

THE HYDROGEN ATOM ACCORDING TO WAVE MECHANICS – II. PARABOLOIDAL COORDINATES

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Abstract

In the second of five parts in a series, the Schroedinger equation is solved in paraboloidal coordinates to yield amplitude functions that enable accurate plots of their surfaces to illustrate the variation of shapes and sizes with quantum numbers n_1 , n_2 , m , for comparison with the corresponding plots of amplitude functions in coordinates of other systems. A useful property of these functions in paraboloidal coordinates is their application to treat the Stark effect, when a hydrogen atom is placed in an isotropic electric field.

Resumen

En el segundo de cinco artículos de esta serie, la ecuación de Schrödinger se resuelve en coordenadas parabólicas para producir funciones de amplitud que permiten gráficos exactos de superficies, para ilustrar la variación de formas y tamaños con números cuánticos n_1 , n_2 y m , y comparar con los gráficos correspondientes de funciones de amplitud en coordenadas de otros sistemas. Una propiedad útil de estas funciones en coordenadas paraboloideas es su aplicación para tratar el efecto Stark, cuando un átomo de hidrógeno se ubica en un campo eléctrico isotrópico.

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

Palabras clave: átomo de hidrógeno, mecánica cuántica, coordenadas parabólicas, orbitales, espectro atómico.

I. INTRODUCTION

In Schroedinger's third article of four in a series of title *Quantisation as a Problem of Proper Values* [1,2,3,4] with which he introduced wave mechanics, he applied his differential equation to the solution of the hydrogen atom in circular paraboloidal coordinates, and specified a method to calculate the intensities of spectral lines [3]. As the type of central field of force in the hydrogen atom is coulombic, the variables in the partial-differential equation are separable in paraboloidal coordinates, to yield three ordinary-differential equations, one for each spatial variable in the definition of a space of three dimensions. In this part II of a series of articles devoted to the hydrogen atom with its coordinates of the governing partial-differential equation separable in four

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systems, we state the temporally independent partial-differential equation and its solution in paraboloidal 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 a paraboloidal 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 the human eye is accustomed.

II. SCHROEDINGER'S EQUATION IN PARABOLOIDAL COORDINATES

We relate these mutually orthogonal circular paraboloidal coordinates u, v, ϕ to cartesian x, y, z , and spherical polar r, θ, ϕ coordinates as algebraic formulae in both direct and inverse relations according to an established convention [6].

$$\begin{aligned} x &= u v \cos(\phi), & y &= u v \sin(\phi), & z &= \frac{1}{2} (u^2 - v^2), & r &= \frac{1}{2} (u^2 + v^2) \\ u^2 &= r + z = r (1 + \cos(\theta)), & v^2 &= r - z = r (1 - \cos(\theta)), & \phi &= \arctan(y/x) \end{aligned}$$

Surfaces of u, v and ϕ as constant quantities are exhibited in figure 1. Although this system of coordinates might be described elsewhere as parabolic, the surfaces of two defining coordinates in three dimensions are clearly paraboloids, or parabolas of revolution, that have circular cross sections, which thus dictate the most informative name of the system. The surfaces of constant u describe confocal paraboloids about the polar axis, z in cartesian coordinates, that open in the direction of negative z or $\theta = \pi$ rad and have a focus at the origin; the surfaces of constant v analogously describe confocal paraboloids that open in the direction of positive z , or $\theta = 0$, and have also a focus at the origin. The limiting cases of u and v tend to a line along axis z as $u \rightarrow 0$ or $v \rightarrow 0$, with $z < 0$ and $z > 0$, respectively, and to a plane perpendicular to axis z as u or v becomes large with $z \gg 0$ or $z \ll 0$, respectively. The surfaces of constant equatorial angle ϕ have the same property as those in spherical polar coordinates – half-planes extending from the polar axis. With appropriate values of u, v and ϕ , a point can clearly locate anywhere in the coordinate space. For use within the volume element in subsequent integrals, the jacobian of the transformation between cartesian and paraboloidal coordinates, as defined above, is $u v (u^2 + v^2)$.

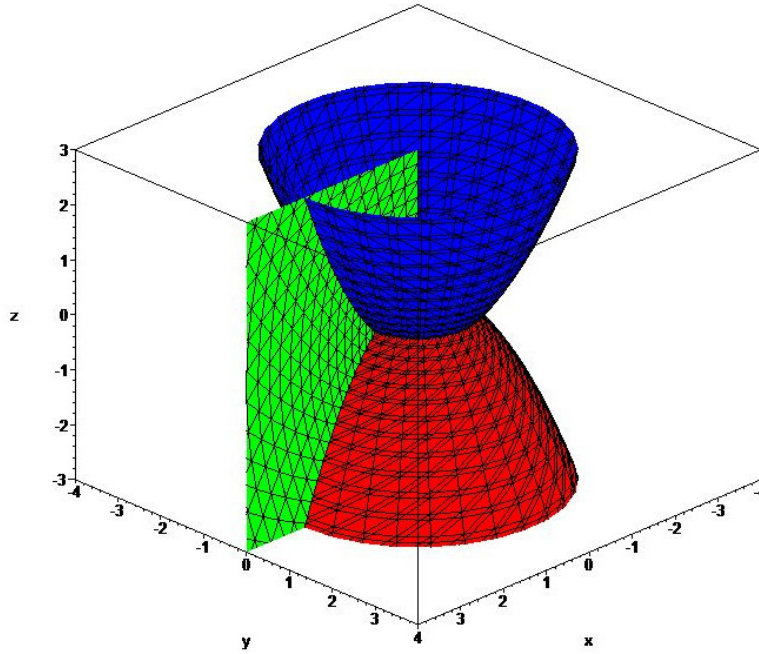


FIGURE 1. Definition of paraboloidal coordinates u, v, ϕ : a paraboloid opening along negative z (red) has $u = 1$ unit and a focus at the origin; another paraboloid (blue), opening along positive z , has $v = 1$ unit and a focus at the origin; a half-plane has equatorial angle $\phi = \pi$ rad with respect to plane xz .

