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Lectures on the Quantum Mechanics of the Electron in Hydrogen atom

Lecture Objectives:

1. To introduce the details of the three dimensional Hamiltonian operator for electron in the hydrogen atom.
2. To introduce the concept of coordinate transformation between Cartesian and polar coordinates in two dimensions and Cartesian and spherical polar coordinates in three dimensions.
3. To express the partial derivatives in both coordinates and to derive the kinetic energy operator for the electron in the hydrogen atom in spherical polar coordinates.
4. To illustrate the separation of the variables for hydrogen atom wave functions (r, θ and ϕ) and write down solutions to the hydrogen atom which are obtained as part of a standard method for solving differential equations.
5. To provide visual aids to analyze the angular distribution of the wave functions and determine the number of nodes, signs of the wave functions in different regions of space and the orthonormality properties of the wave functions.
6. To calculate radial and angular probabilities as well as obtain average values of measurable quantities.
7. To introduce spin of the electron in an ad hoc manner as a fundamental property of the electron and discuss electronic structure and the build-up principle for many-electron atoms.

Lecture Deliverables:

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This is a long lecture. At the end of reading this and doing the calculations as directed, the student will be able to do the following:

1. Visualize the energy levels and write down the wave functions of all one-electron atoms.
2. Write down all the degenerate orbital wave function (angular functions) and identify their functional dependence on the three quantum numbers, n, l and m.
3. Determine the shapes of p, d and f orbitals and the nodes and signs of all angular distributions.
4. Be able to calculate probability densities of different wave functions and identify nodes of them.
5. Be able to calculate most probable radii for all orbitals, average values of radii for all orbitals and average values for kinetic and potential energies for each state of the electron in the hydrogen atom.
6. Be able to verify that the electron cannot be simultaneously located in more than one orbital through calculation of overlaps between wave functions.
7. Br prompted to study the process of solution of the three differential equations (Laguerre equation, Legendre equation and the associated Legendre equation).
8. Be able to organize the orbitals according to an approximate sequence of increasing energies and apply Aufbau principle for arriving at the electronic configuration of polyelectronic atoms.
9. Be able to calculate eigenvalues for states of electron spin in a magnetic field.

Lecture Summary:

1. The Hamiltonian for the electron in the hydrogen atom (that of a reduced mass in the two-body problem of proton-electron) is written in Cartesian coordinates.
2. A procedure for transforming the Cartesian derivatives and wave functions to spherical polar coordinate forms is described and illustrated.

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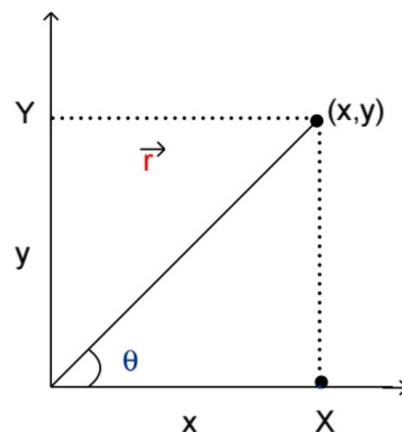This is the subtitle of PDF, Use long text here.

3. The spherical polar form of Hamiltonian is separated into three component differential equations, one each for r, θ and ϕ. The process of separating the equation is instructional to suggest how to handle similar differential equations in physics and engineering and in the use of other coordinate systems.

4. The solutions for the radial and angular parts of the differential equations are enumerated.

5. Visual aids using two and three dimensional animations are provided.

6. The probability density and spherical volume are derived and expectation values of average kinetic and potential energies are given for sample states of the electron.

Lecture Details:

1. Use of partial derivatives and coordinate transformations.

Cartesian to polar coordinates. (Two dimensions)

$$(x, y) \Leftrightarrow (r, \theta)$$

$$x = r \cos \theta$$
$$y = r \sin \theta$$

(1)

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Inverse relation:

$$r = \sqrt{x^2 + y^2}$$

$$\tan\theta = \frac{y}{x} \tag{2}$$

$$\theta = \tan^{-1}\frac{y}{x}$$

A function of $f(x, y)$, if it is to be expressed as a function of, r and θ it is first changed by substituting the above.

Thus, for example,

$$f(x, y) = x^2 y$$

$$= r^2 \cos^2\theta \cdot r\sin\theta$$

$$= r^3 \cos^2\theta \sin\theta = g(r, \theta) \tag{3}$$

$$\frac{\partial f}{\partial x} = 2xy = 2r\cos\theta \cdot r\sin\theta$$

$$= 2r^2 \cos\theta\sin\theta$$

The next step is to define the derivative operator using the coordinate transformation. (4)

After coordinate transformation one gets

$$\frac{\partial f}{\partial x} = \frac{\partial f}{\partial r}\cdot\frac{\partial r}{\partial x} + \frac{\partial f}{\partial \theta}\cdot\frac{\partial \theta}{\partial x} \tag{5}$$

The derivatives of r and θ with respect to x may be calculated as

$$r = \sqrt{x^2 + y^2}$$

$$\theta = \tan^{-1}\frac{y}{x}$$

$$\frac{\partial r}{\partial x} = \frac{x}{\sqrt{x^2 + y^2}} = \cos\theta$$

$$\frac{\partial \theta}{\partial x} = \frac{x^2}{x^2 + y^2} \times \left(\frac{-y}{x^2}\right) = \frac{-y}{x^2 + y^2} = -\frac{\sin\theta}{r} \tag{6}$$

$$\frac{\partial}{\partial x} = \frac{\partial}{\partial r}\cdot\frac{\partial r}{\partial x} + \frac{\partial}{\partial \theta}\cdot\frac{\partial \theta}{\partial x} = \cos\theta\frac{\partial}{\partial r} - \frac{\sin\theta}{r}\frac{\partial}{\partial \theta}$$

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Therefore, the action of the derivative $\dfrac{\partial}{\partial x}$ on the function $f(x,y)$ is the same as the

action of $\cos\theta\,\dfrac{\partial}{\partial r} - \dfrac{\sin\theta}{r}\dfrac{\partial}{\partial\theta}$ on $g(r,\theta)$.

$$g(r,\theta) = r^3\cos^2\theta\sin\theta$$

$$\frac{\partial g}{\partial r} = 3r^2\cos^2\theta\sin\theta \tag{7}$$

$$\frac{\partial g}{\partial\theta} = r^3(-2\cos\theta\sin^2\theta + \cos^3\theta)$$

$$\frac{\partial f}{\partial x} \equiv \left(\cos\theta\,\frac{\partial g}{\partial r} - \frac{\sin\theta}{r}\frac{\partial g}{\partial\theta}\right)$$

$$\left(3r^2\cos^2\theta\sin\theta\right)\cos\theta + r^3\left(-2\cos\theta\sin^2\theta + \cos^3\theta\right)\left(-\frac{\sin\theta}{r}\right)$$

$$= 2r^2\cos^3\theta\sin\theta + 2r^2\cos\theta\sin^3\theta \tag{8}$$

$$= 2r^2\cos\theta\sin\theta$$

The operator $\dfrac{\partial}{\partial x}$ (on $x^2 y$) $= 2xy$ is the same as the operator

$$\left(\cos\theta\frac{\partial}{\partial r} - \frac{\sin\theta}{r}\frac{\partial}{\partial\theta}\right) \text{ on } r^3\cos^2\theta\sin\theta$$

The lesson:

The operator $\dfrac{\partial}{\partial x}$ acts on $= f(x,y)$ to give a result, which is same as the operator

$$\left(\cos\theta\,\frac{\partial}{\partial r} - \frac{\sin\theta}{r}\frac{\partial}{\partial\theta}\right) \text{ on } g(r,\theta)$$

Any other method gives inconsistent results.

