the volume of the positive lobe expands with increasing $d$.

The next amplitude function, $\psi_{1,0,0}$,

$$\psi_{1,0,0} =$$

$$N_{1,0,0}\,\mathbf{e}^{\left(-\frac{d(\xi+\eta)}{4a_0}\right)}\left(\xi-\frac{2a_0\left(1+\sqrt{1+\frac{d^2}{4a_0^2}}\right)}{d}\right)\left(\eta-\frac{2a_0\left(1+\sqrt{1+\frac{d^2}{4a_0^2}}\right)}{d}\right)$$

again expressed with symbolic normalizing factor of algebraic form that becomes converted to the appropriate numerical value, displays a different transition from one limit to the other, as shown in figures 4a, 4b, 4c at distances $d/a_0$ = 1/10, 1.55 and 20 respectively.



**4a**

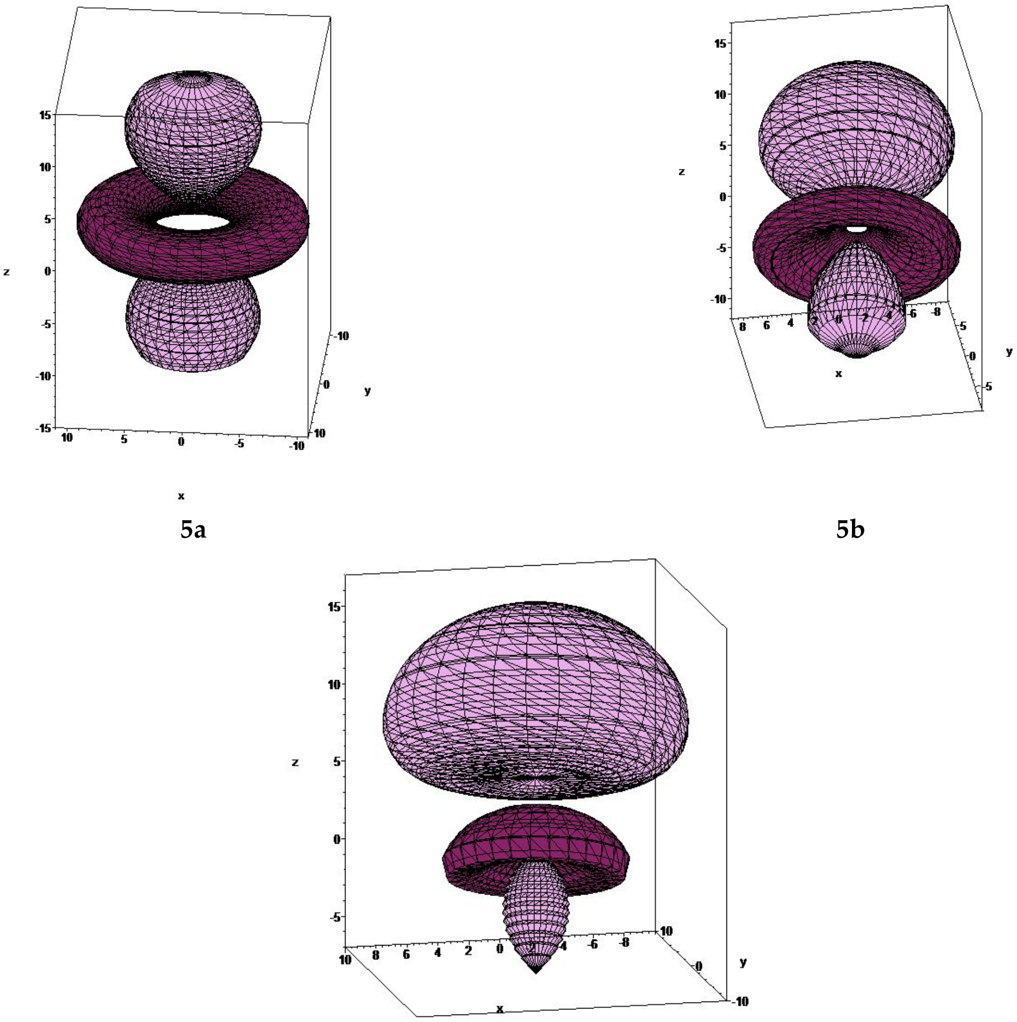
**4b**

**4c**

**FIGURE 4.** Surfaces of $\psi_{1,0,0}$ = 1/100 $a_0^{-3/2}$ at, from top down, a) $d$ = 1/10 $a_0$, b) $d$ = 1.55 $a_0$ and c) $d$ = 20 $a_0$; the positive lobe is brown and the negative lobe is yellow. The surfaces in figures 4a and 4b are cut open to reveal the internal structure.