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. 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 $\psi(u, v, \phi)$ with respect to spatial coordinates u, v, ϕ within an hamiltonian operator H to take into account the kinetic and potential energies of the system; the right side of the equality comprises a product of energy E , as a variable parameter that has no dependence on coordinates, with the same amplitude function. The resultant form, as $H(u, v, \phi) \psi(u, v, \phi) = E \psi(u, v, \phi)$, resembles an eigenvalue relation.

$$\begin{aligned}
 & -\frac{1}{8} \frac{h^2 \left(\frac{\partial}{\partial u} \psi(u, v, \phi) \right)}{\pi^2 \mu (u^2 + v^2) u} - \frac{1}{8} \frac{h^2 \left(\frac{\partial^2}{\partial u^2} \psi(u, v, \phi) \right)}{\pi^2 \mu (u^2 + v^2)} - \frac{1}{8} \frac{h^2 \left(\frac{\partial}{\partial v} \psi(u, v, \phi) \right)}{\pi^2 \mu (u^2 + v^2) v} \\
 & - \frac{1}{8} \frac{h^2 \left(\frac{\partial^2}{\partial v^2} \psi(u, v, \phi) \right)}{\pi^2 \mu (u^2 + v^2)} - \frac{1}{8} \frac{h^2 \left(\frac{\partial^2}{\partial \phi^2} \psi(u, v, \phi) \right)}{\pi^2 \mu (u^2 + v^2) v^2} - \frac{1}{8} \frac{h^2 \left(\frac{\partial^2}{\partial \phi^2} \psi(u, v, \phi) \right)}{\pi^2 \mu (u^2 + v^2) u^2} \\
 & - \frac{1}{4} \frac{Z e^2 \psi(u, v, \phi)}{\pi \epsilon_0 \left(\frac{u^2}{2} + \frac{v^2}{2} \right)} = E \psi(u, v, \phi)
 \end{aligned}$$

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 . After

separation of the variables and solution of the three consequent ordinary-differential equations including definition of the separation parameters or integration constants, the full solution of the above equation has exactly this formula [7].

$$\begin{aligned} \psi(u, v, \phi) = & c (-1)^{|m|} \sqrt{\frac{Z \pi \mu e^2}{\epsilon_0 h^2}} \sqrt{\frac{2 n_1! n_2!}{(n_1 + |m|)! (n_2 + |m|)!}} \\ & \left(\frac{\pi Z e^2 \mu}{h^2 \epsilon_0 (|m| + n_1 + n_2 + 1)} \right)^{(1+|m|)} (u v)^{|m|} e^{\left(-\frac{\pi Z e^2 \mu (u^2 + v^2)}{2 h^2 \epsilon_0 (|m| + n_1 + n_2 + 1)} \right)} e^{i m \phi} \\ & \text{LaguerreL} \left[n_1, |m|, \frac{\pi Z e^2 \mu u^2}{h^2 \epsilon_0 (|m| + n_1 + n_2 + 1)} \right] \\ & \text{LaguerreL} \left[n_2, |m|, \frac{\pi Z e^2 \mu v^2}{h^2 \epsilon_0 (|m| + n_1 + n_2 + 1)} \right] / (\sqrt{2 \pi} (|m| + n_1 + n_2 + 1)) \end{aligned}$$

This formula is accurately normalized such that

$$\int \psi(u, v, \phi)^* \psi(u, v, \phi) dvol = 1,$$

in which *dvol* is a volume element containing the jacobian specified above; the implied triple integration is over all space; an asterisk as raised suffix, so ψ^* of an amplitude function implies a complex conjugate of ψ such that, wherever $i = \sqrt{-1}$ appears in ψ , $-i$ appears in ψ^* . A normalizing factor stated elsewhere [8] is incorrect. The presence of i in an exponential factor as product with ϕ signifies that this formula is complex, thus containing real and imaginary parts. Coefficient c that equals any complex number of modulus unity such as a fourth root of unity – i.e. $\pm 1, \pm \sqrt{-1}$, occurs because Schroedinger's equation 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 $\psi(u, v, \phi)$ as amplitude functions from the temporally independent Schroedinger equation appear in a purely real form, whereas most are complex; with a mathematically valid alternative choice $c = i$, some amplitude functions would be entirely imaginary, but most would still be complex and thus alien to physical space. Choosing instead $c = -1$ or $-i$ merely reverses the phase of an amplitude function or its constituent parts. Parameters that appear in the solution but not in the partial-differential equation take discrete values, imposed by boundary conditions, as follows: m is called the equatorial, or magnetic, quantum number that assumes only integer values and that arises in the solution of the angular equation to define $\Phi(\phi)$, as in spherical polar coordinates; the first arguments of the associated Laguerre functions, n_1 and n_2 , like radial quantum number k among the three quantum numbers pertaining to spherical polar coordinates, must be non-negative integers so that for bound states of the hydrogen atom the Laguerre functions in $U(u)$ and $V(v)$ terminate at finite powers of variable u or v , and remain finite for u or v taking large values, respectively. The sum $n_1 + n_2$ of paraboloidal quantum numbers plays a role similar to that of radial quantum number k among the quantum numbers for spherical polar coordinates [8]; the difference $n_1 - n_2$, or its reverse, might be called an *electric quantum number* [8], because the energy of the linear Stark effect, whereby the H atom interacts with an external electric field, depends on that difference; *vide infra*.