This is the meaning of the equivalence of the two operators.

$$\frac{\partial f}{\partial x} \text{ is } \left(\cos\theta\,\frac{\partial f}{\partial r} - \frac{\sin\theta}{r}\frac{\partial f}{\partial\theta}\right)$$
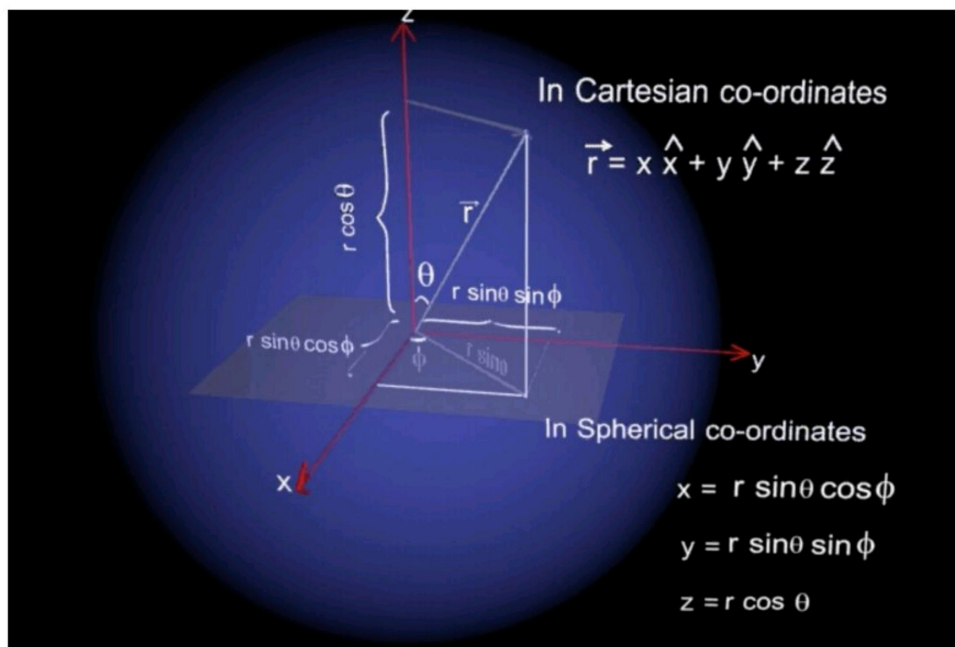
Likewise for $\dfrac{\partial}{\partial y}$:

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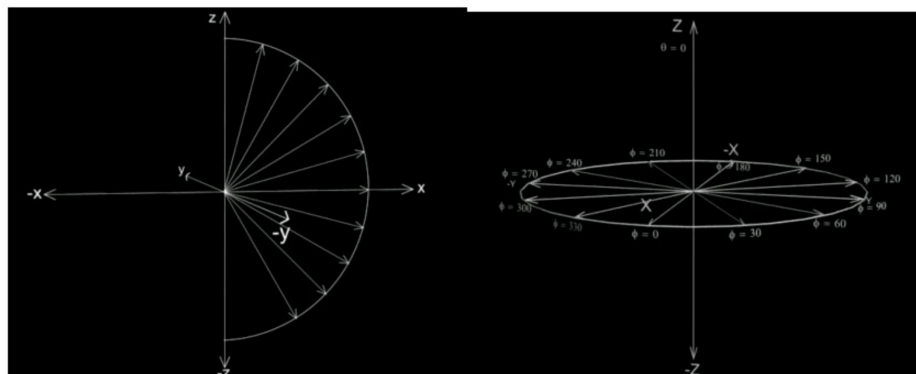
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$$\frac{\partial f}{\partial y} = \frac{\partial r}{\partial y} \cdot \frac{\partial g}{\partial r} + \frac{\partial \theta}{\partial y} \cdot \frac{\partial g}{\partial \theta} = \sin\theta \frac{\partial g}{\partial r} + \frac{\cos\theta}{r} \frac{\partial g}{\partial \theta}$$ (This may be verified by you) (9)

2. **Spherical polar coordinates (three dimensions):** (transformation from Cartesian coordinates)

Here are some pictures to indicate the relations between Cartesian components and spherical polar coordinates in three dimensions.

The range of polar angle θ and the azimuthal angle ϕ for a sphere are shown below:
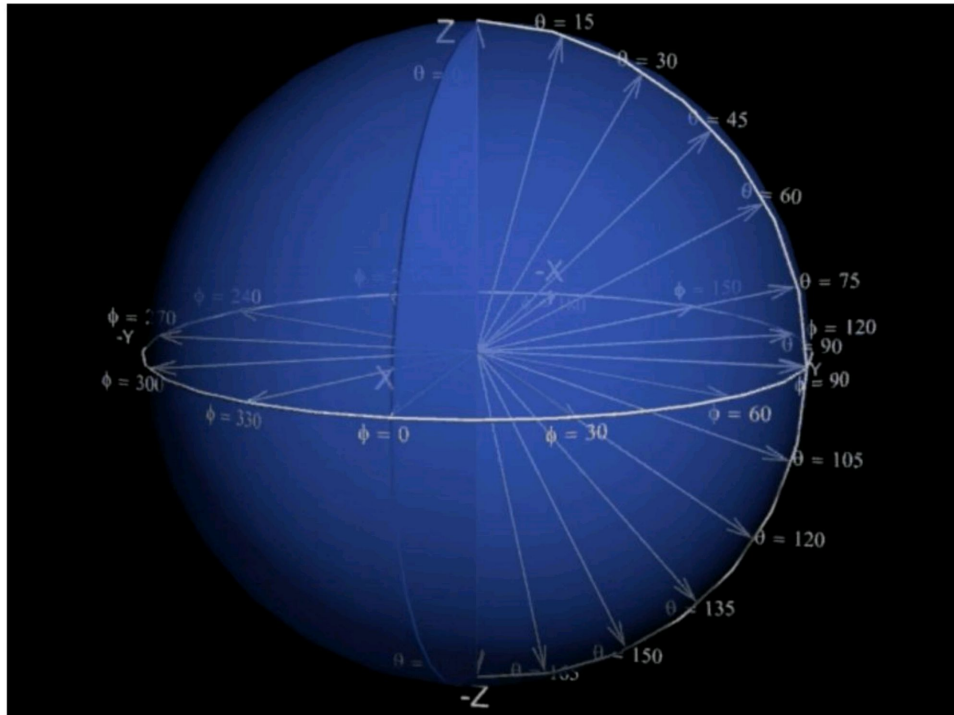
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$$x = r\sin\theta\cos\phi$$
$$y = r\sin\theta\sin\phi \qquad (10)$$
$$z = r\cos\theta$$

Inverse relation:

$$r = \sqrt{x^2 + y^2 + z^2}$$
$$\theta = \tan^{-1}\frac{\sqrt{x^2 + y^2}}{z} \qquad (11)$$
$$\phi = \tan^{-1}\frac{y}{x}$$

Question 1

Verify the inverse transformation relations ($r\theta\phi$)

A function of x, y, z given by $f(x, y, z)$ has derivatives $\dfrac{\partial f}{\partial x}$, $\dfrac{\partial f}{\partial y}$, $\dfrac{\partial f}{\partial z}$ etc.