The shape of the surface at $d$ = 1/10 $a_0$ in figure 4a is essentially identical with that of $\psi_{1,0,0}(r,\theta,\phi)$ in figure 7 [5], having one small and nearly spherical positive lobe totally enclosed within a second, nearly spherical, shell of negative phase. At $d$ = 20 $a_0$, the shape is nearly that of $\psi_{0,1,0}(u,v,\phi)$, just the reverse of that shape in figure 3c along axis $z$. The intermediate shape in figure 4b is chosen at $d$ = 1.55 $a_0$ because at that distance a minute gap opens in the outer shell at the top of the negative lobe, through which the inner positive lobe eventually emerges to be become entirely external, as in figure 4c. These two amplitude functions $\psi_{0,1,0}$ and $\psi_{1,0,0}$, with $\psi_{0,0,1}$ depicted below, have common energy quantum number $n$ = 2.

According to the solution in series [8], the next three amplitude functions involve the roots of a cubic equation, which, according to Viète's method, are expressed algebraically explicitly in terms of trigonometric functions and their inverses, specifically cosine and arc cosine; their forms [8] become consequently too voluminous for convenient presentation here, even with symbolic normalizing factors that would be even more extensive in explicit algebraic presentation. We hence merely present appropriate figures depicting the surfaces of these functions under the same conditions as above, first $\psi_{0,2,0}$ in figures 5a for $d$ = $a_0$/10, 5b for $d$ = 5 $a_0$ and 5c for $d$ = 20 $a_0$.