Whereas the solution of the temporally independent Schroedinger equation in spherical polar coordinates comprises a product of one function of distance $R(r)$, involving radial variable r , and two angular functions $\Theta(\theta)$ and $\Phi(\phi)$ of which the product $Y(\theta,\phi) = \Theta(\theta) \Phi(\phi)$ constitutes spherical harmonics involving angles polar θ and equatorial ϕ , the analogous solution in paraboloidal coordinates comprises a product of two functions of distance variables, $U(u)$ and $V(v)$, and one and the same equatorial angular function $\Phi(\phi)$:

$$\psi(u,v,\phi) = U(u) V(v) \Phi(\phi)$$

each variable u and v has physical dimension of square root of length, so SI unit $m^{1/2}$; $\psi(u,v,\phi)$ has a physical dimension consistent with SI unit $m^{-3/2}$. Since Schroedinger himself [3], both functions $U(u)$ and $V(v)$ are expressed traditionally in terms of Laguerre polynomials for the discrete states, although Kummer and Whittaker functions serve the purpose just as satisfactorily. Just as a Laguerre polynomial in $R(r)$ in spherical polar coordinates contains a sum of quantum numbers that occurs also in the exponent of the temporal factor, so both $U(u)$ and $V(v)$ contain, in the third arguments of their Laguerre functions, a sum $n_1 + n_2 + |m| + 1$; that sum that must take values of a positive integer likewise occurs in the temporal factor, omitted above; we associate that sum with n , an integer quantum number for energy that was originally defined from experiment. For a particular value of energy quantum number n and magnetic quantum number $m = 0$, quantum numbers n_1 and n_2 can be chosen in n distinct ways; for $|m| > 0$, there are two ways of choosing m as $\pm|m|$, which yields a total degeneracy n^2 of amplitude functions, or the corresponding sets of quantum numbers, for a particular value of n and hence the energy associated with a particular amplitude function $\psi(u,v,\phi)$. With coefficient $c = 1$, of n^2 amplitude functions for a given value of n , n functions are real and $n^2 - n$ are complex, hence containing both real and imaginary parts that defy direct plots in less than six spatial dimensions. Whereas in spherical polar coordinates the energy of a H atom not subject to an external electric or magnetic field is formally independent of m , in paraboloidal coordinates under the same conditions the energy depends directly on its absolute value, $|m|$, in combination with quantum numbers n_1 and n_2 , according to the formula above; as $|m|$ is simply equivalent to a lower limit of l in spherical polar coordinates, the same sense of dependence remains in paraboloidal coordinates.

Regarding the frequencies and intensities of spectral lines as the principal observable properties of an atom, as Heisenberg recognised, independent of parochial quantum numbers n_1 , n_2 and m in the case of paraboloidal coordinates, the frequency of a spectral line depends on only the difference of energies of spectrometric states. The energy of each state depends on the inverse square of energy quantum number $n = n_1 + n_2 + |m| + 1$. The intensities are just as readily calculated with paraboloidal amplitude functions [7] as with spherical polar amplitude functions, being proportional to the squares of matrix elements of cartesian coordinate z , or the spherical polar product $r \cos(\theta)$, or the corresponding paraboloidal coordinate $\frac{1}{2}(u^2 - v^2)$ as defined above. The absorption spectrum thus maintains a form exactly as calculated with spherical polar coordinates and depicted in part I of articles in this series [5].

III. GRAPHICAL REPRESENTATIONS OF AMPLITUDE FUNCTION $\Psi(u,v,\phi)$

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 exhibit here some selected examples. As a plot involving three independent variables – spatial coordinates u,v,ϕ – and dependent variable $\psi(u,v,\phi)$ would require at least four

dimensions, the best way to proceed with two dimensions, or three pseudo-dimensions, is to exhibit a surface of constant ψ at a value selected to display the overall spatial properties of a particular real amplitude function in an satisfactory manner, as explained elsewhere [5]. Whereas some textbooks of quantum mechanics in physics discuss amplitude functions of H in paraboloidal coordinates, for instance that by Schiff [9], almost invariably without plots, no known textbook of chemistry even mentions this topic; we hence present here accurate plots of exemplary functions, emphasizing a comparison with related functions expressed in spherical polar coordinates.

The formula of amplitude function $\psi_{0,0,0}$ associated with the state of least energy,

$$\psi_{0,0,0} = \frac{e^3 Z^{\left(\frac{3}{2}\right)} \mu^{\left(\frac{3}{2}\right)} \pi e^{\left(-\frac{Z e^2 \pi \mu (u^2 + v^2)}{2 h^2 \epsilon_0}\right)}}{\epsilon_0^{\left(\frac{3}{2}\right)} h^3},$$

shows no dependence on the angular variable, merely an exponential decay with distance from the origin of the system of coordinates that is effectively at the atomic nucleus, because $u^2 + v^2$ in the exponent is equivalent to distance $2 r$ from the nucleus. With $Z = 1$, we plot a surface of this amplitude function that hence exhibits a spherical shape; its radius is about 2.45×10^{-10} m. The value $\psi_{0,0,0} = 1.46 \times 10^{13} \text{ m}^{-3/2}$ that is chosen for this surface corresponds to both 1/100 of the maximum value of $\psi_{0,0,0}$ at $u = v = 0$ and the volume of $\psi_{0,0,0}^2$ that encloses about 0.995 electronic charge, as explained in part I of this series of papers [5]. The shape and size of this surface of $\psi_{0,0,0}(u,v,\phi)$ in paraboloidal coordinates coincide exactly with the surface of $\psi_{0,0,0}(r,\theta,\phi)$ in spherical polar coordinates. The related surface of $\psi_{0,0,0}^2 = 1.46 \times 10^{26} \text{ m}^{-3}$ is necessarily also spherical and has a radius about 2.55×10^{-10} m; for both this amplitude function and its square, the spherical shape reflects the lack of angular dependence of the electrostatic attraction between the atomic nucleus and the electron in the absence of an electromagnetic field.

