

# THE HYDROGEN ATOM ACCORDING TO WAVE MECHANICS – I. SPHERICAL POLAR COORDINATES

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## Abstract

In the first of five parts in a series, the Schroedinger equation is solved in spherical polar coordinates to yield wave functions that enable an accurate calculation of the frequencies and intensities of lines in the absorption spectrum of the Lyman series in the vacuum-ultraviolet region. Accurate plots of surfaces of amplitude functions illustrate the variation of shapes and sizes varying with quantum numbers  $k$ ,  $l$ ,  $m$  for comparison with the corresponding plots of amplitude functions in other systems of coordinates.

## Resumen

En este primer artículo de cinco, la ecuación de Shroedinger se resuelve usando coordenadas polares esféricas para obtener funciones de onda que facilitan un cálculo preciso de las frecuencias e intensidades del espectro de absorción de una serie de Lyman en la región de ultravioleta al vacío. Los gráficos precisos de las funciones de amplitud muestran la variación de las formas y tamaños con los números cuánticos  $k$ ,  $l$  y  $m$  para comparar con los gráficos correspondientes a las funciones de amplitud en otros sistemas de coordenadas.

**key words:** hydrogen atom, wave mechanics, spherical polar coordinates, orbitals, atomic spectra

**Palabras clave:** átomo de hidrógeno, mecánica cuántica, coordenadas polares esféricas, orbitales, espectro atómico.

## I. INTRODUCTION

Several months after Heisenberg initiated quantum mechanics in 1925 [1], Schroedinger introduced wave mechanics with four articles, of translated title *Quantisation as a Problem of Proper Values* [2,3,4,5], that have since served as a general basis of calculations on microscopic systems for physical and chemical purposes. Heisenberg attacked first the problem of an anharmonic oscillator [1], which eventually involved operations with explicit matrices [6]. Pauli then applied a symbolic method, involving no explicit matrix, to generate the energies of states of the hydrogen atom, but “the calculation of transition probabilities (intensities) [was] omitted from consideration” [7]. In his first article on wave mechanics, Schroedinger solved his differential equation independent of

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time for the hydrogen atom in spherical polar coordinates on assuming an amplitude function of appropriate properties [2], and achieved an account of the energies of the discrete states that was intrinsically no great advance on Bohr's grossly flawed derivation and even on Pauli's quantum-mechanical achievement [7]. In contrast, in an astonishing achievement in his third article, Schroedinger not only analogously solved the differential equation for the hydrogen atom in paraboloidal coordinates [4] but also developed a perturbation theory and calculated the intensities of spectral lines; in a fourth part [5], on incorporating time as a variable, he eliminated the energy parameter from the partial-differential equation, producing a temporal dependence in the resulting wave function.

Among the eleven systems of coordinates [8] that allow a separation of three spatial variables in the Helmholtz equation, or hence also the Laplace equation because that Helmholtz equation contains the laplacian operator, only four systems enable a complete separation of variables of Schroedinger's partial-differential equation for the hydrogen atom to yield ordinary-differential equations, specifically the two specified above plus ellipsoidal coordinates [9], for which only indirect solutions in series had been achieved [10] before the present work, and spheroconical coordinates for which no explicit algebraic solution has ever been reported. The objective of the few articles in this series is to present in turn the solution, derived directly with advanced mathematical software (Maple) for symbolic computation, of Schroedinger's temporally dependent or independent equation in each of the four systems of coordinates, accompanied with numerous accurate illustrations of surfaces of amplitude functions in the various systems, and then to discuss the ramifications of these multiple solutions in a chemical context. Although the governing equations are, of necessity, defined in other systems of coordinates with three spatial dimensions, we view these surfaces invariably in rectangular cartesian coordinates: a computer program translates effectively from another or original system of coordinates, in which the algebra and calculus are performed, to the system to which a human eye is accustomed. The scope of treatments in articles in this series is limited to that appropriate to Schroedinger's equations in a context of pioneer quantum mechanics in its wave-mechanical variety, so neglecting *relativistic* effects, effects of electronic and nuclear intrinsic angular momenta, radiative effects and other aspects that are typically omitted from general undergraduate courses in chemistry and physics.

The most fundamental application of quantum mechanics is in atomic physics, which has also chemical implications. The simplest chemical species is the hydrogen atom,  $^1\text{H}$ , which consists of a simple atomic nucleus – a proton in the most common instance – and one electron, bound through an electrostatic attraction that acts between these particles. Heisenberg recognized that the observable properties of an atom or molecule are the frequencies and intensities of its spectral lines, and that the fundamental properties of an atomic or molecular system that are involved in a calculation of a spectrum are the relative positions and momenta of the particles comprising that system [1]. Within pioneer quantum mechanics, nobody has yet succeeded in predicting the intensities of lines in the discrete spectrum of a hydrogen atom without involving explicitly Schroedinger's amplitude or wave functions, or equivalent. For this reason, even though the latter are incontestably artefacts of both a particular method of calculation and a selected system of coordinates, they seem at present to be unavoidable for a calculation of important observable properties of an atomic or molecular system. In this part I, we review the solution of Schroedinger's equation for the hydrogen atom in spherical polar coordinates, presenting merely the most pertinent equations and formulae as a basis to explain the quintessential mathematical and physical implications. Details of the derivation of the formulae appear elsewhere [11].

## II. SCHROEDINGER'S EQUATION IN SPHERICAL POLAR COORDINATES

The magnitude of a central force on an object depends on only the distance of that object from the origin; the direction of the force is along the line joining the origin and the object. The coulombic attraction is a central force, which implies a conservative field and which signifies that it is expressible as the gradient of a potential energy. Schroedinger's equation for an electron moving in a central force field is invariably separable in spherical polar coordinates, which in Schroedinger's paper is called simply polar coordinates [2]. We assume the electron and the proton, or other atomic nucleus, to constitute point masses that interact according to Coulomb's law; a deviation from that law might imply a non-zero rest mass of a photon, for which no evidence exists, apart from the effects of the finite volume and shape of a massive atomic nucleus, and their isotopic variation, for which experimental evidence exists. We first relate these coordinates, i.e. radial coordinate  $r$ , polar angular coordinate  $\theta$  and equatorial angular coordinate  $\phi$ , to cartesian coordinates  $x, y, z$  as algebraic formulae, according to ISO standard 80000-2:2009,

$$x = r \sin(\theta) \sin(\phi), \quad y = r \sin(\theta) \cos(\phi), \quad z = r \cos(\theta)$$

with domains  $0 \leq r < \infty$ ,  $0 \leq \theta < \pi$ ,  $0 \leq \phi < 2\pi$ , so that axis  $z$  in cartesian coordinates becomes the polar axis in spherical polar coordinates. For the motion of the electron relative to the atomic nucleus, the use of a reduced mass converts the problem of treating two interacting particles into a treatment of effectively a single particle subject to a force field; the motion of the atom as a whole through space is of little interest – only the internal motion produces observable properties readily observable in atomic spectra in absorption or emission. Coordinate  $r$  signifies the distance between reduced mass  $\mu$  and the origin; coordinate  $\theta$  signifies the angle of inclination between a line joining that reduced mass to the origin and polar axis  $z$  in cartesian coordinates; coordinate  $\phi$  signifies the equatorial angle between a half-plane containing that line, between the reduced mass and the origin, and half-plane  $x=0$ ; a half-plane extends from the polar axis to  $\infty$  in any direction. The limiting cases are thus for  $r$  a point at the origin as  $r \rightarrow 0$ , and for  $\theta$  a line along positive axis  $z$  as  $\theta \rightarrow 0$  and along negative axis  $z$  as  $\theta \rightarrow \pi$ . Surfaces of coordinates  $r$ ,  $\theta$  and  $\phi$  as constant quantities are exhibited, with definitions, in figure 1. For use within an integrating element in subsequent integrals, the jacobian of the transformation of coordinates between cartesian and spherical polar, as defined above, is  $r^2 \sin(\theta)$ .

After the separation of the coordinates of the centre of mass of the H atom, Schroedinger's temporally dependent equation in explicit SI units,

$$\left( -\frac{\frac{\partial}{\partial r} \Psi(r, \theta, \phi, t)}{4 \pi^2 r} - \frac{\cos(\theta) \left( \frac{\partial}{\partial \theta} \Psi(r, \theta, \phi, t) \right)}{8 \pi^2 r^2 \sin(\theta)} - \frac{\frac{\partial^2}{\partial \theta^2} \Psi(r, \theta, \phi, t)}{8 \pi^2 r^2} - \frac{\frac{\partial^2}{\partial \phi^2} \Psi(r, \theta, \phi, t)}{8 \pi^2 r^2 \sin(\theta)^2} - \frac{\frac{\partial^2}{\partial r^2} \Psi(r, \theta, \phi, t)}{8 \pi^2} \right) h^2 / \mu - \frac{Z e^2 \Psi(r, \theta, \phi, t)}{4 \pi \epsilon_0 r} = \frac{i h \left( \frac{\partial}{\partial t} \Psi(r, \theta, \phi, t) \right)}{2 \pi}$$

contains within terms on the left side an electrostatic potential energy proportional to  $r^{-1}$  and first and second partial derivatives of an assumed wave function  $\Psi(r, \theta, \phi, t)$  with respect to spatial coordinates  $r, \theta, \phi$ , and on the right side a first partial derivative with respect to time  $t$ . Apart from fundamental physical constants, specifically electric permittivity of free space  $\epsilon_0$ , Planck constant  $h$