**5a**

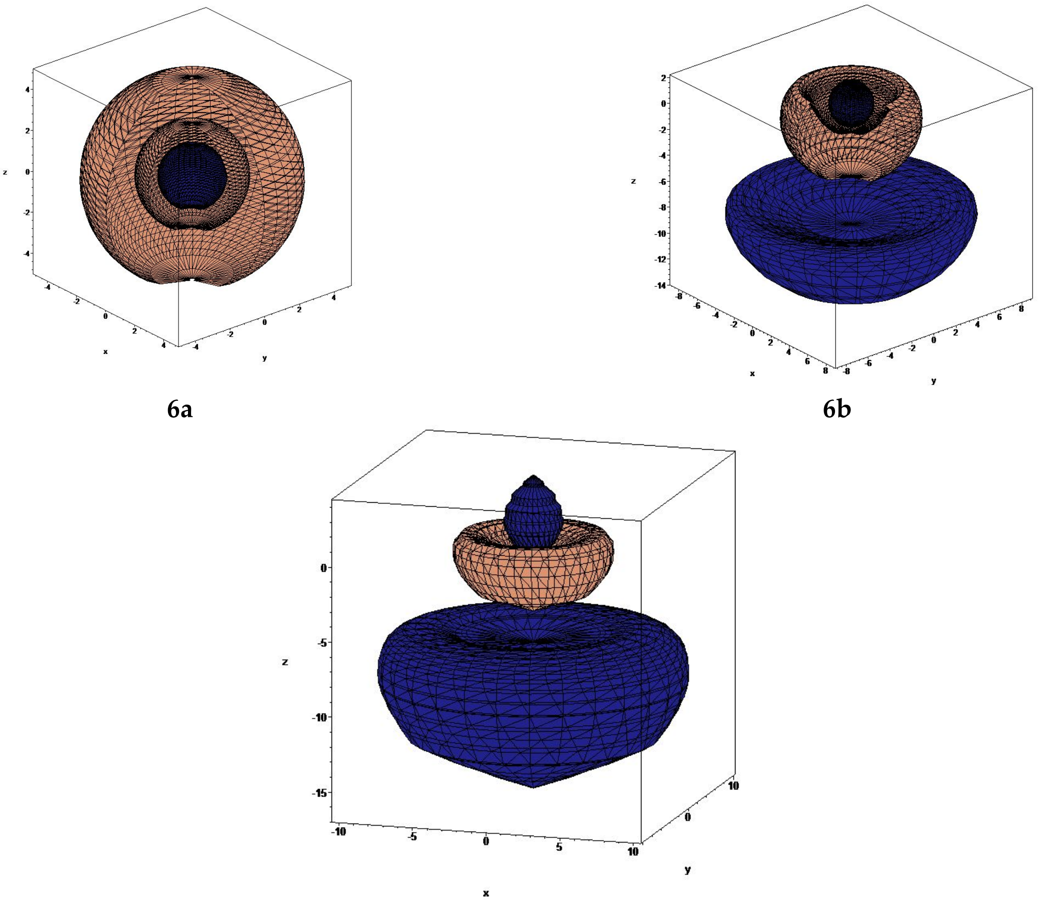
**5b**

**5c**

**FIGURE 5**. Surfaces of $\psi_{0,2,0}$ = 1/100 $a_0^{-3/2}$ at, from top down, a) $d$ = 1/10 $a_0$, b) $d$ = 5 $a_0$ and c) $d$ = 20 $a_0$; the positive lobe is plum colour and the negative lobe is maroon.

Whereas, at $d$ = 1/10 $a_0$, the two positive lobes have practically equal size on either side of a negative torus, similar to $\psi_{0,2,0}(r,\theta,\phi)$ in figure 11 [5], at $d$ = 20 $a_0$, the torus becomes transformed into an inverted bowl, with a small prolate spheroidal lobe below it and above it a large lobe of somewhat oblate spheroidal shape, as in figure 4 [9]. Here the intermediate case is chosen at $d$ = 5 $a_0$, because in that condition the negative lobe exhibits only a small orifice that becomes closed completely at $d$ = 20 $a_0$. Most surface at $d$ = 20 $a_0$ lies above plane $xy$ at $z$ = 0.

The next amplitude function is $\psi_{2,0,0}$ in figure 6a, b, c, with surfaces plotted at $d/a_0$ = 1/10, 1 and 20.