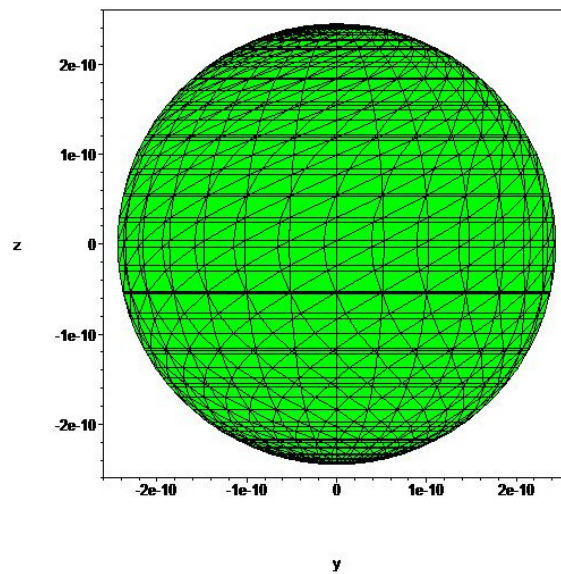


FIGURE 2. Surface of real paraboloidal amplitude function $\psi_{0,0,0} = 1.46 \times 10^{13} \text{ m}^{-3/2}$. Here, and in succeeding plots in three pseudo-dimensions, the unit of length along each coordinate axis is m; notation 2e-10 implies 2×10^{-10} , and analogously, in this and succeeding figures.

The surface of amplitude function $\psi_{1,0,0}$, which incorporates $Z = 1$ here and henceforth,

$$\psi_{1,0,0} = - \frac{e^3 \mu^{\left(\frac{3}{2}\right)} \pi e^{\left(-\frac{e^2 \pi \mu (u^2 + v^2)}{4 h^2 \epsilon_0}\right)} (\pi e^2 \mu u^2 - 2 h^2 \epsilon_0)}{8 \epsilon_0^{\left(\frac{5}{2}\right)} h^5},$$

in figure 3 exhibits a novel shape, unlike that of any amplitude function directly derived in spherical polar coordinates; the domain of ϕ is curtailed at $3 \pi/2$ rad to reveal the interior so as to emphasize the ostensibly peculiar structure. Although the overall shape is axially symmetric about axis z and is roughly spherical, the centre of that sphere is displaced from the origin by about 2×10^{-10} m along positive axis z ; a nodal surface of zero amplitude, of paraboloidal shape, exists between a large positive lobe, extending mostly along positive axis z , and a small negative lobe, extending along negative axis z . The surface of the square of this amplitude function, plotted for $\psi_{1,0,0}^2 = 5 \times 10^{25} \text{ m}^{-3}$, has a similar size and shape.

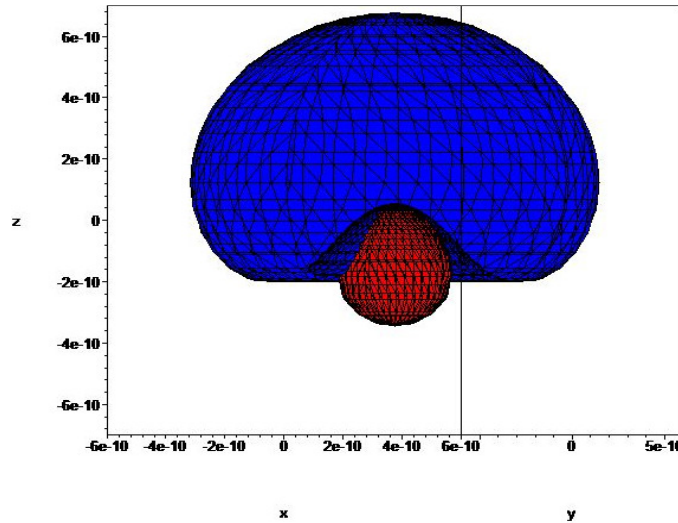


FIGURE 3. Surface of real paraboloidal amplitude function $\psi_{1,0,0} = 1.46 \times 10^{13} \text{ m}^{-3/2}$; the surface is cut open to reveal the structure of the positive lobe (blue) extending mostly above plane $z = 0$ and the negative lobe (red) extending along negative axis z .

Consistent with the complementary shapes of surfaces of u and v of the same value as seen in figure 1, the shape of the surface of $\psi_{0,1,0} = 1.46 \times 10^{13} \text{ m}^{-3/2}$ is exactly the reflection of $\psi_{1,0,0}$ across the plane $z = 0$: a small positive lobe hence extends along positive axis z and a large negative lobe along negative axis z ; the centre of the surface of $\psi_{0,1,0}$ is located about 2×10^{-10} m along negative axis z from the origin. For the real and imaginary parts of complex paraboloidal amplitude functions $\psi_{0,0,1}$ and $\psi_{0,0,-1}$ with equatorial quantum number m different from zero, the shapes and sizes of the surfaces of amplitude functions are essentially identical to those of the corresponding parts of $\psi_{0,1,1}(r, \theta, \phi)$ and $\psi_{0,1,-1}(r, \theta, \phi)$ in spherical polar coordinates, which are in turn identical to $\psi_{0,1,0}(r, \theta, \phi)$ apart from their orientation, except that the real part of $\psi_{0,1,1}(r, \theta, \phi)$ is symmetric about axis y whereas the real part of $\psi_{0,0,1}(u, v, \phi)$ is symmetric about axis x , and vice versa for the imaginary parts. The sum $\psi_{0,1,0}^2 + \psi_{1,0,0}^2 + |\psi_{0,0,1}|^2 + |\psi_{0,0,-1}|^2$ in paraboloidal coordinates plots as a perfect sphere, of radius about 6.4×10^{-10} m.

In figure 4, we show next the surface of paraboloidal amplitude function $\psi_{2,0,0}$, according to this formula.

$$\Psi_{2,0,0} = \frac{e^3 \mu^{\left(\frac{3}{2}\right)} \pi e^{\left(-\frac{e^2 \pi \mu (u^2 + v^2)}{6 h^2 \epsilon_0}\right)} (\pi^2 e^4 \mu^2 u^4 - 12 \pi e^2 h^2 \mu u^2 \epsilon_0 + 18 h^4 \epsilon_0^2)}{162 \epsilon_0^{\left(\frac{7}{2}\right)} h^7}$$

Its surface exhibits three lobes, two of positive phase and one of negative phase between those two, with paraboloidal nodal surfaces between these lobes. Apart from that lobal structure, the overall shape is roughly spherical, of radius 8×10^{-10} m, but the centre of the sphere is located along positive axis z about 4×10^{-10} m from the origin. Amplitude function $\psi_{0,2,0}$ is the reverse of $\psi_{2,0,0}$, roughly spherical in shape but extending mostly along negative axis z and centred near $z = -4 \times 10^{-10}$ m.