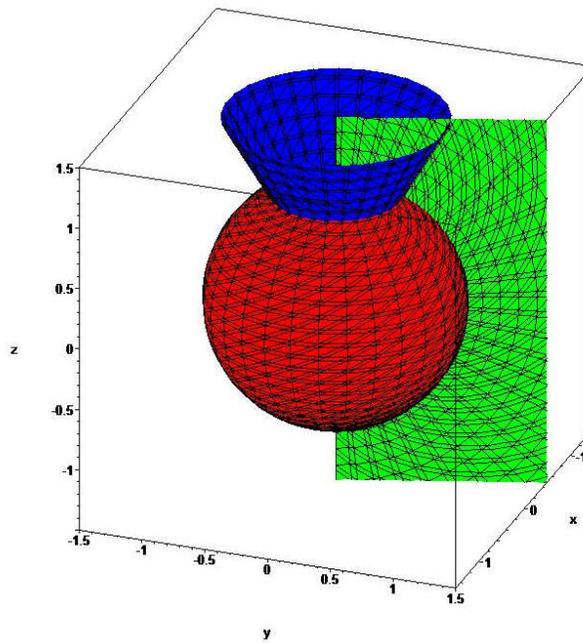
and protonic charge  $e$ , there appear constant parameters  $Z$  for atomic number –  $Z = 1$  for H – and  $\mu = m_e M / (M + m_e)$  for the reduced mass of the atomic system with nuclear mass  $M$ ; this reduced mass is practically equal to the electronic rest mass  $m_e$ . In the limit of infinite nuclear mass, the position of that nuclear mass coincides with the origin of the system of coordinates. After the separation of the variables and the solution of the four consequent ordinary-differential equations including definition of the integration constants and separation parameters, the full solution of the above equation has this form [11].

$$\Psi(r, \theta, \phi, t) = c \sqrt{\frac{Z \pi \mu e^2 k!}{\epsilon_0 h^2 (k + 2l + 1)!}} \left( \frac{2 \mu \pi e^2 Z}{(k + l + 1) h^2 \epsilon_0} \right)^{(l+1)} r^l$$

$$\text{LaguerreL} \left( k, 2l + 1, \frac{2 \pi \mu e^2 Z r}{h^2 \epsilon_0 (k + l + 1)} \right) e^{\left( -\frac{\pi \mu e^2 Z r}{h^2 \epsilon_0 (k + l + 1)} \right)} e^{(im\phi)}$$

$$\sqrt{\frac{(2l + 1)(l - |m|)!}{(l + |m|)!}} \text{LegendreP}(l, |m|, \cos(\theta)) e^{\left( -\frac{i \mu Z^2 e^4 \pi t}{4 h^3 \epsilon_0^2 (k + l + 1)^2} \right)} / ($$

$$2(k + l + 1) \sqrt{\pi})$$



**FIGURE 1.** Definition of spherical polar coordinates  $r, \theta, \phi$ : a sphere (red) has radius  $r = 1$  unit; a cone (blue) has polar angle  $\theta = \pi/6$  rad with respect to polar axis  $+z$ ; a half-plane (green) has equatorial angle  $\pi/10$  rad with respect to plane  $x = 0$ .

The presence of  $i = \sqrt{-1}$  in two exponential factors as product with  $\phi$  or  $t$  signifies that this formula is complex, thus containing real and imaginary parts. Coefficient  $c$ , which here does not denote the speed of light and which equals any complex number of magnitude unity such as a fourth root

of unity – i. e.  $c = \pm 1, \pm i$ , appears because Schroedinger's equation is linear and homogeneous, or equally because Schroedinger's temporally independent equation is of form an eigenvalue relation,

$$H(r, \theta, \phi) \psi(r, \theta, \phi) = E \psi(r, \theta, \phi)$$

in which  $H(r, \theta, \phi)$  denotes a hamiltonian operator with contributions from kinetic and potential energies. A conventional choice  $c = 1$ , which is arbitrary and lacks physical justification, signifies that some amplitude function  $\psi(r, \theta, \phi)$ , as solution from the temporally independent Schroedinger equation with  $m=0$ , appears in a real form, whereas most must be complex; with a mathematically valid alternative choice  $c = i$ , some amplitude functions would be entirely imaginary but most would still be complex. Choosing  $c = -1$  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 indicated below;  $l$  is called the azimuthal quantum number that assumes values of only non-negative integers and that arises in the solution of the angular equation to define  $\Theta(\theta)$ , which also involves  $m$  as its absolute value; product  $Y(\theta, \phi) = \Theta(\theta) \Phi(\phi)$  constitutes a special function known as spherical harmonic to represent functions defined on the surface of a sphere;  $k$  is a radial quantum number that assumes values of only non-negative integers, and arises in the solution of the radial equation to define  $R(r)$ , which also involves quantum number  $l$ . The names of quantum numbers  $k$  and  $m$  hence pertain to the coordinates from which they arise. There is no relative limitation of the values of  $k$  and  $l$ , but, for a given value of  $l$ ,  $m$  assumes  $2l + 1$  integer values from  $-l$  to  $+l$ . The total wave function is thus a product

$$\Psi(r, \theta, \phi, t) = c R(r) \Theta(\theta) \Phi(\phi) \tau(t) = c \psi(r, \theta, \phi) \tau(t)$$

from the normalised solutions of the four separate ordinary-differential equations. The multiplicative terms in the total product that contain no variable serve as normalizing factors, to ensure that, for the amplitude function,

$$\int \psi(r, \theta, \phi)^* \psi(r, \theta, \phi) dvol = 1 ,$$

in which the integration, with  $\psi(r, \theta, \phi)^*$  formed from  $\psi(r, \theta, \phi)$  on replacing  $i$  by  $-i$  and with volume element  $dvol$  incorporating the jacobian specified above, is performed over all space according to the domains of the spatial variables as specified above. Henceforth we take  $c = 1$ .

The coefficient of  $t$  with  $i$  in one exponential term above has the physical dimensions and significance of a radial frequency, as Schroedinger noted [5], but we interpret that quantity in its particular context as energy  $E$  of a particular state divided by Planck constant  $h$ , as Schroedinger also applied. We associate sum  $k + l + 1$ , which must assume a value of a positive integer, in the same exponent with experimental quantum number  $n$  for energy,

$$n = k + l + 1 ;$$

according to the formula for the discrete spectral lines of H derived by Balmer and elaborated by Rydberg, the energy of a discrete state of H is proportional to  $-1/n^2$ . That sum of integers occurs

also in associated Laguerre function  $LaguerreL$  that represents in  $R(r)$  the radial dependence of wave function  $\Psi(r, \theta, \phi, t)$ , but not in associated Legendre function  $LegendreP$  of the first kind,  $\Theta(\theta)$ , that contains the angular dependence on  $\theta$ .

The physical significance of equatorial quantum number  $m$  is that, for a given value of  $l$ ,  $2l + 1$  specifies the number of states, distinguished by their values of  $m$  from  $-l$  to  $+l$ , that have distinct energies for a H atom in the presence of an externally applied magnetic field; that field hence removes a degeneracy whereby multiple states have the same energy. Multiple amplitude functions, corresponding to particular values of  $k, l, m$  and explicitly numbering  $(k + l + 1)^2$ , yield the same energy of a H atom, according to the eigenvalue relation above, in the absence of an externally applied magnetic or electric field; for the solution of Schroedinger's temporally dependent or independent equation in spherical polar coordinates, the energy in the absence of a magnetic field is thus independent of equatorial quantum number  $m$ . The mathematical significance of azimuthal quantum number  $l$  is that it specifies the number of angular nodes of an amplitude function – i.e. the number of times that a particular amplitude function changes sign on  $\theta$  varying between 0 and  $\pi$  rad. The mathematical significance of radial quantum number  $k$  is that it specifies the number of radial nodes of an amplitude function – i.e. the number of times that a particular amplitude function changes sign on  $r$  varying from 0 to  $\infty$ , or the number of zero points of product  $\psi(r,\theta,\phi)^* \psi(r,\theta,\phi) = |\psi(r,\theta,\phi)|^2$  between  $r = 0$  and  $\infty$  in any direction from the origin, Whereas equatorial quantum number  $m$  has hence a direct physical significance, the azimuthal,  $l$ , and radial,  $k$ , quantum numbers have directly a mathematical significance within only a restricted geometric context, and are therefore artifacts of this derivation in spherical polar coordinates; in contrast, product  $l(l + 1)$  has a physical significance as discussed below.

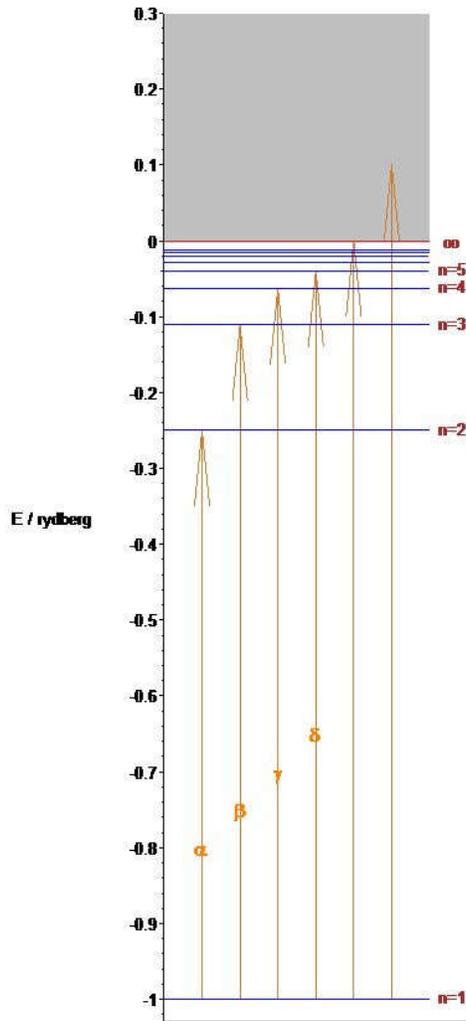
Among many properties of a hydrogen atom that one might explore after having derived explicit formulae for the amplitude or wave functions, we mention only the principal properties that concerned Heisenberg, namely the frequencies and intensities of spectral lines. The frequency  $\nu$  of a spectral line is that of a photon emitted or absorbed by an atom, and bears no direct relation to any purported internal frequency of an atom that produces that spectrum. That optical frequency is specifically the difference of energies,  $E_j$  and  $E_{j'} > E_j$ , of two states of an atom between which an optical transition occurs, divided by Planck's constant, according to Bohr's relation:

$$\nu = (E_{j'} - E_j) / h$$

The energies of states of H defined with energy quantum number  $n = k + l + 1$  are depicted in figure 2, in which energies are expressed in rydberg unit; in terms of fundamental physical constants,

$$1 \text{ rydberg} = m_e e^4 / 8 \epsilon_0^2 c h^3 = 2.179872325 \times 10^{-18} \text{ J}$$

For energies less than a limiting energy as  $n \rightarrow \infty$  that corresponds to ionization of the atom, the energies are discrete, although of formally uncountable number, whereas above that threshold the energies are continuous.