6a

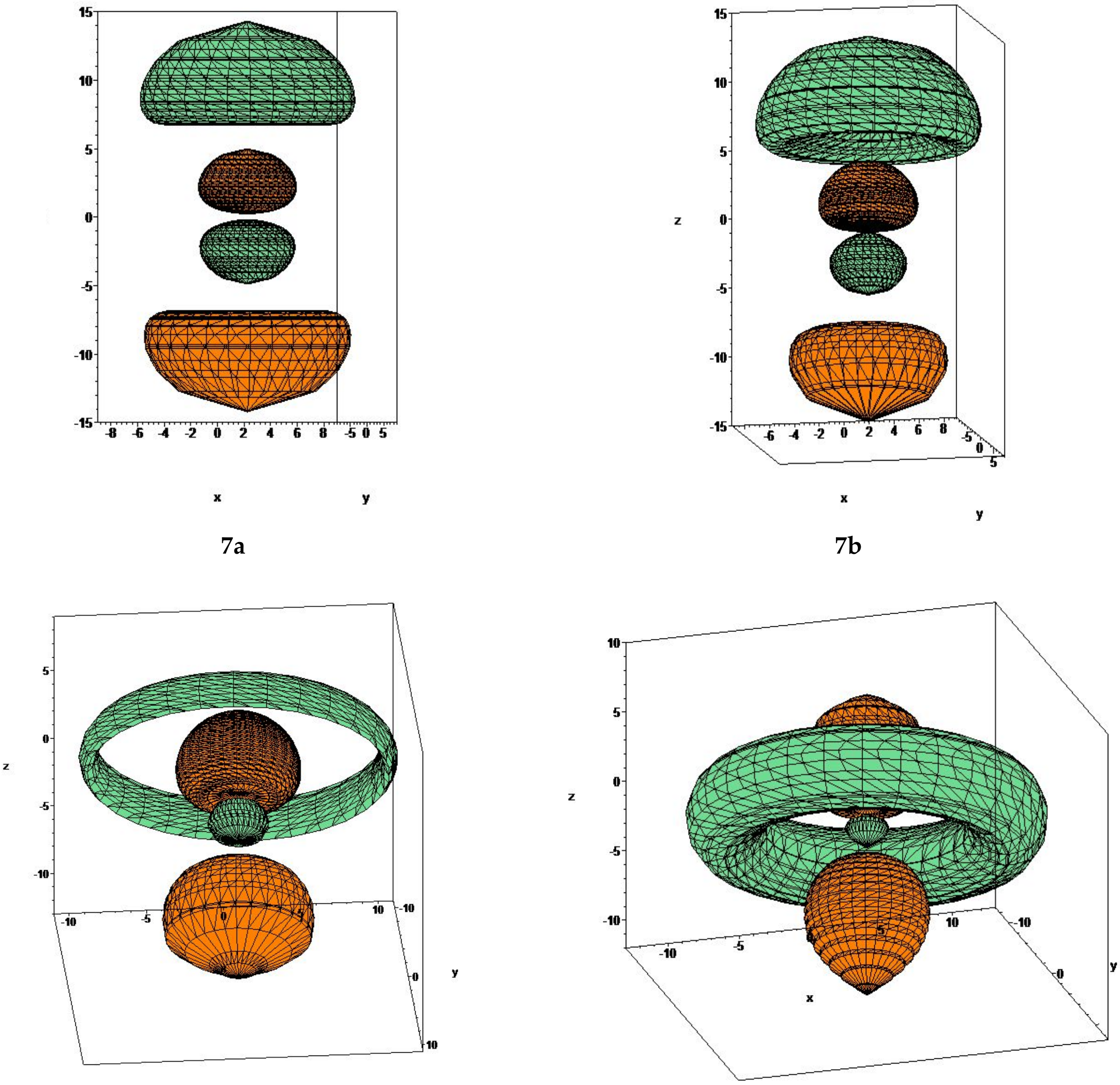
6b

6c

**FIGURE 6.** Surfaces of $\psi_{2,0,0} = 1/100\ a_0^{-3/2}$ at, from top down, a) $d = a_0/10$, b) $d = a_0$ and c) $d = 20a_0$; the positive lobes are navy blue and the negative lobe is tan. In figure 6a, all surfaces are cut open to reveal the interior structure; in figure 6b, only the negative lobe is cut open.

At distance $d$ = 1/10 $a_0$, figure 6a shows a nearly spherical inner lobe of positive phase surrounded by a nearly spherical shell of negative phase; their centres are at approximately the origin of the system of cartesian coordinates. At $d = a_0$, the inner and positive sphere has just emerged from its negative surrounding lobe at the top, but a second positive lobe of bowl shape appears below the negative lobe. At $d$ = 20 $a_0$, the upper positive lobe has a prolate spheroidal shape, partially below the rim of a negative lobe of bowl shape, and the lower positive lobe has almost a hemispherical shape, just the reverse of figure 5c along polar axis $z$. Most surface of this amplitude function is below plane $xy$ at $z$ = 0.

The next amplitude function is $\psi_{1,1,0}$, of which surfaces in figures 7a,b,c,d appear at $d = a_0/10$, $a_0$, 5 $a_0$ and 20 $a_0$, respectively.



7a

7b

7c

7d

**FIGURE 7.** Surfaces of $\psi_{1,1,0} = 1/100\ a_0^{-3/2}$ at, from top down, a) $d = 1/10\ a_0$, b) $d = a_0$, c) $d = 5\ a_0$ and d) $d = 20\ a_0$; the positive lobes have coral colour, the negative lobes aquamarine.

The total surface of $\psi_{1,1,0} = 1/100\ a_0^{-3/2}$ at $d = 1/10\ a_0$ comprises four lobes, two of each phase, one small lobe of each phase between the other small lobe and a large lobe; this pattern correlates with $\psi_{1,1,0}(r,\theta,\phi)$. At $d = a_0$, the upper negative lobe increases in breadth, but at $d = 5\ a_0$ it becomes a torus surrounding the upper part of a positive lobe; at $d = 20\ a_0$ that torus has moved to plane $xy$ nearly at $z = 0$, at which it surrounds the other small negative lobe that is nearly spherical at the origin. The two positive lobes have prolate spheroidal shapes and are nearly symmetrically disposed across plane $xy$ at $z = 0$. The latter shape correlates with $\psi_{1,1,0}(u,v,\phi)$ in paraboloidal coordinates. The latter three amplitude functions have energy quantum number $n = 3$.

Amplitude function $\psi_{0,0,1}$, or equivalently $\psi_{0,0,-1}$, has both real and imaginary parts, according to the presence of an exponential factor containing **i** $m\,\phi$ with equatorial quantum number $m = 1$, in which $\mathbf{i} = \sqrt{-1}$ .

$$\psi_{0,\,0,\,1} = N_{0,\,0,\,1}\,\mathbf{e}^{\left(-\frac{d\,(\xi+\eta)}{4\,a_0}\right)}\sqrt{(\xi^2-1)\,(-\eta^2+1)}\;\mathbf{e}^{(i\,\phi)}$$

Figure 8 presents the imaginary part of this amplitude function, of which the shape and size of the surface are practically invariant with varying distance $d$.