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If the function is expressed in terms of r, θ, ϕ then the derivative can be expressed in terms of $\frac{\partial}{\partial r}$, $\frac{\partial}{\partial \theta}$, $\frac{\partial}{\partial \phi}$ as

$$\frac{\partial f}{\partial x} = \frac{\partial f}{\partial r} \cdot \frac{\partial r}{\partial x} + \frac{\partial f}{\partial \theta} \cdot \frac{\partial \theta}{\partial x} + \frac{\partial f}{\partial \phi} \cdot \frac{\partial \phi}{\partial x} \tag{12}$$

Likewise

$$\frac{\partial f}{\partial y} = \frac{\partial f}{\partial r} \cdot \frac{\partial r}{\partial y} + \frac{\partial f}{\partial \theta} \cdot \frac{\partial \theta}{\partial y} + \frac{\partial f}{\partial \phi} \cdot \frac{\partial \phi}{\partial y} \tag{13}$$

and

$$\frac{\partial f}{\partial z} = \frac{\partial f}{\partial r} \cdot \frac{\partial r}{\partial z} + \frac{\partial f}{\partial \theta} \cdot \frac{\partial \theta}{\partial z} + \frac{\partial f}{\partial \phi} \cdot \frac{\partial \phi}{\partial z} \tag{14}$$

Thus the derivative equivalence is

$$\frac{\partial}{\partial x} = \frac{\partial r}{\partial x} \cdot \frac{\partial}{\partial r} + \frac{\partial \theta}{\partial x} \cdot \frac{\partial}{\partial \theta} + \frac{\partial \phi}{\partial x} \cdot \frac{\partial}{\partial \phi}$$

and similarly for other derivatives $\frac{\partial}{\partial y}$ and $\frac{\partial}{\partial z}$

Problem 2

Express $\frac{\partial}{\partial y}$ **and** $\frac{\partial}{\partial z}$ **in terms of** $\frac{\partial}{\partial r}$, $\frac{\partial}{\partial \theta}$, $\frac{\partial}{\partial \phi}$.

The quantities we need to know:

$$\frac{\partial r}{\partial x}, \frac{\partial \theta}{\partial x} \text{ and } \frac{\partial \phi}{\partial x} \text{ for } \frac{\partial}{\partial x}$$

$$\frac{\partial r}{\partial y}, \frac{\partial \theta}{\partial y} \text{ and } \frac{\partial \phi}{\partial y} \text{ for } \frac{\partial}{\partial y}$$

$$\frac{\partial r}{\partial z}, \frac{\partial \theta}{\partial z} \text{ and } \frac{\partial \phi}{\partial z} \text{ for } \frac{\partial}{\partial z}$$

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$$r = \sqrt{x^2 + y^2 + z^2}$$

$$\frac{\partial r}{\partial x} = \frac{x}{\sqrt{x^2 + y^2 + z^2}} = \sin\theta\cos\phi$$

$$\frac{\partial r}{\partial y} = \frac{y}{\sqrt{x^2 + y^2 + z^2}} = \sin\theta\sin\phi \tag{15}$$

$$\frac{\partial r}{\partial z} = \frac{z}{\sqrt{x^2 + y^2 + z^2}} = \cos\theta$$

$$\theta = \tan^{-1}\frac{\sqrt{x^2 + y^2}}{z}$$

$$\frac{\partial \theta}{\partial x} = \frac{z^2}{x^2 + y^2 + z^2} \times \frac{1}{z} \cdot \frac{x}{\sqrt{x^2 + y^2}} = \frac{\cos\theta\cos\phi}{r}$$

$$\frac{\partial \theta}{\partial y} = \frac{z^2}{x^2 + y^2 + z^2} \times \frac{1}{z} \cdot \frac{y}{\sqrt{x^2 + y^2}} = \frac{\cos\theta\sin\phi}{r} \tag{16}$$

$$\frac{\partial \theta}{\partial z} = \frac{z^2}{x^2 + y^2 + z^2} \times \left(-\frac{1}{z^2}\right) \cdot \sqrt{x^2 + y^2} = \frac{-\sin\theta}{r}$$

$$\phi = \tan^{-1}\frac{y}{x}$$

$$\frac{\partial \phi}{\partial x} = \frac{x^2}{x^2 + y^2} \times y\left(-\frac{1}{x^2}\right) = -\frac{\sin\phi}{r\sin\theta}$$

$$\frac{\partial \phi}{\partial y} = \frac{x^2}{x^2 + y^2} \times \frac{1}{x} = \frac{\cos\phi}{r\sin\theta} \tag{17}$$

$$\frac{\partial \phi}{\partial z} = 0$$

$$\frac{\partial}{\partial x} = \sin\theta\cdot\cos\phi\frac{\partial}{\partial r} + \frac{\cos\theta\cos\phi}{r}\cdot\frac{\partial}{\partial\theta} - \frac{\sin\phi}{r\sin\theta}\cdot\frac{\partial}{\partial\phi}$$

$$\frac{\partial}{\partial y} = \sin\theta\cdot\sin\phi\frac{\partial}{\partial r} + \frac{\cos\theta\sin\phi}{r}\cdot\frac{\partial}{\partial\theta} + \frac{\cos\phi}{r\sin\theta}\cdot\frac{\partial}{\partial\phi} \tag{18}$$

$$\frac{\partial}{\partial z} = \cos\theta\cdot\frac{\partial}{\partial r} - \frac{\sin\theta}{r}\cdot\frac{\partial}{\partial\theta}$$

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3. **The Laplacian in spherical polar coordinates:**

$$\frac{\partial^2 f}{\partial x^2} \Rightarrow \frac{\partial^2 f}{\partial x^2} = \frac{\partial}{\partial x}\left(\frac{\partial f}{\partial x}\right)$$

$$= \left(\sin\theta\cos\phi\frac{\partial}{\partial r} + \frac{\cos\theta\cos\phi}{r}\frac{\partial}{\partial\theta} - \frac{\sin\phi}{r\sin\theta}\frac{\partial}{\partial\phi}\right) \cdot \left(\sin\theta\cos\phi\frac{\partial f}{\partial r} + \frac{\cos\theta\cos\phi}{r}\frac{\partial f}{\partial\theta} - \frac{\sin\phi}{r\sin\theta}\frac{\partial f}{\partial\phi}\right)$$

$$= \begin{bmatrix} \sin^2\theta\cos^2\phi\dfrac{\partial^2 f}{\partial r^2} - \dfrac{\sin\theta\cos^2\phi\cos\theta}{r^2}\dfrac{\partial f}{\partial\theta} + \dfrac{\sin\theta\cos\theta\cos^2\phi}{r}\dfrac{\partial^2 f}{\partial r\partial\theta} \\[2mm] + \dfrac{\cos\phi\sin\phi}{r^2}\dfrac{\partial f}{\partial\phi} - \dfrac{\sin\phi\cos\phi}{r}\dfrac{\partial^2 f}{\partial r\partial\phi} + \dfrac{\cos^2\theta\cos^2\phi}{r}\dfrac{\partial f}{\partial r} \\[2mm] + \dfrac{\cos\theta\sin\theta\cos^2\phi}{r}\dfrac{\partial^2 f}{\partial\theta\partial r} - \dfrac{\cos\theta\sin\theta\cos^2\phi}{r^2}\dfrac{\partial f}{\partial\theta} + \dfrac{\cos^2\theta\cos^2\phi}{r^2}\dfrac{\partial^2}{\partial\theta^2} \\[2mm] + \dfrac{\cos^2\theta\cos\phi\sin\phi}{r^2\sin^2\theta}\dfrac{\partial f}{\partial\phi} - \dfrac{\cos\theta\cos\phi\sin\phi}{r^2\sin\theta}\dfrac{\partial^2 f}{\partial\theta\partial\phi} + \dfrac{\sin^2\phi}{r}\dfrac{\partial f}{\partial r} \\[2mm] - \dfrac{\sin\phi\cos\phi}{r}\dfrac{\partial^2 f}{\partial\phi\partial r} + \dfrac{\sin^2\phi\cos\theta}{r^2\sin\theta}\dfrac{\partial f}{\partial\theta} - \dfrac{\sin\phi\cos\theta\cos\phi}{r^2\sin\theta}\dfrac{\partial^2 f}{\partial\phi\partial\theta} \\[2mm] + \dfrac{\sin\phi\cos\phi}{r^2\sin^2\theta}\dfrac{\partial f}{\partial\phi} + \dfrac{\sin^2\phi}{r^2\sin^2\theta}\dfrac{\partial^2 f}{\partial\phi^2} \end{bmatrix}$$