**FIGURE 2.** Energies of continuous states with positive energies and of discrete states with negative energies, relative to  $E = 0$  that pertains to a proton and an electron infinitely separate and at rest; energies at five discrete values bear labels of energy quantum number  $n$  from 1 to 5. In order of increasing length, four vertical arrows with greek letters indicate transitions between discrete states, observed in absorption in the Lyman series of lines in the vacuum-ultraviolet spectral region; two further arrows indicate a minimum ionization and a transition into the continuum of energies above the threshold of ionization.

The electric-dipolar moment appropriate to an optical transition in absorption from a state with quantum numbers  $k, l, m$  to another state with quantum numbers  $k', l', m'$  involving component  $z$ , with  $z = r \cos(\theta)$ , of the electric component of the electromagnetic field is calculated, in the length representation and with spherical polar coordinates, as quantity  $\langle e z \rangle = \langle e r \cos(\theta) \rangle$  involving integration over the corresponding wave functions that hence include the temporal dependence.

$$\langle e z \rangle = \int_0^\infty \int_0^\pi \int_0^{2\pi} \Psi_{k', l', m'}(r, \theta, \phi, t) * e r \cos(\theta) \Psi_{k, l, m}(r, \theta, \phi, t) r^2 \sin(\theta) d\phi d\theta dr$$

In this triple integral over the spatial coordinates,  $\Psi^*$  denotes a complex-conjugate wave function in terms of spatial  $r, \theta, \phi$  and temporal  $t$  variables and of quantum numbers  $k', l', m'$ ; a transformation from  $\Psi$  to  $\Psi^*$  involves the replacement everywhere of  $i$  by  $-i$ . For this observable property, intensity, as for any other observable property, the chosen value of coefficient  $c$  in the definition of the wave function above is hence immaterial. The intensity of an optical transition is proportional to the square of the above matrix element for the electric-dipolar moment of that transition, which is thus independent of the sense of  $z$  and of time  $t$ . In Dirac's notation with *bra* and *ket*, for a H atom ( $Z = 1$ ), an optical transition corresponding to vertical arrow  $\alpha$  in figure 2 is indicated from the state of least accessible energy specified with quantum numbers  $k = 0, l = 0, m = 0$ , so  $n = k + l + 1 = 1$ , to the first excited state, specified with quantum numbers  $k' = 0, l' = 1, m' = 0$ , so  $n = 2$ . This matrix element of dipolar moment is calculated symbolically to have this value:

$$\langle 0, 1, 0 | e z | 0, 0, 0 \rangle = \frac{128 \sqrt{2} h^2 \epsilon_0 \mathbf{e} \left( \left( -\frac{3 i \mu Z^2 e^4 \pi}{16 h^3 \epsilon_0^2} \right) t \right)}{243 Z e \pi \mu}$$

The states, denoted  ${}^2S$  for the electronic ground state and  ${}^2P$  for an excited state accessible therefrom in absorption, are distinct from the amplitude or wave functions expressed in a particular coordinate system with which calculations might be made, but for the particular transition indicated we associate the amplitude function specified with quantum numbers  $k=0, l=0, m=0$  uniquely with state  ${}^2S$  and amplitude function with quantum numbers  $k=0, l=1, m=0$  with state  ${}^2P$ . In the latter formula we interpret the coefficient, with  $i$ , of  $t$  in the exponent to specify the optical frequency, i.e. the angular frequency of the photon that is absorbed when a H atom undergoes the pertinent transition with a gain of one unit, in terms of  $h/2\pi$ , of angular momentum through conservation of that quantity; the circular frequency is hence

$$\nu = \frac{3 \mu Z^2 e^4}{32 h^3 \epsilon_0^2}$$

A contrast with the above interpretation of the coefficient of  $i t$  in the exponent of the wave function itself, as energy divided by Planck constant, is noteworthy. In figure 3, we show quantitatively the absorption spectrum of the H atom below the threshold of ionization: the scale of the abscissa variable has unit  $10^{15}$  Hz = PHz for frequency  $\nu$ ; because the intensities of transitions decrease rapidly with increasing frequency, for illustrative purposes the ordinate scale is logarithmic in a quantity  $10^3 f$ ; oscillator strength  $f$  is a dimensionless quantity that serves as an appropriate measure of intensity. The greek letters above the spectral lines in figure 3 pertain to the designations of features of the spectrum of the H atom in the vacuum-ultraviolet region, in which transitions in absorption occur from the ground state  $|0,0,0\rangle$  to states denoted  $|k, 1, 0\rangle$  with values of  $k$  increasing from zero, and correlate with the same greek letters in figure 2. The absorption spectrum in the continuous region above the minimum energy of ionization is calculated quantitatively elsewhere [12]; like the discrete spectrum, the intensity per unit energy in the continuous spectrum diminishes rapidly with energy increasing above the threshold of ionization.

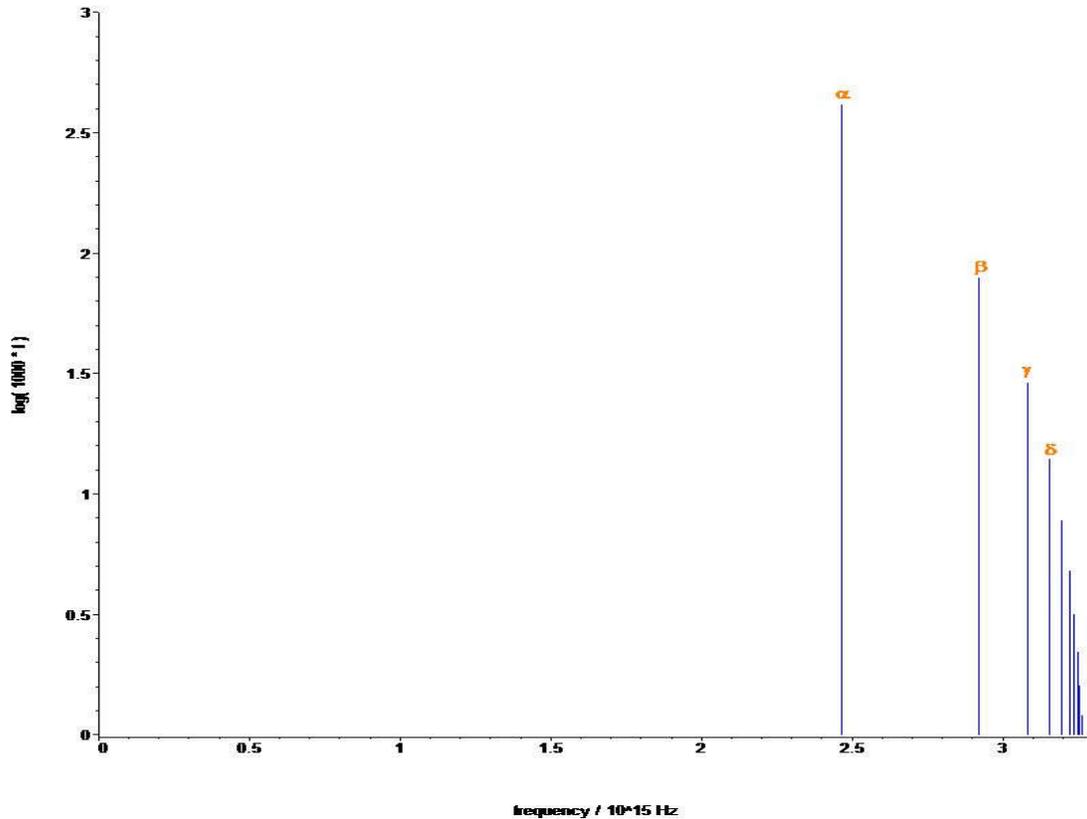


FIGURE 3. Quantitative representation of the absorption spectrum of the H atom for transitions from the ground state to ten discrete excited states as lines at particular frequencies/ $10^{15}$  Hz with intensities according to  $\log_{10}(10^3 f)$ ;  $f$  denotes the oscillator strength.

### III. GRAPHICAL REPRESENTATIONS OF AMPLITUDE FUNCTION $\psi(r, \theta, \phi)$

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, here follow plots of the surfaces of selected amplitude functions. As a plot involving three independent variables – spatial coordinates  $r, \theta, \phi$  – and one dependent variable  $\psi(r, \theta, \phi)$  would require four spatial 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 in a satisfactory manner. Because in many published papers and textbooks these surfaces are portrayed inaccurately, we explain our procedure to produce an accurate plot, deploying first for this purpose amplitude function  $\psi_{0,0,0}$ . Its formula,

$$\psi_{0,0,0} = \frac{e^3 \mu^{(3/2)} Z^{(3/2)} \pi e \left( \frac{\pi \mu Z e^2 r}{h^2 \epsilon_0} \right)}{h^3 \epsilon_0^{(3/2)}},$$

shows no dependence on angular variables, merely an exponential decay with distance  $r$  of the reduced mass from the origin of coordinates that effectively marks the location of the atomic nucleus. By assumption, the electron interacts with the nuclear matter only through the electrostatic interaction; with point particles, the probability of finding the electron is maximum at the atomic nucleus, at which the amplitude function has a cusp: i.e.  $d\psi/dr$  is discontinuous at the origin. We plot this dependence on  $r$  in figure 4 to demonstrate pertinent properties.