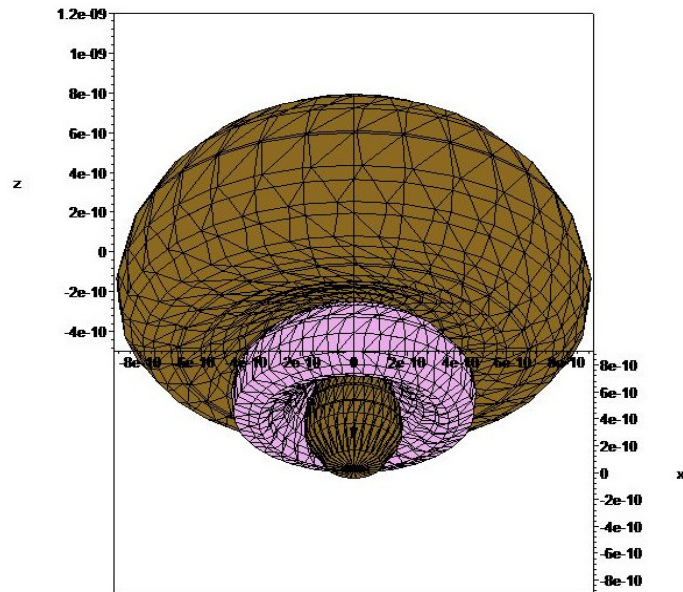


FIGURE 4. Surface of real paraboloidal amplitude function $\psi_{2,0,0} = 1.46 \times 10^{13} \text{ m}^{-3/2}$; the largest and smallest lobes (sienna) have positive phase, the intermediate lobe (plum) has a negative phase.

The surface of amplitude function $\psi_{1,1,0}$,

$$\Psi_{1,1,0} = \frac{e^3 \mu^{\left(\frac{3}{2}\right)} \pi e^{\left(-\frac{e^2 \pi \mu (u^2 + v^2)}{6 h^2 \epsilon_0}\right)} (\pi e^2 \mu u^2 - 3 h^2 \epsilon_0) (\pi e^2 \mu v^2 - 3 h^2 \epsilon_0)}{81 \epsilon_0^{\left(\frac{7}{2}\right)} h^7},$$

which, like the preceding two functions, $\psi_{2,0,0}$ and $\psi_{0,2,0}$, corresponds to energy quantum number $n = 3$, is shown in figure 5. In this case a small positive lobe of slightly oblate spheroidal shape is centred at the origin; a large positive lobe is a torus, with two pronouncedly spheroidal negative lobes directed along positive and negative axis z separated by the small positive lobe. The overall shape is roughly oblate spheroidal; its square exhibits a similar shape.

As an example of a novel complex amplitude function, we show in figure 6 the surface of the real part of $\psi_{1,0,1}$ that conforms to this formula:

$$\psi_{1,0,1} = \frac{e^5 \mu^{\left(\frac{5}{2}\right)} 2^{\left(\frac{1}{2}\right)} \pi^2 u v e^{\left(-\frac{e^2 \pi \mu u^2 + e^2 \pi \mu v^2 - 6 i \phi h^2 \epsilon_0}{6 h^2 \epsilon_0}\right)} (\pi e^2 \mu u^2 - 6 h^2 \epsilon_0)}{162 \epsilon_0^{\left(\frac{7}{2}\right)} h^7}$$

Of four lobes, two are large and two are small, one each of each phase. The shapes of lobes in this figure are common to $\psi_{1,0,1}$, $\psi_{1,0,-1}$, $\psi_{0,1,1}$ and $\psi_{0,1,-1}$ in their real or imaginary parts; they are symmetric across planes $y = 0$ or $x = 0$. For $\psi_{1,0,1}$ or $\psi_{1,0,-1}$, the large lobes lie mostly above plane $z = 0$, as for $\psi_{1,0,0}$, whereas for $\psi_{0,1,1}$ or $\psi_{0,1,-1}$ the large lobes lie mostly on the negative side of plane $z = 0$, as for $\psi_{0,1,0}$. The surfaces of the squares of $\psi_{1,0,1}$ and $\psi_{1,0,-1}$ are identical, and resemble the shapes of the surfaces of $\psi_{1,0,0}$, shown in figure 3, and $\psi_{0,1,0}$, except that there is a tunnel of zero electronic density along the polar axis, making the shapes toroidal.

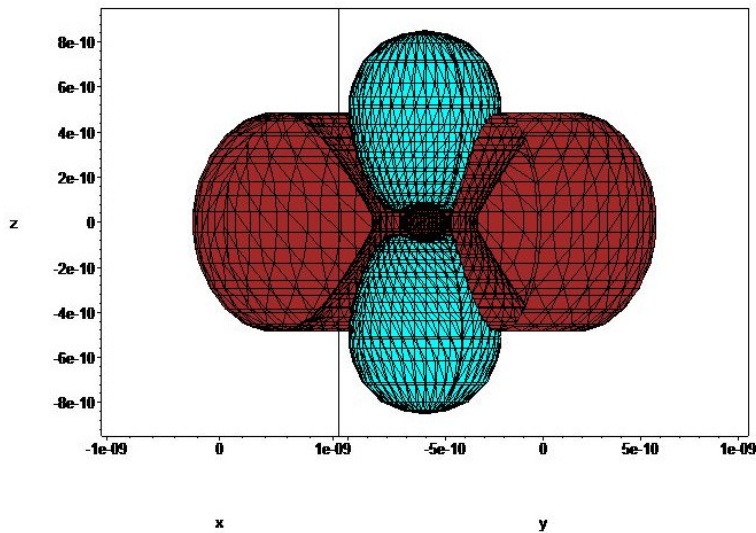


FIGURE 5. Surface of real paraboloidal amplitude function $\psi_{1,1,0} = 1.46 \times 10^{13} \text{ m}^{-3/2}$, cut open to reveal the interior structure; two negative lobes (cyan) are separated by a small positive oblate spheroidal lobe (brown) around the origin, all partially surrounded with a large positive torus (brown).