$$(19)$$

$$\frac{\partial^2 f}{\partial y^2} = \frac{\partial}{\partial y}\left(\frac{\partial f}{\partial y}\right)$$

$$= \left(\sin\theta\sin\phi\frac{\partial}{\partial r} + \frac{\cos\theta\sin\phi}{r}\frac{\partial}{\partial\theta} + \frac{\cos\phi}{r\sin\theta}\frac{\partial}{\partial\phi}\right) \cdot \left(\sin\theta\sin\phi\frac{\partial f}{\partial r} + \frac{\cos\theta\sin\phi}{r}\frac{\partial f}{\partial\theta} + \frac{\cos\phi}{r\sin\theta}\frac{\partial f}{\partial\phi}\right)$$

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$$\Rightarrow \left[\begin{array}{c} \sin^2\theta\sin^2\phi\dfrac{\partial^2}{\partial r^2} - \dfrac{\sin\theta\cos\theta\sin^2\phi}{r^2}\dfrac{\partial f}{\partial\theta} + \dfrac{\sin\theta\cos\theta\sin^2\phi}{r}\dfrac{\partial^2 f}{\partial r\partial\theta} \\[2mm] -\dfrac{\cos\phi\sin\phi}{r^2}\dfrac{\partial f}{\partial\phi} + \dfrac{\sin\phi\cos\phi}{r}\dfrac{\partial^2 f}{\partial r\partial\phi} + \dfrac{\cos^2\theta\sin^2\phi}{r}\dfrac{\partial f}{\partial r} \\[2mm] +\dfrac{\cos\theta\sin\theta\sin^2\phi}{r}\dfrac{\partial^2 f}{\partial\theta\partial r} - \dfrac{\cos\theta\sin\theta\sin^2\phi}{r^2}\dfrac{\partial f}{\partial\theta} + \dfrac{\cos^2\theta\sin^2\phi}{r^2}\dfrac{\partial^2 f}{\partial\theta^2} \\[2mm] -\dfrac{\cos^2\theta\cos\phi\sin\phi}{r^2\sin^2\theta}\dfrac{\partial f}{\partial\phi} + \dfrac{\cos\theta\cos\phi\sin\phi}{r^2\sin\theta}\dfrac{\partial^2 f}{\partial\theta\partial\phi} + \dfrac{\cos^2\phi}{r}\dfrac{\partial f}{\partial r} \\[2mm] +\dfrac{\sin\phi\cos\phi}{r}\dfrac{\partial^2 f}{\partial\phi\partial r} + \dfrac{\cos^2\phi\cos\theta}{r^2\sin\theta}\dfrac{\partial f}{\partial\theta} \\[2mm] +\dfrac{\cos\phi\cos\theta\sin\phi}{r^2\sin\theta}\dfrac{\partial^2 f}{\partial\phi\partial\theta} - \dfrac{\cos\phi\sin\phi}{r^2\sin^2\theta}\dfrac{\partial f}{\partial\phi} + \dfrac{\cos^2\phi}{r^2\sin^2\theta}\dfrac{\partial^2 f}{\partial\phi^2} \end{array} \right]$$

(20)

$$\frac{\partial^2 f}{\partial z^2} = \frac{\partial}{\partial z}\left(\frac{\partial f}{\partial z}\right)$$

$$= \left(\cos\theta\frac{\partial}{\partial r} - \frac{\sin\theta}{r}\frac{\partial}{\partial\theta}\right)\left(\cos\theta\frac{\partial f}{\partial r} - \frac{\sin\theta}{r}\frac{\partial f}{\partial\theta}\right)$$

$$= \left[\begin{array}{c} \cos^2\theta\dfrac{\partial^2 f}{\partial r^2} + \dfrac{\cos\theta\sin\theta}{r^2}\dfrac{\partial f}{\partial\theta} - \dfrac{\cos\theta\sin\theta}{r}\dfrac{\partial^2 f}{\partial r\partial\theta} + \dfrac{\sin^2\theta}{r}\dfrac{\partial f}{\partial r} \\[2mm] -\dfrac{\sin\theta\cos\theta}{r}\dfrac{\partial^2 f}{\partial\theta\partial r} + \dfrac{\sin\theta\cos\theta}{r^2}\dfrac{\partial f}{\partial\theta} + \dfrac{\sin^2\theta}{r^2}\dfrac{\partial^2 f}{\partial\theta^2} \end{array} \right]$$

(21)

$$\frac{\partial^2 f}{\partial x^2} + \frac{\partial^2 f}{\partial y^2} + \frac{\partial^2 f}{\partial z^2} =$$

$$\left\{\sin^2\theta\left(\cos^2\phi + \sin^2\phi\right) + \cos^2\theta\right\}\frac{\partial^2 f}{\partial r^2} + \left\{\begin{array}{c}\dfrac{\cos^2\theta}{r}\left(\cos^2\phi + \sin^2\phi\right) + \\[2mm] \dfrac{\left(\cos^2\phi + \sin^2\phi\right)}{r} + \dfrac{\sin^2\theta}{r}\end{array}\right\}\frac{\partial f}{\partial r}$$

$$+ \left\{\frac{\cos^2\theta\left(\cos^2\phi + \sin^2\phi\right)}{r^2} + \frac{\sin^2\theta}{r^2}\right\}\frac{\partial^2 f}{\partial\theta^2}$$

$$+ \left\{\frac{-\cos\theta\sin\theta\left(\cos^2\phi + \sin^2\phi\right)}{r^2} + \frac{\cos\theta}{r^2\sin\theta}\left(\sin^2\phi + \cos^2\phi\right) + \frac{\sin\theta\cos\theta}{r^2}\right\}\frac{\partial f}{\partial\theta}$$

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$$+ \left\{ \frac{\left(\sin^2\phi + \cos^2\phi\right)}{r^2\sin^2\theta} \frac{\partial^2 f}{\partial\phi^2} \right\} \quad . \tag{22}$$

All other terms cancel each other with the substitutions like $\dfrac{\partial^2 f}{\partial r\,\partial\theta} = \dfrac{\partial^2 f}{\partial\theta\,\partial r}$.

Thus:

$$\frac{\partial^2 f}{\partial x^2} + \frac{\partial^2 f}{\partial y^2} + \frac{\partial^2 f}{\partial z^2} = \frac{\partial^2 f}{\partial r^2} + \frac{2}{r}\frac{\partial f}{\partial r} + \frac{1}{r^2}\frac{\partial^2 f}{\partial\theta^2} + \frac{\cos\theta}{r^2\sin\theta}\frac{\partial f}{\partial\theta} + \frac{1}{r^2\sin^2\theta}\frac{\partial^2 f}{\partial\phi^2}$$

$$= \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial f}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2} \tag{25}$$

as is commonly written in the text books.