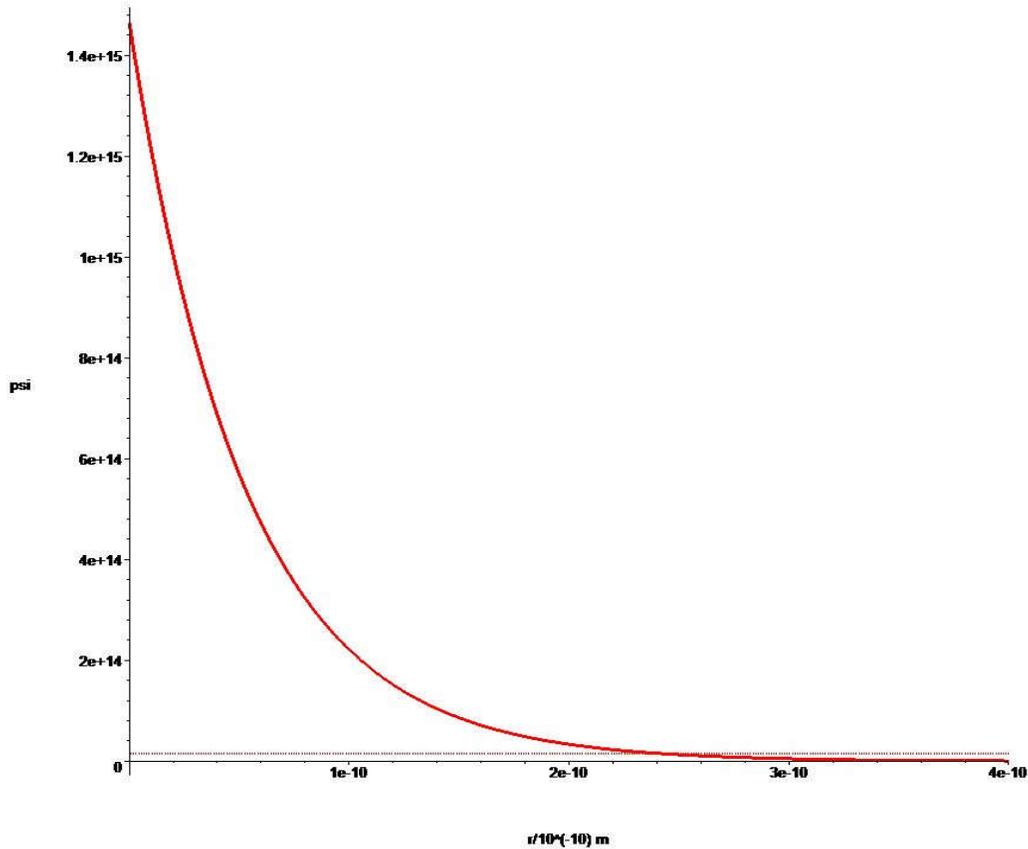


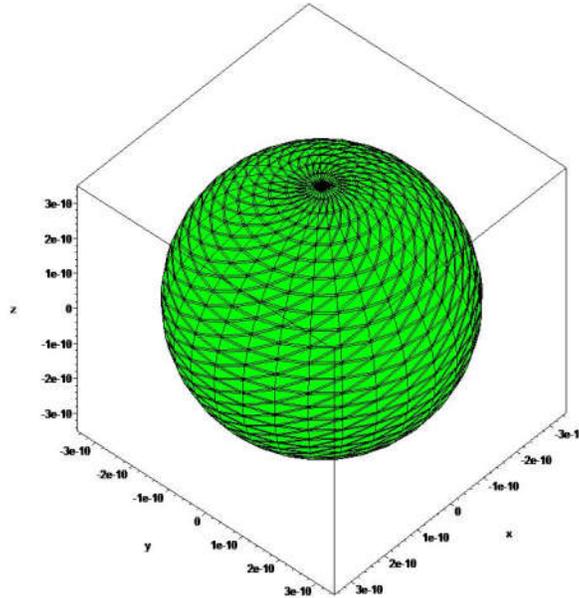
FIGURE 4. Radial dependence of  $\psi_{0,0,0}/m^{-3/2}$ ; the intersection of the dotted line with the curve indicates the point at which 0.995 of the density of electronic charge is within that distance from the origin of coordinates. Here, and in succeeding plots, notation 2e+14 implies  $2 \times 10^{14}$ ; 2e-10 implies  $2 \times 10^{-10}$ , and analogously for other values.

In figure 4, a dotted line intersects the curve depicting the radial dependence of  $\psi_{0,0,0}$  at a point  $r_c$  chosen such that 0.995 of the total density of electronic charge according to an integral,

$$\int_0^{r_c} \psi(0, 0, 0)^2 4 \pi r^2 dr$$

is within a domain  $0 \dots r_c$ ; for  $\psi_{0,0,0}$ , that distance is  $r_c = 2.45 \times 10^{-10}$  m. When we plot a surface of constant  $\psi_{0,0,0} = 1.43 \times 10^{13} \text{ m}^{-3/2}$ , which is 0.01 times the maximum value of  $\psi_{0,0,0}$ , at  $r = 0$ , we obtain necessarily a sphere, having the stated radius  $r_c$ , because  $\psi_{0,0,0}$  exhibits no angular dependence. We

must adopt such a strategy to derive a meaningful idea of any *size* or *shape* of an amplitude function, or the corresponding density of electronic charge that is proportional to  $|\psi^2|$  or  $\psi^*\psi$  according to Born's interpretation, because amplitude function  $\psi_{0,0,0}$  has zero value only as  $r \rightarrow \infty$ ; i.e. according to Schrodinger's amplitude function, a single H atom in its ground state occupies the entire universe, but not to the practical exclusion of other atoms!



**FIGURE 5.** Surface of  $\psi_{0,0,0} = 1.43 \times 10^{13} \text{ m}^{-3/2}$ . Here, and in succeeding plots in three pseudo-dimensions, the unit of length along each coordinate axis is m.

We next consider amplitude function  $\psi_{1,0,0}$  that has this explicit formula,

$$\Psi_{1,0,0} = -\frac{1}{8} \frac{\sqrt{2} e^3 \mu^{(3/2)} Z^{(3/2)} \pi (\pi Z e^2 \mu r - 2 h^2 \epsilon_0) e^{\left(-1/2 \frac{\pi \mu Z e^2 r}{h^2 \epsilon_0}\right)}}{\epsilon_0^{(5/2)} h^5}$$

first as its radial profile, shown in figure 6 with two dotted lines at  $\pm 3.17 \times 10^{12} \text{ m}^{-3/2}$ . The intersection of the line at  $-3.17 \times 10^{12} \text{ m}^{-3/2}$  with the curve at  $r_c = 7.2 \times 10^{-10} \text{ m}$  indicates the distance within which 0.995 of the total electronic charge is contained. Two other intersections of the curve with those two lines occur, both near  $1.07 \times 10^{-10} \text{ m}$ ; the latter location marks the presence of a nodal surface, the single spherical surface between  $r = 0$  and  $r \rightarrow \infty$  at which function  $\psi_{1,0,0}$  has zero amplitude and  $\psi_{1,0,0}^2 = 0$ , consistent with radial quantum number  $k = 1$ . An explanation of the appearance of that surface is that, relative to the phase convention set on assuming  $c = 1$  in the solution of the temporally dependent Schrodinger equation, the phase of the amplitude function changes from positive to negative at that distance,  $1.07 \times 10^{-10} \text{ m}$ , as depicted in figure 6. For that reason we find three concentric spheres, of which the radii correspond to the distances at which the dotted lines intersect the curve in figure 6; at all those three points, the magnitude of  $\psi_{1,0,0}$  is equal to that at the third point, at  $r_c$ , at which 0.995 of the total electronic charge is contained within

that radius. Figure 7 shows a complete inner sphere that has a positive phase, and two spheres of negative phase cut open to show that inner sphere. These plotted surfaces of  $\psi_{0,0,0}$  and  $\psi_{1,0,0}$  and the explanation underlying their generation provide a basis for further plots to illustrate salient features of selected amplitude functions.

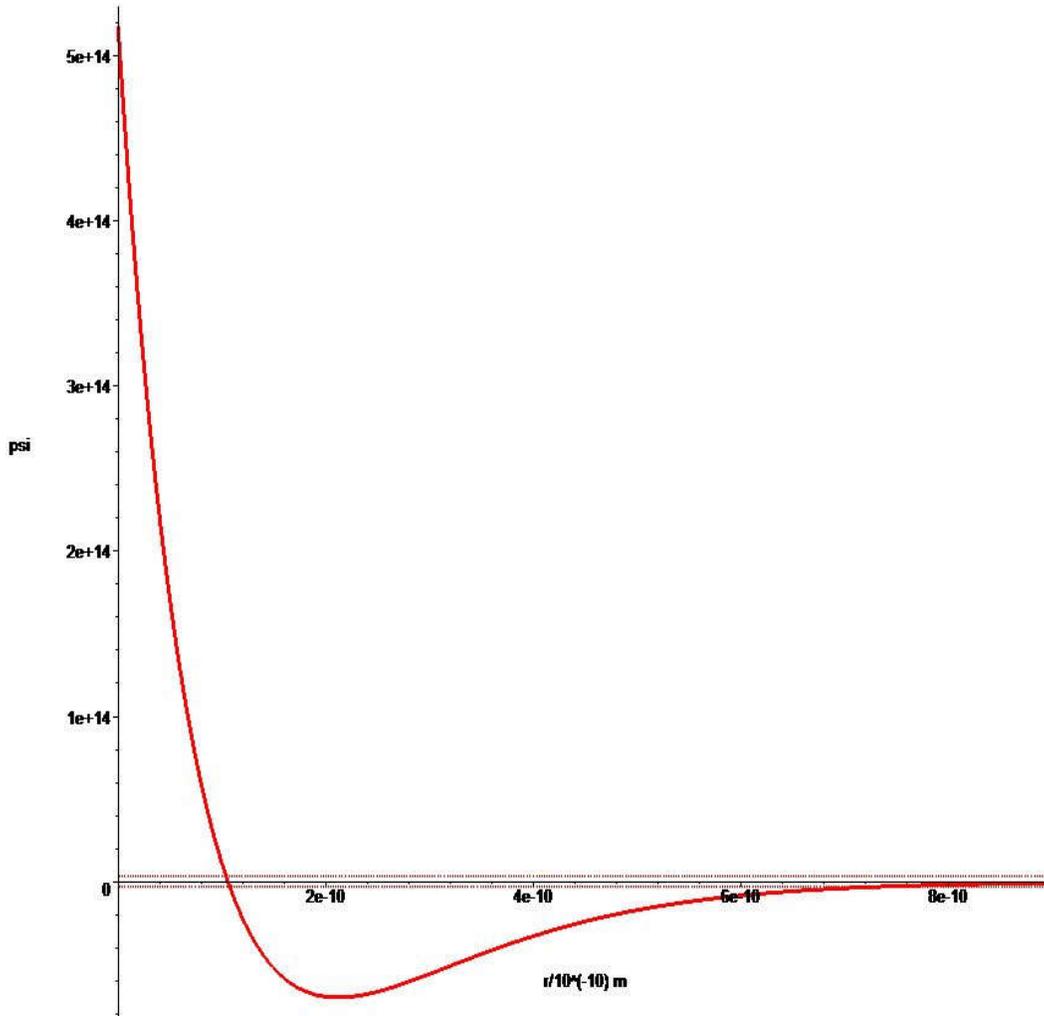


FIGURE 6. Radial dependence of  $\psi_{1,0,0}$ ; the intersection, farthest from the origin, of the lower dotted line with the curve indicates the point at which 0.995 of the electronic charge occurs within that distance from the origin of coordinates.