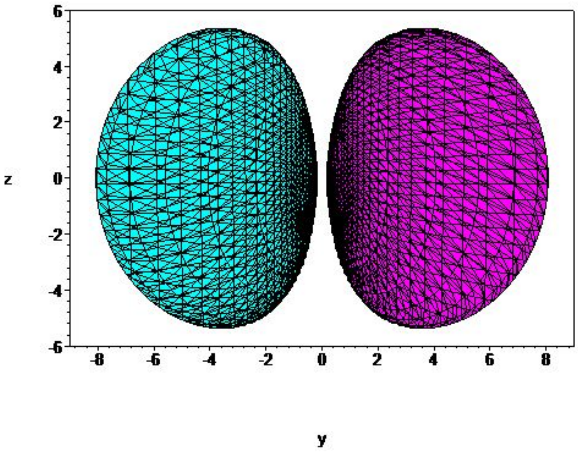


**FIGURE 8.** Surface of the imaginary part of $\psi_{0,0,1} = 1/100\ a_0^{-3/2}$ at $d = 1/10\ a_0$; the positive lobe is magenta and the negative lobe is cyan.

This surface is characteristic of $\psi_{0,0,1}(r,\theta,\phi)$ or $\psi_{0,0,-1}(r,\theta,\phi)$, and equivalently $\psi_{0,0,1}(u,v,\phi)$ or $\psi_{0,0,-1}(u,v,\phi)$, in either real or imaginary part. Although all preceding figures show surfaces of the depicted amplitude functions of which the surfaces are axially symmetric about the polar axis $z$, this surface is axially symmetric about cartesian axis $y$; its real counterpart is analogously axially symmetric about axis $x$, and the real and imaginary parts of $\psi_{0,0,-1}$ have analogous spatial dispositions axially symmetric about the same axes $x$ and $y$, respectively.

## IV. DISCUSSION

The three or four plots in each composite figure 3 - 7 demonstrate clearly how the familiar shape of the surface of an ellipsoidal amplitude function [*5*] for distance $d$ between foci nearly zero, which resembles a surface of an amplitude function in spherical polar coordinates, transforms into a much less familiar shape resembling the surface of a corresponding amplitude function in paraboloidal coordinates [*9*], as $d$ increases to a large value. The number of such amplitude functions that are available for this purpose is limited at present because of the problem of the complex nature of confluent Heun functions in the directly derived amplitude functions and because of the intractability of explicit algebraic solutions of quartic polynomials in the indirectly derived functions [*8*]. When one is able to plot real amplitude functions in both limiting cases and deduces the appropriate correlation, it is not difficult to imagine the course of the gradual transformation between those two limiting cases with increasing or decreasing distance $d$ between the foci of the ellipsoids; the two limiting cases must conform to the same value of energy quantum number $n$. As all these amplitude functions are common to the hydrogen atom, they must be convertible from one form, in one coordinate system, to another form in a separate coordinate system; this property would enable further explicit formulae to be generated through a transformation of coordinates, but the resulting expressions likely have a complicated algebraic form.

Much interest in the hydrogen atom treated in ellipsoidal coordinates arises because of the features pertinent to a system with two coulombic centres, such as $H_2^+$, for which ellipsoidal coordinates have long been applied [*6*]. Following the pioneering work of Burrau [*10*] and Wilson [*11,12*], Teller recognised that the amplitude functions from the solution of Schroedinger's equation in ellipsoidal coordinates to treat interatomic interactions in a diatomic molecule were applicable also to the hydrogen atom itself [*13*]. These ellipsoidal amplitude functions that result from the solution of Schroedinger's equation, either directly containing confluent Heun functions as presented above or indirectly through solution in series [*8*], are hence most appropriate for the treatment of a hydrogen atom, or analogous atomic ion with one electron, interacting with a point charge, located at the dummy focus; in such a case the atomic amplitude function, or atomic orbital, becomes *de facto* a molecular orbital. Other applications arise in an investigation of diatomic molecules or their ions in Rydberg states, or in other excited states [*14*]. As these confluent Heun functions become developed, these applications will become increasingly practical with the direct solutions of the Schroedinger equation.

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