4. **The volume element and limits of integration in spherical polar coordinate system:**

In Cartesian coordinate system in three dimensions (x, y, z), the primitive volume element is $dV = d\tau = dx\,dy\,dz$. In polar coordinate system as above, the volume element is expressed in terms of the infinitesimal elements dr, $d\theta$ and $d\phi$ as

$$dx\,dy\,dz = \det\begin{vmatrix} \frac{\partial x}{\partial r} & \frac{\partial x}{\partial\theta} & \frac{\partial x}{\partial\phi} \\ \frac{\partial y}{\partial r} & \frac{\partial y}{\partial\theta} & \frac{\partial y}{\partial\phi} \\ \frac{\partial z}{\partial r} & \frac{\partial z}{\partial\theta} & \frac{\partial z}{\partial\phi} \end{vmatrix} dr\,d\theta\,d\phi \tag{26}$$

where we use the absolute value of the determinant. The derivatives are easy to calculate given that

$$x = r\sin\theta\cos\phi$$
$$y = r\sin\theta\sin\phi .$$
$$z = r\cos\theta$$

Therefore,

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$$dxdydz = \det \begin{vmatrix} \sin\theta\cos\phi & r\cos\theta\cos\phi & -r\sin\theta\sin\phi \\ \sin\theta\sin\phi & r\cos\theta\sin\phi & r\sin\theta\cos\phi \\ \cos\theta & -r\sin\theta & 0 \end{vmatrix} drd\theta d\phi = r^2\sin\theta drd\theta d\phi \tag{27}$$

The limits of integration in Cartesian coordinates are extended throughout the three dimensional space, namely, $x \to -\infty$ to ∞, $y \to -\infty$ to ∞ and $z \to -\infty$ to ∞. The same universal volume in three dimensional space is obtained by the limits $r \to 0$ to ∞, $\theta \to 0$ to π and $\phi \to 0$ to 2π.

See my animation on spherical coordinate limits.

Therefore average values calculated in the spherical polar coordinate system would use the limits and the volume elements as

$$\int_{r=0}^{\infty} r^2\, dr \int_{\theta=0}^{\pi} \sin\theta\, d\theta \int_{\phi=0}^{2\pi} d\phi \cdots .$$

5. The Hamiltonian for the hydrogen atom:

The quantum mechanical Hamiltonian for hydrogen atom is expressed using a simple separation of coordinates of the nucleus from that of the electron using classical two-body kinematics. The translational energy of the atom being due to the kinetic energy of the atom as a whole, it is not considered. The relative motion is that of the two-body system with the reduced mass given by,

$$\mu = \frac{m_p m_e}{m_p + m_e} \approx m_e \quad \text{since} \quad m_p \gg m_e \quad \text{and} \quad m_p + m_e \simeq m_p. \tag{28}$$

Since this is the mass of the electron, the relative motion of the electron is due to the kinetic and potential energy of the electron with the nucleus being assumed stationary. This is also referred to later as the Born-Oppenheimer approximation. Thus the electron coordinates may be referred to the axis system centered on the nucleus and the kinetic energy and potential energies of the electron are given by,

$$T = \frac{p_e^2}{2m_e} = \frac{(p_e)_x^2 + (p_e)_y^2 + (p_e)_z^2}{2m_e} \quad \text{and} \quad V = -\frac{Ze^2}{4\pi\varepsilon_0 r}, \tag{29}$$

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where Ze is the charge on the nucleus and r is the distance between the point charges. This is a classical approximation. In quantum mechanics, the corresponding quantities are given by operators, resulting in the Hamiltonian,

$$H = -\frac{\hbar^2}{2m_e}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right) - \frac{Ze^2}{4\pi\varepsilon_0\sqrt{x^2+y^2+z^2}} \quad , \tag{30}$$

where the wave function for the electron is expressed in the position coordinates of the electron x, y, z with the origin at the nucleus. The solution of the Schrödinger equation is thus the solution of the differential equation

$$H\psi(x,y,z) = \left\{-\frac{\hbar^2}{2m_e}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right) - \frac{Ze^2}{4\pi\varepsilon_0\sqrt{x^2+y^2+z^2}}\right\}\psi(x,y,z) = E\psi(x,y,z)$$

$$\tag{31}$$

The stability of the Hydrogen atom is still an unexplained interplay between the electron's potential energy balanced by its kinetic energy. Neither of them can be determined exactly in the classical sense without losing complete information about the other since the two energy terms, as operators, do not commute with each other. Thus kinetic energy and potential energy of the electron in the hydrogen atom cannot be simultaneously, and accurately, determined, but the overall energy can be, by the solution of the Schrödinger equation as above. This is best done, using spherical polar coordinates by expressing the Hamiltonian in spherical polar coordinates, and that was the object of the previous section in this lecture notes. Expressed in such a coordinate system, the potential energy depends only on the radial distance r and therefore, the r-dependent kinetic energy and potential energy terms can be separated out and solved as a radial distance problem. The overall energy of the system gets absorbed in the radial equation and the remaining terms of the kinetic energy are solved as angular problem. The details of the separation procedure are given below.

First write down the Schrodinger equation in spherical polar coordinates

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

$$\psi(x,y,z) \equiv \Psi(r,\theta,\phi)$$

$$H(r,\theta,\phi)\Psi(r,\theta,\phi)$$

$$= \left\{ -\frac{\hbar^2}{2m_e}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right] - \frac{Ze^2}{4\pi\varepsilon_0 r}\right\}\Psi(r,\theta,\phi)$$

$$= E\Psi(r,\theta,\phi)$$

$$(32)$$

$$\Psi(r,\theta,\phi) = R(r)\Theta(\theta)\Phi(\phi)$$

$$\Rightarrow \left\{ \begin{array}{l} \dfrac{1}{r^2}\dfrac{d}{dr}\left(r^2\dfrac{dR}{dr}\right)\Theta(\theta)\Phi(\phi) + \dfrac{1}{r^2\sin\theta}\dfrac{d}{d\theta}\left(\sin\theta\dfrac{d\Theta}{d\theta}\right)R(r)\Phi(\phi) \\[3mm] + \dfrac{1}{r^2\sin^2\theta}\left(\dfrac{d^2\Phi}{d\phi^2}\right)R(r)\Theta(\theta) \end{array}\right\}\left(\dfrac{-\hbar^2}{2m_e}\right)$$

$$- \left\{\frac{z_e^2}{4\pi\varepsilon_0 r} + E\right\}R(r)\Theta(\theta)\Phi(\phi) = 0$$

$$(33)$$

Multiply by r^2, divide by $R(r)\Theta(\theta)\Phi(\phi)$. The equation separates into an r-only-dependent and a $\theta\phi$ dependent-part terms.

$$\Rightarrow \frac{-\hbar^2}{2m_e}\left[\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{2m_e r^2}{\hbar^2}\left(\frac{z_e^2}{4\pi\varepsilon_0 r} + E\right)\right]$$

$$\frac{-\hbar^2}{2m_e}\left[\frac{1}{\sin\theta\,\Theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + \frac{1}{\Phi\sin^2\theta}\frac{d^2\Phi}{d\phi^2}\right] = 0$$

$$(34)$$

The second line in the above can be identified with the square of the orbital angular momentum of the electron (around the nucleus) and can be identified as follows:

$$\frac{-\hbar^2}{2m_e}\left[\frac{1}{\sin\theta\,\Theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + \frac{1}{\Phi\sin^2\theta}\frac{d^2\Phi}{d\phi^2}\right] = -\frac{\hbar^2 L^2}{2m_e}$$

$$(35)$$

which remains a constant. We shall therefore equate the $\theta\phi$ dependent parts to a constant $-\beta$, then the r dependent part of the equation becomes