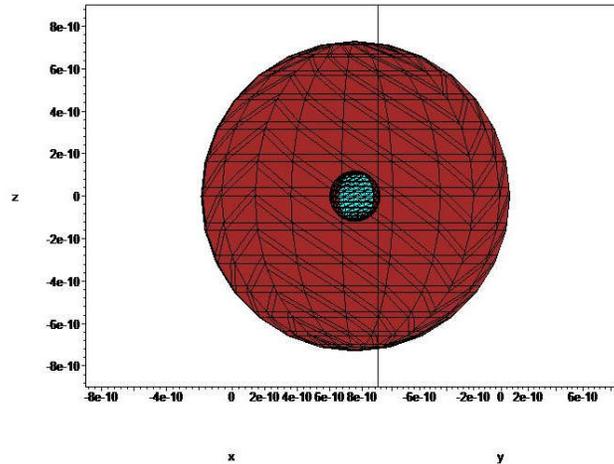
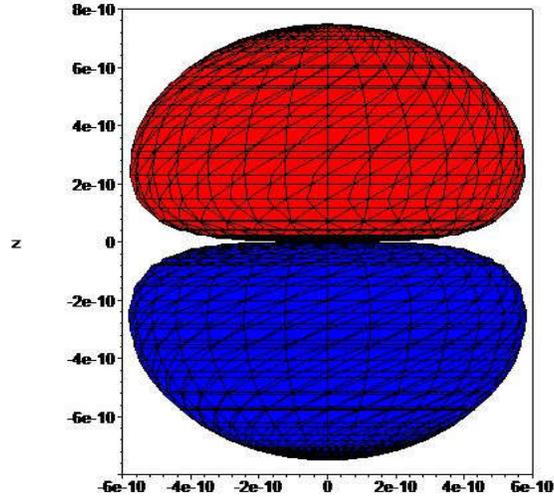


FIGURE 7. Surfaces of amplitude function  $\psi_{1,0,0} = \pm 3.17 \times 10^{12} \text{ m}^{-3/2}$ ; of three spheres, the inner one (cyan) contains the amplitude function in its positive phase; in a thick shell between an intermediate sphere (brown), of radius only slightly larger than that of the inner sphere, and the outer sphere (also brown), both shown cut open with  $\phi = 0 \dots 3\pi/2$  rad, the amplitude function has a negative phase corresponding to the profile in figure 6.

We consider next  $\psi_{0,1,0}$ , according to this formula:

$$\psi_{0,1,0} = \frac{\sqrt{2} e^5 \mu^{\left(\frac{5}{2}\right)} Z^{\left(\frac{5}{2}\right)} \pi^2 r e^{\left(-\frac{\pi \mu Z e^2 r}{2 h^2 \epsilon_0}\right)} \cos(\theta)}{8 h^5 \epsilon_0^{\left(\frac{5}{2}\right)}}$$

Consistent with azimuthal quantum number  $l = 1$ , we expect one angular node in the domain  $\theta = 0 \dots \pi$ , which is shown in figure 8 to lie in plane  $z = 0$  or  $\theta = \pi/2$ . This figure exhibits two lobes, each almost hemispherical but with rounded edges: the positive lobe for  $\psi_{0,1,0} > 0$  is axially symmetric about axis  $z$  with  $z > 0$ ; the negative lobe for  $\psi_{0,1,0} < 0$  is also axially symmetric about axis  $z$  but with  $z < 0$ ; a narrow gap between those surfaces contains a nodal plane between these two lobes at which  $\psi_{0,1,0} = 0$ . At the selected value  $|\psi_{0,1,0}| = 3.17 \times 10^{12} \text{ m}^{-3/2}$  for this surface, the same as for  $\psi_{1,0,0}$ , the maximum extent of the surface along axis  $z$ , about  $1.5 \times 10^{-9} \text{ m}$ , is slightly larger than the maximum extent perpendicular to this direction, about  $1.2 \times 10^{-9} \text{ m}$ , contrary to what one might expect from published plots of only the angular parts or of qualitative sketches based mostly on wishful thinking. The overall shape, nearly spherical or slightly prolate spheroidal, is consistent with a coulombic attraction between a proton and an electron that has no angular dependence. The square of this amplitude function has essentially the same *relative size and shape*.



**FIGURE 8.** Surface of amplitude function  $\psi(0,1,0) = \pm 3.17 \times 10^{12} \text{ m}^{-3/2}$ ; the upper lobe (red) has a positive phase, the lower lobe (blue) negative.

Like most amplitude functions expressed in spherical polar coordinates, amplitude functions  $\psi_{0,1,1}$  and  $\psi_{0,1,-1}$  are complex: for a given value of energy quantum number  $n$ , explicitly  $n^2 - n$  functions have both real and imaginary parts for the choice of coefficient  $c = 1$ . For this function,

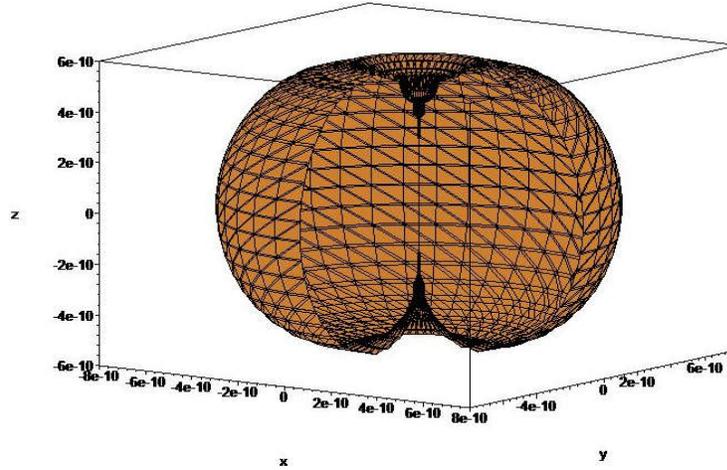
$$\Psi_{0,1,1} = \frac{e^5 \mu^{\left(\frac{5}{2}\right)} Z^{\left(\frac{5}{2}\right)} \pi^2 r e^{\left(-\frac{\pi \mu Z e^2 r}{2 h^2 \epsilon_0}\right)} \sin(\theta) (\cos(\phi) + i \sin(\phi))}{8 h^5 \epsilon_0^{\left(\frac{5}{2}\right)}}$$

of which the real part contains the cosine function, its plot generates a figure identical with that in figure 8 except that it is axially symmetric about axis  $y$  instead of axis  $z$ ; the plot of the imaginary part, containing the sine function, is, analogously, axially symmetric about axis  $x$ ; i.e. each such surface is the same as that in figure 8 but rotated about axis  $x$  or  $y$ . Their positive lobes extend along the respective positive axes  $y$  and  $x$ , and their negative lobes along the same negative axes. A more intriguing aspect is the square of either  $\psi_{0,1,1}$  or  $\psi_{0,1,-1}$ , which are identical according to this formula because the dependence on  $\phi$  is lost in the square,

$$\Psi_{0,1,1}^2 = \frac{1}{64} \frac{\mu^5 Z^5 e^{10} \pi^4 r^2 e^{\left(-\frac{\pi \mu Z e^2 r}{h^2 \epsilon_0}\right)} \sin(\theta)^2}{h^{10} \epsilon_0^5}$$

and which, cut open to reveal the inner structure, is depicted accurately in figure 9; there is explicitly zero density of  $\psi_{0,1,1}^2$  or electronic charge along polar axis  $z$  at which  $r \sin(\theta) = \theta = 0$  or  $\pi$  rad. Whereas both  $\psi_{0,1,0}$  and its square display an overall shape of slightly prolate spheroid with a plane of zero amplitude or density between two nearly hemispherical lobes, the square of either

$\psi_{0,1,1}$  or  $\psi_{0,1,-1}$ , calculated as  $|\psi_{0,1,1}|^2 = \psi_{0,1,1}^* \psi_{0,1,1}$  or analogously, displays as an oblate toroid with zero density along polar axis  $z$ . The extent of this toroid at the given value of  $\psi_{0,1,1}^2$  is about  $1.15 \times 10^{-9}$  m along axis  $z$  and  $1.3 \times 10^{-9}$  m perpendicular to this axis. The surface of sum  $\psi_{0,1,0}^2 + |\psi_{0,1,1}|^2 + |\psi_{0,1,-1}|^2 = 1.0 \times 10^{25} \text{ m}^{-3}$  displays as a perfect sphere, of diameter  $1.55 \times 10^9$  m with the same criterion of enclosed electronic charge.



**FIGURE 9.** Surface of squared amplitude function  $\psi_{0,1,1}^2 = 1.0 \times 10^{25} \text{ m}^{-3}$ , shown cut open with  $\phi = 0 \dots 3 \pi/2$  rad to reveal the zero density along polar axis  $z$ .