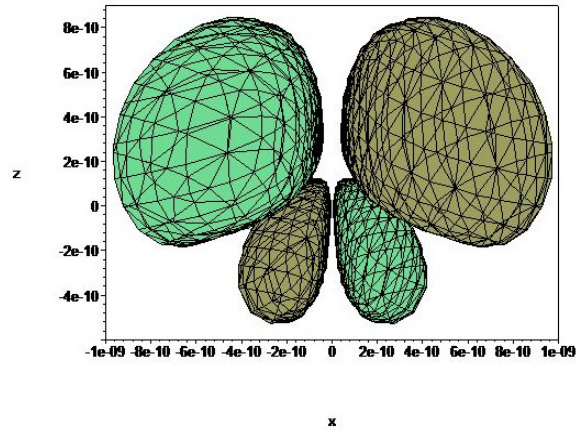


FIGURE 6. Surface of the real part of complex paraboloidal amplitude function $\psi_{0,1,1} = 1.46 \times 10^{13} \text{ m}^{-3/2}$; the positive lobes (khaki) and negative lobes (aquamarine) are symmetric with respect to plane xz .

In contrast, for complex paraboloidal amplitude functions $\psi_{0,0,2}$ and $\psi_{0,0,-2}$ in their real or imaginary parts, the surfaces have four lobes of equal size, extending along axes x and y for $\psi_{0,0,2}$ and $\psi_{0,0,-2}$ in their real parts and between these axes for their imaginary parts, so rotated by $\pi/8$ rad from one another. As an example in figure 7, we display the shape of the surface of the real part of $\psi_{0,0,2}$ that conforms to this formula.

$$\psi_{0,0,2} = \frac{e^7 \mu^{\left(\frac{7}{2}\right)} \pi^3 u^2 v^2 e^{\left(-\frac{e^2 \pi \mu (u^2 + v^2)}{6 h^2 \epsilon_0}\right)} \cos(2\phi)}{162 h^7 \epsilon_0^{\left(\frac{7}{2}\right)}}$$

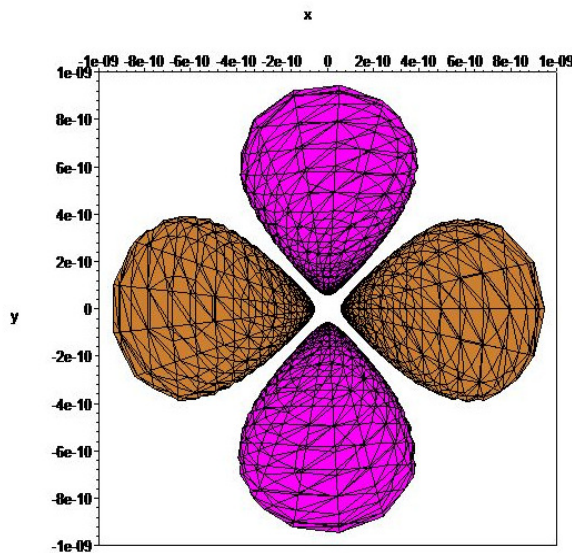


FIGURE 7. Surface of the real part of complex paraboloidal amplitude function $\psi_{0,0,2} = 1.46 \times 10^{13} \text{ m}^{-3/2}$; the lobes of positive phase (golden) lie along axis y and those of negative phase (magenta) along axis x .

These surfaces of complex paraboloidal amplitude functions $\psi_{0,0,\pm 2}$ in their real and imaginary parts thus resemble the surfaces of spherical polar amplitude functions $\psi_{0,2,\pm 2}(r,\theta,\phi)$, analogously to the respective surfaces of $\psi_{0,0,\pm 1}$ and $\psi_{0,1,\pm 1}(r,\theta,\phi)$. The shapes of the surfaces of the squares of $\psi_{0,0,2}$ and $\psi_{0,0,-2}$ are identical to each other, and constitute oblate tori surrounding the polar axis.

As a further example, figure 8 displays the surface of paraboloidal amplitude function $\psi_{1,2,0}$, according to this formula,

$$\psi_{1,2,0} = -e^3 \mu^{\left(\frac{3}{2}\right)} \pi e^{\left(-\frac{e^2 \pi \mu (u^2 + v^2)}{8 h^2 \epsilon_0}\right)} (\pi e^2 \mu u^2 - 4 h^2 \epsilon_0) (\pi^2 e^4 \mu^2 v^4 - 16 \pi e^2 h^2 \mu v^2 \epsilon_0 + 32 h^4 \epsilon_0^2) \Big/ \left(2048 \epsilon_0^{\left(\frac{9}{2}\right)} h^9\right)$$

which exhibits four spheroidal lobes, two of each phase, and two tori, one of each phase, all symmetric about the polar axis. These features of tori and spheroids are typical of the shapes of surfaces of real paraboloidal amplitude functions with energy quantum number n greater than 3.