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$$\frac{-\hbar^2}{2m_e}\left[\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{1}{R}\frac{2m_e\,r^2}{\hbar^2}\left(\frac{z_e^2}{r}+E\right)\right]-\beta=0$$

Eq. (5)

The $\theta\phi$ equation is

$$\frac{-\hbar^2}{2m_e}\left[\frac{1}{\sin\theta\,\Theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)+\frac{1}{\Phi\sin^2\theta}\frac{d^2\Phi}{d\phi^2}\right]+\beta=0 \qquad (36)$$

Separate the $\theta\phi$ equation by setting

$$\beta'=\frac{2\,m_e}{\hbar^2}\beta$$

Multiply by $\sin^2\theta$ and rearrange them

$$\left[\frac{\sin\theta}{\Theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)-\beta'\sin^2\theta\right]+\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2}=0 \qquad (37)$$

The Φ equation may be equated to a negative constant (must satisfy periodic boundary condition; $-m^2$ does not do that)

$$\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2}=-m^2$$

$$\Phi(\phi)=\frac{1}{\sqrt{2\pi}}e^{im\phi}\quad m=0,\pm1,\pm2\cdots \qquad (38)$$

Then the Θ equation is

$$\sin\theta\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)-\left(\beta'\sin^2\theta+m^2\right)\Theta=0$$

choose $\cos\theta=x,\ \theta=0\to\pi\Rightarrow x=+1\to-1$

$$\frac{d}{d\theta}\Rightarrow\frac{d}{dx}\cdot\frac{dx}{d\theta}\quad=-\sin\theta\frac{d}{dx}$$

$$=-\sqrt{1-x^2}\frac{d}{dx};\ \Theta(\theta)=P(x)$$

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$$\Rightarrow -\sqrt{1-x^2}\,\sqrt{1-x^2}\,\frac{d}{dx}\left(\sqrt{1-x^2}\,(-1)\sqrt{1-x^2}\,\frac{dP}{dx}\right)$$

$$-\left[\beta'\left(1-x^2\right)+m^2\right]P(x)=0 \tag{39}$$

or

$$\left(1-x^2\right)\frac{d}{dx}\left(\left(1-x^2\right)\frac{dP}{dx}\right)-\left[\beta'\left(1-x^2\right)+m^2\right]P(x)=0$$

The choice $\beta'=-l(l+1)$, where l is a positive integer (0,1,2,3, …) enables the theta (x) equation to give converged solution. With the choice $m=0$ this equation is identified with the celebrated **Legendre equation**. For the choices $\beta'=-l(l+1)$ and $m\neq 0$, it is the same as the **associated Legendre equation**. In the solution of the Legendre equation, you will see why this choice for β' is both reasonable and acceptable.

The angular part given by the product $\Theta(\theta)\Phi(\phi)$ is known in mathematics literature as SPHERICAL HARMONICS. The overall solution $\Psi(r,\theta,\phi)=R(r)\Theta(\theta)\Phi(\phi)$ is dependent on three quantum numbers, n, l, m where the possible values for the quantum numbers are

$n=1,\ 2,\ 3,\ \dots$
$l=0,\ 1,\ 2,\ \cdots,\ n-1$
$m=0,\ \pm1,\ \pm2,\ \cdots,\ \pm l$.

The eigenfunctions of the Hamiltonian and the eigenvalues are of the following form when the three equations are solved analytically using a power series method to solve the second order differential equations for the radial part and the angular part, namely

$$H\Psi_{nlm}(r,\theta,\phi)=HR_n^l(r)Y_l^m(\theta,\phi)=E_n R_n^l(r)Y_l^m(\theta,\phi);$$

$$E_n=-\frac{hcR_H}{n^2}$$

The energy depends on only the quantum number n, known as the principal quantum number. The quantum numbers l and m are known as azimuthal and magnetic quantum numbers, respectively. The specific forms for lower order spherical harmonics are given below:

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$$Y_0^0(\theta,\phi) = \sqrt{\frac{1}{4\pi}}$$

$$Y_1^0(\theta\phi) = \sqrt{\frac{3}{4\pi}}P_1^0(\cos\theta) = \sqrt{\frac{3}{4\pi}}\cos\theta$$

$$Y_1^1(\theta\phi) = -\sqrt{\frac{3}{4\pi}}\times\frac{1}{2}\sin\theta e^{i\phi} = -\sqrt{\frac{3}{8\pi}}\sin\theta e^{i\phi}$$

$$Y_1^{-1}(\theta\phi) = -\sqrt{\frac{3}{4\pi}}\times 2\times(-1)\frac{1}{2}\sin\theta e^{-i\phi} = \sqrt{\frac{3}{8\pi}}\sin\theta e^{-i\phi}$$

(40)

$$Y_2^0(\theta\phi) = \sqrt{\frac{5}{4\pi}}\frac{1}{2}(3\cos^2\theta-1) = \sqrt{\frac{5}{16\pi}}(3\cos^2\theta-1)$$

$$Y_2^1(\theta\phi) = -\sqrt{\frac{15}{8\pi}}\cos\theta\sin\theta e^{i\phi}$$

$$Y_2^{-1}(\theta\phi) = \sqrt{\frac{15}{8\pi}}\cos\theta\sin\theta e^{-i\phi}$$

$$Y_2^2(\theta\phi) = \sqrt{\frac{5}{4\pi}}\times\frac{1}{24}\,3\sin^2\theta e^{2i\phi} = \sqrt{\frac{15}{32\pi}}\sin^2\theta e^{2i\phi}$$

$$Y_2^{-2}(\theta\phi) = \sqrt{\frac{5}{4\pi}}\times 24\times\frac{1}{8}3\sin^2\theta e^{-2i\phi} = \sqrt{\frac{15}{32\pi}}\sin^2\theta e^{-2i\phi}$$

(41)

$$Y_3^0(\theta\phi) = \sqrt{\frac{7}{16\pi}}(5\cos^3\theta-3\cos\theta)$$

$$Y_3^{\pm 1}(\theta\phi) = \mp\sqrt{\frac{21}{64\pi}}\sin\theta(5\cos^2\theta-1)e^{\pm i\phi}$$

$$Y_3^{\pm 2}(\theta\phi) = \sqrt{\frac{105}{32\pi}}\sin^2\theta\cos\theta e^{\pm 2i\phi}$$

$$Y_3^{\pm 3}(\theta\phi) = \mp\sqrt{\frac{35}{64\pi}}\sin^3\theta e^{\pm 3i\phi}$$

(42)

The angular functions are homogenous functions in $\sin\theta$ and $\cos\theta$ with the degree l.

Thus a function like $3\cos^2\theta-1$ is a homogeneous function written as

$3\cos^2\theta-\sin^2\theta-\cos^2\theta=2\cos^2\theta-\sin^2\theta$ which is second degree, namely $l=2$; a

function like

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$$5\cos^3\theta - 3\cos\theta = 5\cos^3\theta - 3\cos\theta\left(\sin^2\theta + \cos^2\theta\right)$$
$$= 2\cos^3\theta - 3\cos\theta\sin^2\theta$$

is of third degree, namely $l = 3$. Every such function has l angular nodes.