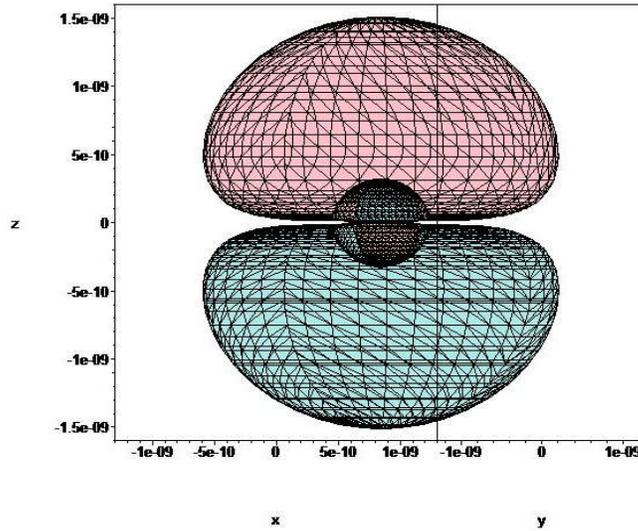
A plot of amplitude function  $\psi_{2,0,0}$  exhibits two nodal concentric spherical surfaces, consistent with  $k = 2$ , between one inner sphere of positive phase and two larger spherical shells, of successively negative and positive phases, analogously to  $\psi_{1,0,0}$  in figure 6 that displays only one inner spherical nodal surface; with the surfaces set for  $|\psi_{2,0,0}| = 1.23 \times 10^{12} \text{ m}^{-3/2}$ , the diameters/ $10^{-10}$  m of the nodal surfaces are equal to about 2 and 8. According to our stated criterion of enclosed electronic charge being 0.995 of the total negative charge, the diameter of the outer sphere is  $2.8 \times 10^{-9}$  m, increased from  $0.49 \times 10^{-9}$  m for  $\psi_{0,0,0}$  and  $1.44 \times 10^{-9}$  m for  $\psi_{1,0,0}$ .

We show in figure 10 the surface of  $\psi_{1,1,0}$  that has this formula,

$$\Psi_{1,1,0} = -\frac{1}{81} \frac{\sqrt{2} e^5 \mu^{(5/2)} Z^{(5/2)} \pi^2 (\pi Z e^2 \mu r - 6 h^2 \epsilon_0) r e^{\left(-\frac{1}{3} \frac{\pi \mu Z e^2 r}{h^2 \epsilon_0}\right)} \cos(\theta)}{\epsilon_0^{(7/2)} h^7}$$

Like figure 8 that shows two nearly hemispherical lobes, figure 10 shows two large nearly hemispherical lobes, one of positive and one of negative phase, each with an embedded small nearly hemispherical lobe of opposite phase near the origin, all symmetric about axis  $z$ . For  $\psi_{1,1,0} = \pm 1.23 \times 10^{12} \text{ m}^{-3/2}$ , the maximum extent of the surface along axis  $z$  is about  $2.8 \times 10^{-9}$  m, and  $2.4 \times 10^{-9}$  m perpendicular to this direction, so slightly prolate spheroidal in overall shape. For  $\psi_{1,1,1}$  or  $\psi_{1,1,-1}$  that has both real and imaginary parts, those parts exhibit an identical shape and size axially symmetric about axes  $y$  or  $x$ , respectively, analogous to the relation between  $\psi_{0,1,0}$  depicted in figure 8 and  $\psi_{0,1,1}$  or  $\psi_{0,1,-1}$ , but rotated about axis  $y$  or  $x$ . The surface representing sum  $\psi_{1,1,0}^2 + \psi_{1,1,1}^*$

$\psi_{1,1,1} + \psi_{1,1,-1}^* \psi_{1,1,-1} = 1.25 \times 10^{24} \text{ m}^{-3}$  is again a perfect sphere, of diameter about  $3 \times 10^{-9} \text{ m}$ , with no internal structure.



**FIGURE 10.** Surface of amplitude function  $\psi_{1,1,0} = \pm 1.23 \times 10^{12} \text{ m}^{-3/2}$  shown cut open with  $\phi = 0 \dots 3\pi/2$  rad to exhibit the inner structure; phases positive (pink) and negative (light blue) are indicated.

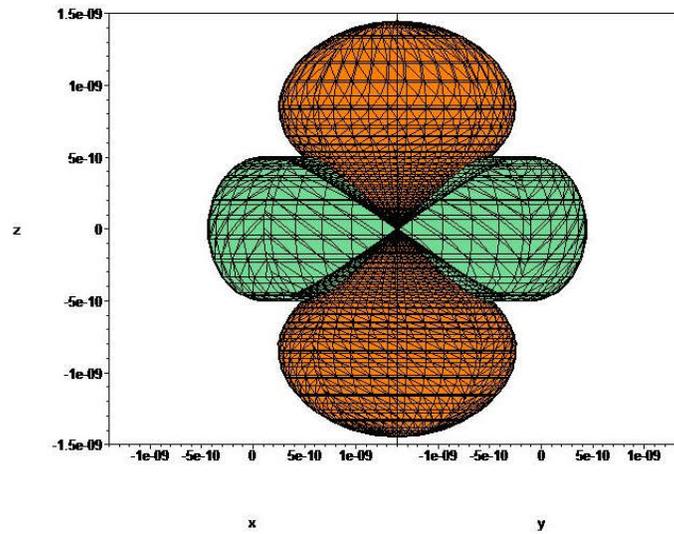
As an amplitude function that presents further features, we consider  $\psi_{0,2,0}$  that implies  $l = 2$ , according to this formula:

$$\Psi_{0,2,0} = \frac{1}{486} \frac{\sqrt{6} e^7 \mu^{(7/2)} Z^{(7/2)} \pi^3 r^2 e^{\left(-\frac{1}{3} \frac{\pi \mu Z e^2 r}{h^2 \epsilon_0}\right)} (3 \cos(\theta)^2 - 1)}{\epsilon_0^{(7/2)} h^7}$$

Its surface with  $\psi_{0,2,0} = \pm 1.23 \times 10^{12} \text{ m}^{-3/2}$  appears in figure 11. In accordance with  $k = 0$ , there is no radial node – along a line in any direction from the origin, the amplitude function does not change sign, but from polar angle  $\theta = 0$  to  $\theta = \pi$  rad there are two changes of sign, from positive to negative and back to positive, consistent with  $l = 2$ . The shape might be described as a torus of positive phase separating two, somewhat conical, negative lobes. The figure is axially symmetric about axis  $z$ ; its maximum extents/ $10^{-9} \text{ m}$  are 2.9 along polar axis  $z$  and 2.6 perpendicular to that axis, so again slightly prolate spheroidal in overall shape. The square of this amplitude function has approximately the same *relative size and shape*.

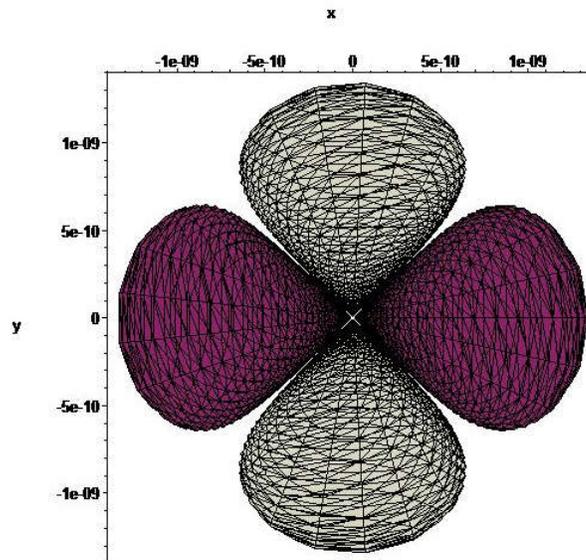
For contrast we show surfaces of the real and imaginary parts of complex amplitude function  $\psi_{0,2,2}$  expressed with  $\phi$  in trigonometric form as

$$\Psi_{0,2,2} = -\frac{1}{162} \frac{e^7 \mu^{(7/2)} Z^{(7/2)} \pi^3 r^2 e^{\left(-\frac{\pi \mu Z e^2 r}{3 h^2 \epsilon_0}\right)} \sin(\theta)^2 (\cos(2\phi) + i \sin(2\phi))}{h^7 \epsilon_0^{(7/2)}}$$

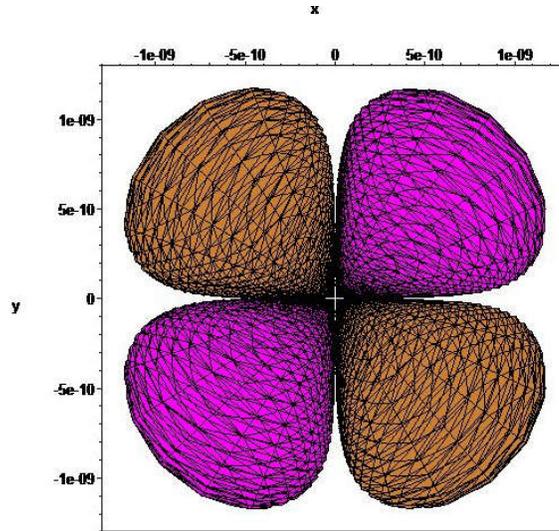


**FIGURE 11.** Surface of amplitude function  $\psi_{0,2,0} = \pm 1.23 \times 10^{12} \text{ m}^{-3/2}$ , shown cut open with  $\phi = 0 \dots 3\pi/2$  rad to reveal the angular nodes and lack of radial node; coral colour indicates a positive phase, aquamarine negative.

The real part of the surface of this amplitude function  $\psi_{0,2,2}$ , containing  $\cos(2\phi)$  and shown in figure 12, and the imaginary part, containing  $\sin(2\phi)$  and shown in figure 13, reveal a four-fold symmetry about axis  $z$ , apart from their phases.



**FIGURE 12.** Surface of real part of amplitude function  $\psi_{0,2,2} = \pm 1.23 \times 10^{12} \text{ m}^{-3/2}$ ; the wheat lobes have positive phase, the maroon lobes negative.



**FIGURE 13.** Surface of imaginary part of amplitude function  $\psi(0,2,2) = \pm 1.23 \times 10^{12} \text{ m}^{-3/2}$ ; the golden lobes have positive phase, the magenta lobes negative.