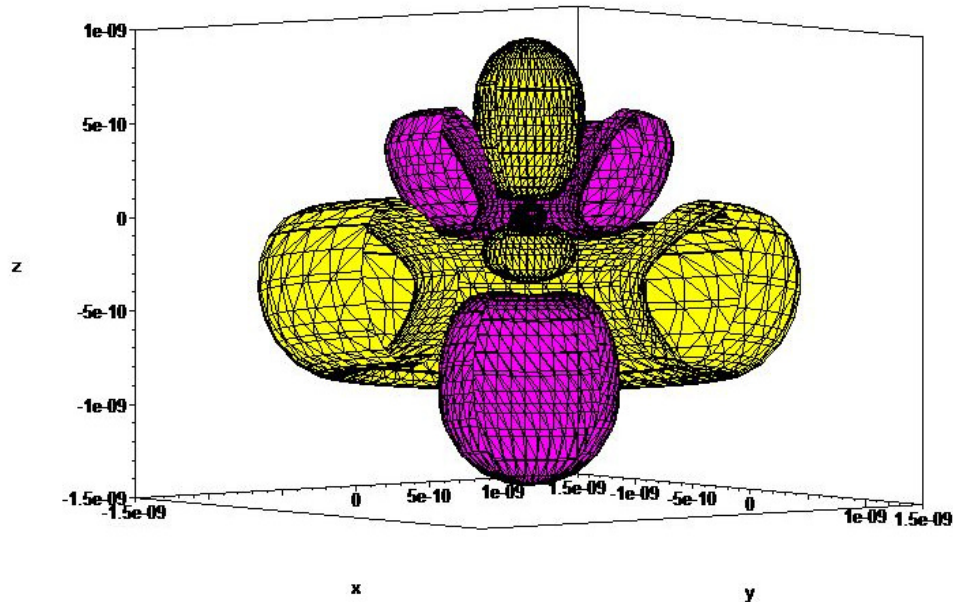


FIGURE 8. Surface of real paraboloidal amplitude function $\psi_{1,2,0} = 1.46 \times 10^{13} \text{ m}^{-3/2}$, cut open to reveal the interior structure; the large torus (yellow) has a negative phase and the small torus (magenta) a positive phase; of the four spheroidal lobes, the largest (magenta) has a positive phase, and the smallest also of positive phase (magenta) is between two larger spheroidal lobes of negative phase.

IV. DISCUSSION

Schroedinger developed this solution of his equation in paraboloidal coordinates [3] primarily as a method to treat, with perturbation theory that he concurrently developed, the Stark effect on the hydrogen atom, explicitly the shifting and splitting of spectral lines as a result of

hydrogen atoms being subjected to a uniform electric field. To take such account, he added to the hamiltonian a term $e F z = \frac{1}{2} e F (u^2 - v^2)$ for a uniform electric field of strength F in direction $+z$, i.e. so to define the polar axis; the additional term was treated as a perturbation of the system. The consequent energy of a state corresponding to quantum numbers n_1 , n_2 and m becomes

$$E = - \frac{\mu Z^2 e^4}{8 h^2 \epsilon_0^2 (n_1 + n_2 + |m| + 1)^2} + \frac{3 \mu e^4 (n_1 + n_2 + |m| + 1) (n_1 - n_2) F}{8 h^2 \epsilon_0^2 Z}$$

in which the first term is precisely the energy of that state in the absence of the field, $F = 0$; the second term shows the linear dependences on both that mild field and the difference between quantum numbers n_1 and n_2 , i.e. the *electric quantum number*. For $n_1 > n_2$, the electron is predominantly located with $z > 0$, consistent with the raising of the energy through the potential energy of the electron and the external field. Figures 2 – 8 show that, for amplitude functions with $n_1 = n_2$, plane $z = 0$ is a plane of symmetry. With increasing strength of the electric field, an additional term, quadratic in F , appears, and eventually, at large fields, further terms become significant. In all cases the magnitude of the Stark effect depends also on the magnitude of equatorial quantum number m , as shown in the above formula for the linear Stark effect for instance. Regarding an homogeneous magnetic field acting on a hydrogen atom ^1H , the problem is complicated because of the presence of magnetic dipole moments associated with the intrinsic angular momenta of both electron and proton, known as spin. Neglect of the effect of *electron spin* yields a variation of the energy of the atom linearly proportional to magnetic quantum number m , considered to be the *normal* Zeeman effect, but in practice the energy of interaction of the electron spin with its motion about the atomic nucleus is larger than the energy change due to the external magnetic field, up to flux density $B_z = 10$ T. Taking into account also the purported electron spin involves a treatment that yields the *anomalous* Zeeman effect, but spherical polar coordinates are suitable for this calculation.

Other contexts in which these paraboloidal coordinates are particularly useful include the photoelectric effect, the Compton effect and a collision of an electron with a H atom; in each case a particular direction in space is distinguished according to some external force [8]: that direction becomes the polar axis about which equatorial angle ϕ is measured with respect to a reference plane. Although paraboloidal coordinates might appear to obscure the innate spherical symmetry of an isolated H atom, in nearly any practical experiment on these atoms, apparently apart from a measurement of the simple spectrum of an unperturbed system, that spherical symmetry is lost. Any chemical application of the amplitude functions of a H atom, in particular, inevitably involves an interaction with another chemical species, which defines a particular direction to become prospectively the polar axis. From a chemical or physical point of view, a consideration of the H atom in paraboloidal coordinates seems more important than in spherical polar coordinates, but ellipsoidal coordinates are more practical than either spherical polar or paraboloidal. We consider this matter further in Part III on ellipsoidal coordinates.

Quantum numbers in each set n_1 , n_2 , m and each amplitude function that they designate, with their corresponding plots, are all parochial to this system of paraboloidal coordinates, just as quantum numbers k , l , m and their associated amplitude functions are parochial to the system of spherical polar coordinates, and have no meaning beyond the context of the same particular system of coordinates; equatorial quantum number fortuitously happens to be common to both systems because equatorial angle ϕ is likewise a common coordinate. With $n = n_1 + n_2 + |m| + 1$, the

total number of states or amplitude functions for n of given value is equal to that number n with $m = 0$ plus twice the sum with $m \neq 0$,

$$n + 2 \left(\sum_{m=1}^{n-1} (n-m) \right) = n^2,$$

the same as for spherical polar coordinates.