The radial solution is given using a polynomial set known as Laguerre polynomials. They are indexed by two quantum numbers and have the general form

$$R_n^l(r) = N(n,l)\left(\frac{Zr}{a_0}\right)^l P^{n-l-1}(Zr/a_0)e^{-Zr/na_0} \tag{43}$$

where the function $P^{n-l-1}(Zr/a_0)$ is known as the Laguerre polynomial of order $n-l-1$. Since there are that many zeroes for the polynomial all of which are real, the number of radial nodes will be $n-l-1$. The quantity $N(n,l)$ is the normalization constant, to be identified below. They are listed below for $n=1$ to $n=3$ and for all possible l, as

n,l	$R_n^l(r)$	Function
1,0	$R_1^0(r)$	$2\left(\dfrac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$
2,0	$R_2^0(r)$	$2\left(\dfrac{Z}{2a_0}\right)^{3/2}\left(1-\dfrac{Zr}{2a_0}\right)e^{-Zr/2a_0}$
2,1	$R_2^1(r)$	$\dfrac{2}{\sqrt{3}}\left(\dfrac{Z}{2a_0}\right)^{3/2}\left(\dfrac{Zr}{2a_0}\right)e^{-Zr/2a_0}$
3,0	$R_3^0(r)$	$2\left(\dfrac{Z}{3a_0}\right)^{3/2}\left(1-2\left(\dfrac{Zr}{3a_0}\right)+\dfrac{2}{3}\left(\dfrac{Zr}{3a_0}\right)^2\right)e^{-Zr/3a_0}$
3,1	$R_3^1(r)$	$4\sqrt{2}\left(\dfrac{Z}{3a_0}\right)^{3/2}\left(\dfrac{Zr}{3a_0}\right)\left(1-\dfrac{1}{2}\left(\dfrac{Zr}{3a_0}\right)\right)e^{-Zr/3a_0}$
3,2	$R_3^2(r)$	$\dfrac{2\sqrt{2}}{3\sqrt{5}}\left(\dfrac{Z}{3a_0}\right)^{3/2}\left(\dfrac{Zr}{3a_0}\right)^2 e^{-Zr/3a_0}$

With the definition of the radial function and the angular parts as above, it is easy to visualize that there are n^2 orbital functions for any principal quantum number n. This is because, for any n, we have

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$$\sum_{l=0}^{n-1}(2l+1)=1+3+5+\cdots+2n-1=n^2$$ as the degeneracy of the orbital quantum number

since all energies for a given n are identical. These are known, for

$l=0,\ l=1,\ l=2,\ l=3,\ldots$ as $ns,\ np,\ nd, nf,\ldots$, orbitals respectively, wherever the

quantum numbers obey the conditions.

Therefore, the table of orbitals from 1s to 3f orbitals are given below with all the normalization constants included. The normalization integral is to be understood as follows:

$$\int_0^\infty r^2\,dr\int_0^\pi \sin\theta\,d\theta\int_0^{2\pi}d\phi\left[R_n^l(r)\right]^2\left|Y_l^m(\theta,\phi)\right|^2=1\ . \tag{44}$$

This integral is the product of an integral of a radial distribution function and an angular distribution function as

$$\int_0^\infty r^2\,dr\left[R_n^l(r)\right]^2\otimes\int_0^\pi \sin\theta\,d\theta\int_0^{2\pi}d\phi\left|Y_l^m(\theta,\phi)\right|^2=1.$$

The function $r^2\,dr\left[R_n^l(r)\right]^2$ is the probability of finding the electron in a spherical shell

enclosed by two spheres of radius r and $r+dr$ It is called radial probability. The other,

$\left|Y_l^m(\theta,\phi)\right|^2\sin\theta d\theta d\phi$ is the angular probability of locating the electron in an angular area

on a sphere trapped between θ and $\theta+d\theta$ and ϕ and $\phi+d\phi$.

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n,l,m	Orbital	Function
1,0,0	$1s$	$\dfrac{1}{\sqrt{\pi}}\left(\dfrac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$
2,0,0	$2s$	$\dfrac{1}{\sqrt{8\pi}}\left(\dfrac{Z}{a_0}\right)^{3/2}\left(1-\dfrac{Zr}{2a_0}\right) e^{-Zr/2a_0}$
2,1,0	$2p$	$\dfrac{1}{\sqrt{\pi}}\left(\dfrac{Z}{2a_0}\right)^{3/2}\left(\dfrac{Zr}{2a_0}\right) e^{-Zr/2a_0}\cos\theta$
2,1,±1	$2p$	$\mp\dfrac{1}{\sqrt{2\pi}}\left(\dfrac{Z}{2a_0}\right)^{3/2}\left(\dfrac{Zr}{2a_0}\right) e^{-Zr/2a_0}\sin\theta\, e^{\pm i\phi}$
3,0,0	$3s$	$\dfrac{1}{\sqrt{\pi}}\left(\dfrac{Z}{3a_0}\right)^{3/2}\left(1-2\left(\dfrac{Zr}{3a_0}\right)+\dfrac{2}{3}\left(\dfrac{Zr}{3a_0}\right)^2\right) e^{-Zr/3a_0}$
3,1,0	$3p$	$\sqrt{\dfrac{24}{\pi}}\left(\dfrac{Z}{3a_0}\right)^{3/2}\left(\dfrac{Zr}{3a_0}\right)\left(1-\dfrac{1}{2}\left(\dfrac{Zr}{3a_0}\right)\right) e^{-Zr/3a_0}\cos\theta$
3,1,±1	$3p$	$\mp\sqrt{\dfrac{12}{\pi}}\left(\dfrac{Z}{3a_0}\right)^{3/2}\left(\dfrac{Zr}{3a_0}\right)\left(1-\dfrac{1}{2}\left(\dfrac{Zr}{3a_0}\right)\right) e^{-Zr/3a_0}\sin\theta\, e^{\pm i\phi}$
3,2,0	$3d$	$\sqrt{\dfrac{1}{18\pi}}\left(\dfrac{Z}{3a_0}\right)^{3/2}\left(\dfrac{Zr}{3a_0}\right)^2 e^{-Zr/3a_0}\left(3\cos^2\theta-1\right)$
3,2,±1	$3d$	$\mp\sqrt{\dfrac{1}{3\pi}}\left(\dfrac{Z}{3a_0}\right)^{3/2}\left(\dfrac{Zr}{3a_0}\right)^2 e^{-Zr/3a_0}\cos\theta\sin\theta\, e^{\pm i\phi}$
3,2,±2	$3d$	$\sqrt{\dfrac{1}{12\pi}}\left(\dfrac{Z}{3a_0}\right)^{3/2}\left(\dfrac{Zr}{3a_0}\right)^2 e^{-Zr/3a_0}\sin^2\theta\, e^{\pm 2i\phi}$