The maximum extent of the displayed surface of the real part of  $\psi_{0,2,2} = \pm 1.23 \times 10^{12} \text{ m}^{-3/2}$  along axes  $x$  and  $y$  is  $2.7 \times 10^{-9} \text{ m}$ , but the thickness of the body, parallel to axis  $z$ , is only about  $1.8 \times 10^{-9} \text{ m}$ ; the imaginary part has similar dimensions but its orientation is rotated about polar axis  $z$  by  $\pi/8$  rad. The surface of the square of  $\psi_{0,2,2}$ , calculated as  $\psi_{0,2,2}^* \psi_{0,2,2}$ , resembles a torus with a narrow core along axis  $z$  that is empty of electronic charge, similar to that in figure 9. The surfaces of  $\psi_{0,2,-2} = \pm 1.23 \times 10^{12} \text{ m}^{-3/2}$  in their real and imaginary parts are practically identical to those of the corresponding parts of  $\psi_{0,2,2} = \pm 1.23 \times 10^{12} \text{ m}^{-3/2}$ . The surfaces of  $\psi_{0,2,1}$  and  $\psi_{0,2,-1}$  are analogous to those of the imaginary parts of  $\psi_{0,2,2}$  and  $\psi_{0,2,-2}$  except that they display a nearly four-fold symmetry about axes  $x$  and  $y$ , respectively, rather than about polar axis  $z$ ; their lobes extend only between the cartesian axes, as in figure 13, rather than along axes as in figure 12. The surface of the square of  $\psi_{0,2,1}$ , calculated as  $\psi_{0,2,1}^* \psi_{0,2,1} = 1.5 \times 10^{24} \text{ m}^{-3}$ , is shown in figure 14; it exhibits a narrow core of zero electronic charge density along polar axis  $z$  and a nodal plane at  $z = 0$  at which the electronic charge density is also zero. Its maximum extent parallel to axis  $z$  is  $2.1 \times 10^{-9} \text{ m}$  and perpendicular to polar axis  $z$  is  $2.3 \times 10^{-9} \text{ m}$ , making its overall shape approximately slightly oblate spheroidal.

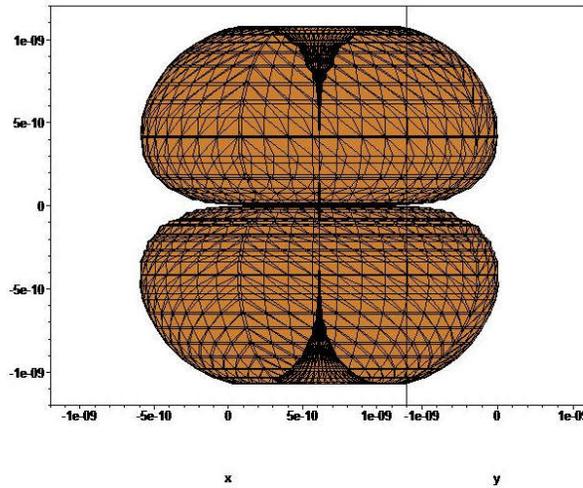
According to the same criterion of enclosed electronic charge, the surface of sum

$$|\Psi_{0,2,0}|^2 + |\Psi_{0,2,1}|^2 + |\Psi_{0,2,-1}|^2 + |\Psi_{0,2,2}|^2 + |\Psi_{0,2,-2}|^2 = 1.5 \times 10^{24} \text{ m}^{-3}$$

of the squared amplitude functions for  $k = 0$  and  $l = 2$  is a perfect sphere of diameter  $2.9 \times 10^{-9} \text{ m}$ .

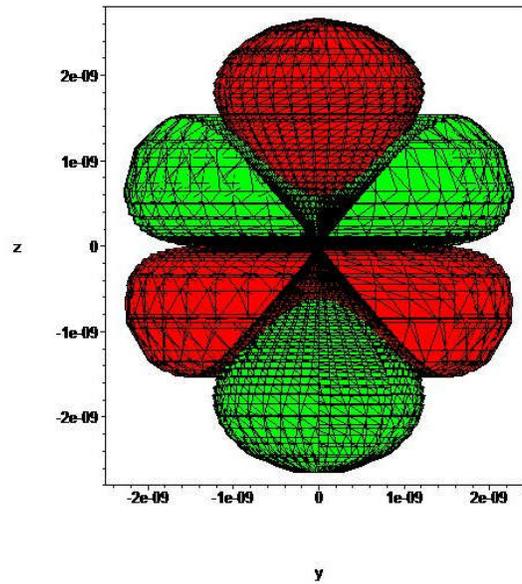
As examples of the general features of surfaces of spherical polar amplitude functions with further values of azimuthal quantum number  $l$ , we show in figure 15 the surface of  $\psi_{0,3,0}$ ,

$$\Psi_{0,3,0} = \frac{1}{15360} \frac{\sqrt{5} e^9 \mu^{(9/2)} Z^{(9/2)} \pi^4 r^3 e^{\left(-\frac{1}{4} \frac{\pi \mu Z e^2 r}{h^2 \epsilon_0}\right)} \cos(\theta) (5 \cos(\theta)^2 - 3)}{h^9 \epsilon_0^{(9/2)}}$$



**FIGURE 14.** Surface of  $|\psi_{0,2,1}|^2 = \psi_{0,2,1}^* \psi_{0,2,1} = 1.5 \times 10^{24} \text{ m}^{-3}$ , shown cut open with  $\phi = 0 \dots 3 \pi/2$  rad to expose zero density along polar axis  $z$  and in plane  $z = 0$ .

which exhibits the corresponding numbers of angular nodes,  $l = 3$ , with two tori of roughly conical cross section separating two roughly conical lobes along the polar axis, but no radial node.

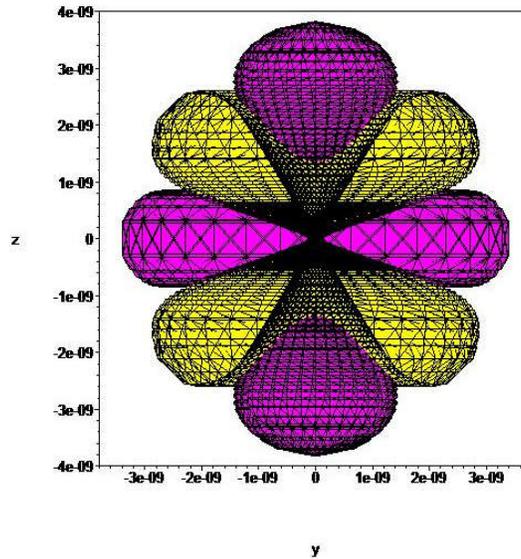


**FIGURE 15.** Surface of spherical polar amplitude function  $\psi_{0,3,0} = \pm 1.85 \times 10^{11} \text{ m}^{-3/2}$ , shown cut open with  $x = -2.5 \times 10^{-9} \dots 0.5 \times 10^{-9} \text{ m}$  to expose the nodal surfaces; the red lobes have positive phase, the green lobes negative.

Figure 16 displays a surface of  $\psi_{0,4,0}$ ,

$$\Psi_{0,4,0} = \frac{1}{13125000} \sqrt{70} e^{11} \mu^{(11/2)} Z^{(11/2)} \pi^5 r^4 e^{\left( -\frac{1}{5} \frac{\pi \mu Z e^2 r}{h^2 \epsilon_0} \right)} \frac{(35 \cos(\theta)^4 - 30 \cos(\theta)^2 + 3)}{\epsilon_0^{(11/2)} h^{11}}$$

with  $l = 4$ , which exhibits three tori of roughly conical cross section separating two lobes of roughly conical shape.



**FIGURE 16.** Surface of spherical polar amplitude function  $\psi_{0,4,0} = \pm 1.1 \times 10^{11} \text{ m}^{-3/2}$ , shown cut open with  $x = -2.8 \times 10^{-9} \dots 0.8 \times 10^{-9} \text{ m}$  to expose the nodal surfaces; the violet lobes have positive phase, the yellow lobes negative.

Many other plots of surfaces of amplitude functions or their squares might be presented, but the examples provided above likely demonstrate both the qualitative and the quantitative features of these functions in spherical polar coordinates as solutions of Schroedinger's temporally independent equation that is applicable to states of the hydrogen atom with discrete energies.

#### IV. DISCUSSION

Although the treatment of the hydrogen atom, or a hydrogenic atom with one electron or the Kepler problem or the central-field problem as alternative descriptions, with Schroedinger's equation temporally dependent or independent in spherical polar coordinates is much discussed elsewhere, a principal objective here is to emphasize the particular quantitative aspects of this system of coordinates for comparison with the results in other systems in succeeding parts of this series. A treatment of this system of spatial coordinates comprising  $r$ ,  $\theta$  and  $\phi$  yields results in the form of amplitude functions involving quantum numbers  $k$ ,  $l$  and  $m$ ; we summarize this condition according to notation  $\psi_{k,l,m}(r,\theta,\phi)$  for the amplitude function. Including the temporal variable to specify the wave function as  $\Psi_{k,l,m}(r,\theta,\phi,t)$  produces no advantage because the temporal part of the solution of Schroedinger's equation is, naturally, common to all pertinent systems of coordinates in a non-relativistic sense; energy quantum number  $n$  results from an analysis of experiments in the form of optical spectra, and the form of its dependence is duly reproduced in the theoretical derivation incorporating a temporal dependence as summarized above for spherical polar coordinates when we associate  $k + l + 1$  with  $n$ .

With each plot presented here is specified an explicit formula of the particular associated amplitude function to emphasize that these plots depict mathematical functions; for the same reason, these functions include explicitly the pertinent fundamental physical constants, evaluated for all purposes rigorously in SI units. *A shape of a surface illustrated in any such plot implies an*

associated formula, and vice versa; such a shape is meaningless in the absence of both such a formula and the specified system of coordinates, and even a specific constant value of that formula. An accurate surface of each such amplitude function displayed within a preceding plot hence pertains to a particular value of that function  $\psi_{k,l,m}$  or its square; such an amplitude function has an accompanying unit in terms of a unit of length to the appropriate power, specifically  $\text{m}^{-3/2}$  in SI units for  $\psi$ , and accordingly  $\text{m}^{-3}$  for  $\psi^2$ ; integration over all space effectively multiplies the units of the squared amplitude function by  $\text{m}^3$ , generating a dimensionless value of that integral that we might associate with unit probability according to Born's interpretation. The shape of the surface depends also on the chosen value of  $\psi$  or  $\psi^2$  for that surface to some extent; the criterion for the value of  $\psi$  might be chosen to differ from that of  $\psi^2$  containing 0.995 of the total electronic charge, which would accordingly affect the shape, and size, of the surface.