The preceding plots of surfaces of amplitude functions in paraboloidal coordinates show that, in general, these functions are asymmetric to the plane $z = 0$ or for which $u^2 = v^2$ unless $n_1 = n_2$; for $n_1 > n_2$ most electronic charge is located in the half space in which $z > 0$, and conversely for $n_1 < n_2$. A comparison of plots of surfaces of amplitude functions in spherical polar and paraboloidal coordinates makes clear that the shapes and sizes of the surfaces of the real and imaginary parts of complex paraboloidal amplitude functions $\psi_{0,0,1}(u,v,\phi)$ and $\psi_{0,0,-1}(u,v,\phi)$ are essentially identical with those of the corresponding parts of $\psi_{0,1,1}(r,\theta,\phi)$ and $\psi_{0,1,-1}(r,\theta,\phi)$ in spherical polar coordinates, except that the real part of $\psi_{0,1,1}(r,\theta,\phi)$ is symmetric about axis y whereas the real part of $\psi_{0,0,1}$ is symmetric about axis x , and vice versa. For the paraboloidal and spherical polar amplitude functions, there are relations, not one to one as for the complex functions specified above, but as a sum or difference of amplitude functions in one system of coordinates to generate a particular amplitude function in another system with a common value of energy, and hence energy quantum number n . This condition necessarily follows from the solution of the same hydrogen atom under the same conditions, for instance, a non-relativistic treatment in three spatial dimensions in the absence of an external field. As instances of formulae for interconversion of these functions between $\psi_{n_1,n_2,m}(u,v,\phi)$ and $\psi_{k,l,m}(r,\theta,\phi)$, which correspond merely to transformations of coordinates, we state the following results for the sum,

$$\psi_{0,1,0}(r,\theta,\phi) + \psi_{1,0,0}(r,\theta,\phi) = \sqrt{2} \psi_{1,0,0}(u,v,\phi)$$

or the inverse relation,

$$\sqrt{2} \psi_{1,0,0}(r,\theta,\phi) = \psi_{0,1,0}(u,v,\phi) + \psi_{1,0,0}(u,v,\phi)$$

and for the difference,

$$\psi_{0,1,0}(r,\theta,\phi) - \psi_{1,0,0}(r,\theta,\phi) = \sqrt{2} \psi_{0,1,0}(u,v,\phi)$$

and its inverse relation.

$$\sqrt{2} \psi_{0,1,0}(r,\theta,\phi) = \psi_{0,1,0}(u,v,\phi) - \psi_{1,0,0}(u,v,\phi)$$

Analogous sums and differences – linear combinations of multiple functions in general – connect any amplitude function in spherical polar coordinates with appropriately selected functions in paraboloidal coordinates, provided that energy quantum number n is common to each set; for the above relations $n = 2$. Schroedinger mentioned this interconversion in his second lecture to the Royal Institution in London, 1928 [10]. The identity of surfaces of the separate real or imaginary parts of $\psi_{0,0,1}(u,v,\phi)$ and $\psi_{0,0,-1}(u,v,\phi)$ with those of the corresponding parts of $\psi_{0,1,1}(r,\theta,\phi)$ and $\psi_{0,1,-1}(r,\theta,\phi)$ fails to hold directly for amplitude functions with $n > 2$, but remains applicable to the appropriate linear combinations of complex amplitude functions of one coordinate system to

generate a particular complex amplitude function in another system. Linear combinations of degenerate amplitude functions with common energy quantum number n , which are consequently likewise solutions of the same Schroedinger equation with the same energy, correspond to merely a rotation of the axes in the same system of coordinates or to another choice of system of coordinates [9]. Such degeneracy occurs in general when the amplitude equation is solvable in multiple ways – either for distinct systems of coordinates or within a single coordinate system variously oriented. For $l = 0$ in spherical polar coordinates, the amplitude function is spherically symmetric, so having the same form for any orientation of the polar axis. For paraboloidal coordinates, quantum number l for angular momentum is undefined, even though the component of angular momentum along the polar axis is well defined according to equatorial quantum number m ; the only intrinsically spherically symmetric surface of an amplitude function, or of one of its lobes, occurs for $n_1 = n_2 = m = 0$, applicable to the ground state of this H atom with a plot shown in figure 2; in this case the solutions for the amplitude equation derived in spherical polar and paraboloidal coordinates are equivalent. With the amplitude functions as defined above, we calculate an expectation value of the square of angular momentum L^2 in its external motion for any state defined with quantum numbers n_1, n_2, m as

$$\langle L^2 \rangle = \frac{1}{4} \frac{((n_1 + n_2 + 1)|m| + m^2 + n_1 + 2n_1n_2 + n_2)h^2}{\pi^2},$$

which accordingly depends on all three quantum numbers, like the energy of that state. From that formula one might derive an expectation value for l ,

$$l = -\frac{1}{2} + \sqrt{(|m| + n_1 + n_2 + 1)(|m| + 1) + 2n_1n_2 - |m| - \frac{3}{4}} h/2\pi,$$

which clearly assumes no integer or half-integer value except when $n_1 = n_2 = 0$ giving $l = |m|$, and which might otherwise have little meaning as a quantum number; taking $|m|$ as being a lower limit of l is clearly preferable. The coefficient of $h/2\pi$ in the above formula is thus effectively an expectation value of l for states associated with amplitude functions expressed in paraboloidal coordinates. For comparison, in spherical polar coordinates, the total square of angular momentum, hence a scalar quantity and having no directional dependence, has value $l(l+1)$

$\left(\frac{h}{2\pi}\right)^2$ involving quantum number l , of which the numerical coefficient of $\left(\frac{h}{2\pi}\right)^2$ assumes an integer value only for $l = 0$. For both systems of coordinates, the component L_z of angular momentum parallel to the polar axis is given by $m h/2\pi$, which is independent of quantum numbers n_1 and n_2 but limited by l .

The preceding results in the form of formulae for amplitude functions $\psi(u,v,\phi)$, their associated quantum numbers n_1, n_2, m , and the surfaces of those functions are all clearly parochial to these paraboloidal coordinates, just as the corresponding quantities for spherical polar coordinates are parochial to those coordinates. An analogous conclusion is inevitable for the solution of Schroedinger's equation in ellipsoidal and spheroconical coordinates, presented in further papers of this series.

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