The important results of the preceding treatment are that spatial coordinates  $r, \theta, \phi$  in this spherical polar system lead irrevocably, on solution of Schroedinger's equations, to formulae expressed in terms of quantum numbers  $k, l, m$ . Unlike energy quantum number  $n$  that is independent of any system of coordinates and that arises indisputably from experiment, quantum numbers  $k$  and  $l$  have only a parochial significance: they are artifacts of this particular system and can be accordingly expected to have no meaning for the formulae and shapes of surfaces of amplitude functions apart from this system. Whereas equatorial quantum number  $m$  is directly related to the angular-momentum properties of the atom in states that are independent of coordinates in a chosen system,  $l$  is only indirectly related, because the squared total angular momentum  $L^2$ , hence a scalar quantity with no directional property, is equal to  $l(l+1)h^2/4\pi^2$ . For each value of  $k+l+1$ , there are  $2l+1$  values of  $m$ ; the values of  $l$  run from 0 to  $n-1 = k+l$ . There are hence quantum numbers in

$$\sum_{l=0}^{n-1} (2l+1) = n^2$$

sets that specify a particular amplitude function for each value of  $n$ ; among these orthogonal functions, for coefficient  $c = 1$ ,  $n^2 - n$  functions are complex, so having real and imaginary parts; apart from any other consideration, the fact of these imaginary parts means that these functions have no direct physical reality. There are also  $n^2$  spectrometric states for each value of  $n$ . We reiterate that there is, in general, no direct relation between a spectrometric state, as denoted below, and a particular amplitude function  $\psi_{k,l,m}$  corresponding to quantum numbers  $k, l, m$  in a specific set; the ground state is an exception to this condition. The importance of this reasoning becomes incontestable when one proceeds to contemplate solutions of Schroedinger's equation temporally independent with coordinates in other systems and their associated quantum numbers, as discussed in succeeding parts of articles in this series. The designation of a spectrometric state of the hydrogen atom is based conventionally on a value of azimuthal quantum number  $l$  – S states for  $l = 0$ , P states for  $l = 1$ , D states for  $l = 2$  et cetera, originating in the terminology of Liveing and Dewar for sharp, principal and diffuse series of lines in atomic spectra; the quantum number for energy might be included in such a designation as  $n l$ , and all states are doublet states, indicated as a prefixed superscript, when the purported intrinsic angular momentum of the electron is taken also into account, to yield a term symbol such as  $1^2\text{S}, 2^2\text{S}, 2^2\text{P}$  et cetera. Such an intrinsic angular momentum is beyond the purview of Schroedinger's treatment. The line marked  $\alpha$  in the discrete absorption spectrum in figure 3, of least energy of the photon, hence represents a transition that might be denoted  $2^2\text{P} \leftarrow 1^2\text{S}$ ; all such spectral lines have fine structure, not indicated in figure 3

because its calculation is beyond the scope of pioneer quantum mechanics and is related to the coupling of intrinsic electronic and nuclear angular momenta.

The Zeeman effect, whereby spectral lines split and have their frequencies or wave lengths altered when a sample of atoms is subjected to an external magnetic field, is related to component  $L_z$  of electronic angular momentum due to its motion, which yields equatorial quantum number  $m$ . Although a treatment of this Zeeman effect is practicable with amplitude functions in spherical polar coordinates, to produce the *normal* Zeeman effect, taking into consideration also the intrinsic angular momentum of the electron -- its purported spin -- produces the *anomalous* Zeeman effect. Because such an electron spin is beyond the scope of the Schroedinger equation as presented above, we omit this discussion.

The *shapes* of surfaces of these amplitude functions  $\psi_{k,l,m}(r,\theta,\phi)$  are likewise parochial; they are hence artifacts of this particular system, and accordingly lack meaning beyond this system, as is demonstrated on comparison with shapes of surfaces of amplitude functions in other systems of coordinates, presented in further articles in this series. The *sizes* of the surfaces of these amplitude functions at the selected values according to a particular criterion of enclosed electronic charge are, in contrast, a result of the coulombic potential energy, and are seen to be approximately common to amplitude functions, expressed in various coordinates, corresponding to the same energy quantum number  $n$ . In the preceding figures, the shapes of the nodal surfaces that lie between lobes of opposite phase are spheres centred at the origin, or cones centred about the polar axis, or planes containing the cartesian axes, reflecting the nature of the system of spherical polar coordinates  $r, \theta, \phi$ , respectively.

Apart from any fine structure that results from the purported electronic spin, the energy of a discrete state of a H atom is commonly stated to depend only on  $n$ ; as  $n$  must be regarded as the energy quantum number, such a statement appears tautological. For only a hydrogenic atom, as defined above, is the energy synonymous with an energy quantum number. As  $n$  represents, for only spherical polar (and spheroconical) coordinates, a sum  $k + l + 1$ , the energy of a discrete state hence depends equivalently on quantum numbers  $k$  and  $l$ , but not on  $m$  in the absence of an external field applied to the atom. Whereas  $l$  has an indirect connexion with angular momentum, as explained above, an interpretation of  $k$  other than as signifying the number of radial nodes is challenging. For instance, the mean distance of the electron from the origin near the atomic nucleus for atomic number  $Z$ , or expectation value  $\langle r \rangle$ , as a function of quantum numbers is, expressed in terms of Bohr radius  $a_0$ ,

$$\langle r \rangle = \frac{a_0}{Z} \left( \frac{3}{2} k^2 + 3 k l + l^2 + 3 k + \frac{5}{2} l + \frac{3}{2} \right),$$

which depends, to comparable extents, on both  $k$  and  $l$ , which can vary independently. In the absence of an externally applied electric or magnetic field, the independence of the energy on equatorial quantum number  $m$  is attributed to the isotropic nature of space: there is no preferred axis or direction.

One might seek to overcome the complex nature of amplitude functions on forming linear combinations of two or more functions with the same values of quantum numbers  $k$  and  $l$ , but different  $m$ , such as in the following examples. This sum of two particular amplitude functions,

$$\frac{\Psi_{0,1,1} + \Psi_{0,1,-1}}{\sqrt{2}} = \frac{\sqrt{2} e^5 Z^{\left(\frac{5}{2}\right)} \mu^{\left(\frac{5}{2}\right)} \pi^2 r e^{\left(-\frac{Z e^2 \pi \mu r}{2 h^2 \varepsilon_0}\right)} \sin(\theta) \cos(\phi)}{8 \varepsilon_0^{\left(\frac{5}{2}\right)} h^5}$$

produces a plot exactly like that in figure 8 except that the axis of cylindrical symmetry is  $x$  instead of  $z$ . The difference of the same two particular amplitude functions, divided by  $i$ ,

$$\frac{\Psi_{0,1,1} - \Psi_{0,1,-1}}{\sqrt{2} i} = \frac{\sqrt{2} e^5 Z^{\left(\frac{5}{2}\right)} \mu^{\left(\frac{5}{2}\right)} \pi^2 r e^{\left(-\frac{Z e^2 \pi \mu r}{2 h^2 \varepsilon_0}\right)} \sin(\theta) \sin(\phi)}{8 \varepsilon_0^{\left(\frac{5}{2}\right)} h^5}$$

likewise produces a plot exactly like that in figure 8 except that the axis of cylindrical symmetry is  $y$  instead of  $z$ , but both such plots depend on an arbitrary choice of coefficient  $c = 1$ . The value of  $l$  for the sum and difference appears to remain unity, but the value of equatorial quantum number  $m$  is indeterminate – until one recognizes that those results simply correspond to a rotation of the coordinate axes [13] to redirect  $\psi_{0,1,0}$ . Such a rotation hence implies again no direct physical reality.

Another notable aspect of the figures showing surfaces of constant amplitude is the dominance of the polar axis, to which polar angle  $\theta$  is referred. Although an amplitude function such as  $\psi_{0,1,1}(r,\theta,\phi)$  is not axially symmetric with respect to this polar axis, its square acquires that property. Despite this apparent special spatial feature, in the absence of an externally applied electric or magnetic field a hydrogen atom is *spherically symmetric* – there is no preferred axis of symmetry, as mentioned above. The solution of Schroedinger's equation, temporally dependent or independent, in spherical polar coordinates is valid only under conditions of rigorously spherical symmetry -- no other matter in the system, no externally applied electric field. A related aspect is the small extent of a deviation from spherical symmetry demonstrated by the only slightly prolate or oblate spheroidal overall shapes of the surfaces of amplitude functions and their squares. A major distinction between the surfaces of amplitude functions  $\psi_{0,0,0}$  and  $\psi_{1,0,0}$  in figures 5 and 7 or between  $\psi_{0,1,0}$  and  $\psi_{1,1,0}$  in figures 8 and 10 is the appearance of an inner sphere, in the functions with  $l = 0$ , or two hemispheres, for  $l = 1$ . This feature is common to all further amplitude functions in spherical polar coordinates in which radial quantum number  $k$  increases by one unit between two instances; when  $k$  increases by two units, the distinction amounts to two further inner spheres or their parts or two further radial or spherical nodal surfaces. This property is a direct result of the fundamental significance of this quantum number  $k$ : it specifies the number of radial nodes. Likewise, as is evident from figures 5, 8, 11, 15 and 16, quantum number  $l$  specifies the number of angular nodes. As amplitude functions for  $l > 4$  have no practical application in a chemical or physical context, further plots of surfaces to show the shapes are of negligible interest.

A claim [14] to have obtained an additional solution of Schroedinger's equation in rectangular or cartesian coordinates is misleading because those four coordinates  $(x,y,z,r)$  include also the radial distance  $r$ . The other coordinates provide, as ratios of cartesian coordinates and their combinations, an alternative to spherical harmonics, and allow eigenfunctions of angular momentum to avoid reference to polar angles. This system of coordinates must be considered to be merely a variant of spherical polar coordinates.

In a subsequent part of this sequence of articles, we form an overview of all solutions of Schroedinger's temporally dependent equation in the four systems of coordinates, the quantum numbers in their corresponding sets and the related properties.

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