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n,l,m	Label	Function
4,0,0	$4s$	$\dfrac{1}{\sqrt{\pi}}\left(\dfrac{Z}{4a_0}\right)^{\frac{3}{2}}\left(1-3\left(\dfrac{Zr}{4a_0}\right)+2\left(\dfrac{Zr}{4a_0}\right)^2-\dfrac{1}{3}\left(\dfrac{Zr}{4a_0}\right)^3\right)e^{-Zr/4a_0}$
4,1,0	$4p$	$\sqrt{\dfrac{5}{\pi}}\left(\dfrac{Z}{4a_0}\right)^{\frac{3}{2}}\left(\dfrac{Zr}{4a_0}\right)\left(1-\dfrac{Zr}{4a_0}+\dfrac{1}{5}\left(\dfrac{Zr}{4a_0}\right)^2\right)e^{-Zr/4a_0}\cos\theta$
4,1,±1	$4p$	$\mp\sqrt{\dfrac{5}{2\pi}}\left(\dfrac{Z}{4a_0}\right)^{\frac{3}{2}}\left(\dfrac{Zr}{4a_0}\right)\left(1-\dfrac{Zr}{4a_0}+\dfrac{1}{5}\left(\dfrac{Zr}{4a_0}\right)^2\right)e^{-Zr/4a_0}\sin\theta e^{\pm i\phi}$
4,2,0	$4d$	$\dfrac{1}{2\sqrt{\pi}}\left(\dfrac{Z}{4a_0}\right)^{\frac{3}{2}}\left(\dfrac{Zr}{4a_0}\right)^2\left(1-\dfrac{1}{3}\left(\dfrac{Zr}{4a_0}\right)\right)e^{-Zr/4a_0}\left(3\cos^2\theta-1\right)$
4,2,±1	$4d$	$\mp\sqrt{\dfrac{3}{2\pi}}\left(\dfrac{Z}{4a_0}\right)^{\frac{3}{2}}\left(\dfrac{Zr}{4a_0}\right)^2\left(1-\dfrac{1}{3}\left(\dfrac{Zr}{4a_0}\right)\right)e^{-Zr/4a_0}\sin\theta\cos\theta e^{\pm i\phi}$
4,2,±2	$4d$	$\dfrac{1}{2}\sqrt{\dfrac{3}{2\pi}}\left(\dfrac{Z}{4a_0}\right)^{\frac{3}{2}}\left(\dfrac{Zr}{4a_0}\right)^2\left(1-\dfrac{1}{3}\left(\dfrac{Zr}{4a_0}\right)\right)e^{-Zr/4a_0}\sin^2\theta e^{\pm 2i\phi}$
4,3,0	$4f$	$\dfrac{1}{6\sqrt{5\pi}}\left(\dfrac{Z}{4a_0}\right)^{\frac{3}{2}}\left(\dfrac{Zr}{4a_0}\right)^3 e^{-Zr/4a_0}\left(5\cos^3\theta-3\cos\theta\right)$
4,3,±1	$4f$	$\mp\dfrac{1}{4\sqrt{15\pi}}\left(\dfrac{Z}{4a_0}\right)^{\frac{3}{2}}\left(\dfrac{Zr}{4a_0}\right)^3 e^{-Zr/4a_0}\left(5\cos^2\theta-1\right)\sin\theta e^{\pm i\phi}$
4,3,±2	$4f$	$\dfrac{1}{2\sqrt{6\pi}}\left(\dfrac{Z}{4a_0}\right)^{\frac{3}{2}}\left(\dfrac{Zr}{4a_0}\right)^3 e^{-Zr/4a_0}\sin^2\theta\cos\theta e^{\pm 2i\phi}$
4,3,±3	$4f$	$\mp\dfrac{1}{12\sqrt{\pi}}\left(\dfrac{Z}{4a_0}\right)^{\frac{3}{2}}\left(\dfrac{Zr}{4a_0}\right)^3 e^{-Zr/4a_0}\sin^3\theta e^{\pm 3i\phi}$

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Animations and Figures:

Spherical Harmonics in two and three dimensions (Real and imaginary parts of $Y_l^m(\theta,\phi)$ for $l = 0,1,2,3$. There are sixteen figures in the pages below for all angular orbitals of elements that appear in the periodic table.

$$l = 0, \quad m = 0 \quad \text{Constant} = \frac{1}{\sqrt{4\pi}}$$

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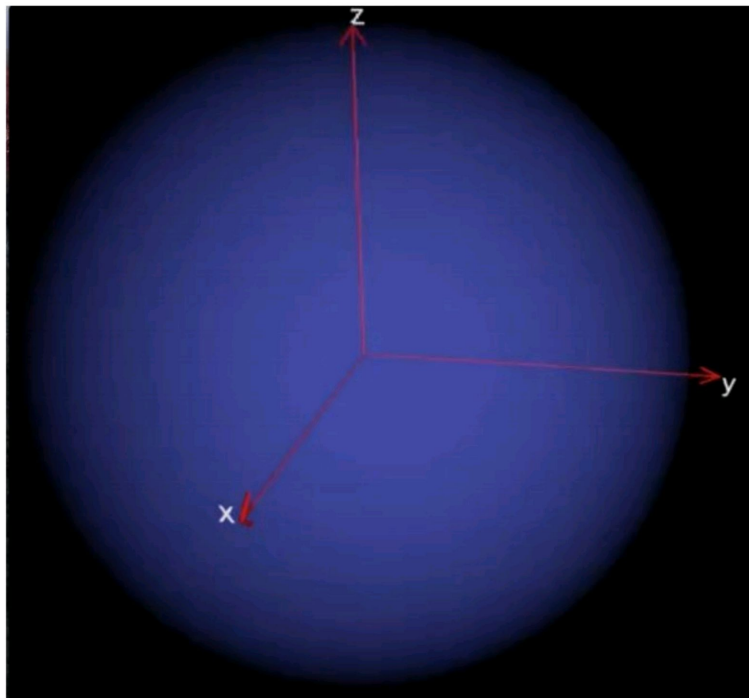
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$$l=1,\quad m=0\quad Y_1^0(\theta,\phi)\ \propto\cos\theta\qquad p_z$$

	Polar plot of function cos(θ)	⏮ ⏪ ⏹ ▶ ⏩ ⏭

PROCEDURE

1. Vary angle theta made by the vector with **z** axis for values ($0 \leqslant \theta \leqslant \pi$)
2. Draw circle of radius **r = cos(θ)**. Mark the point of intersection of circle with the vector
3. This plot is made for $\phi = 0$

θ	cos(θ)
0	1
15	0.965926
30	0.866025
45	0.70711
60	0.5
75	0.25882
90	0
105	-0.25882
120	-0.5
135	-0.70711
150	-0.86603
165	-0.96593
180	-1

Polar plot of cos(θ) ($0 \leqslant \theta \leqslant \pi$)
$\phi = 0$

■ positive value of the function
■ negative value of the function

+ ve
- ve

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$$l = 1, \quad m = 1 \quad \mathrm{Re}\left[Y_1^1(\theta,\phi) \right] \propto \sin\theta \cos\phi \quad p_x$$

Polar plot of function $(\sin(\theta)\cos(\phi))$ ⏮ ⏪ ⏹ ▶ ⏩ ⏭

PROCEDURE

1. Vary angle theta made by the vector with **z** axis for values $(0 \leqslant \theta \leqslant \pi)$
2. Draw circle of radius $r = (\sin(\theta)\cos(\phi))$. Mark the point of intersection of circle with the vector
3. This plot is made for $\phi = 0$ (or $\cos\phi = 1$)

Polar plot of $(\sin(\theta)\cos(\phi))$
$(0 \leqslant \theta \leqslant \pi)$; $\phi = 0$ (or $\cos\phi = 1$)

θ	sin(θ)
0	0
15	0.2588
30	0.5
45	0.7071
60	0.8660
75	0.9659
90	1
105	0.9659
120	0.8660
135	0.7071
150	0.5
165	0.2588
180	0

positive value of the function

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$$l = 1, \quad m = 1 \quad \text{Im}\left[Y_1^1(\theta,\phi)\right] \propto \sin\theta\sin\phi; \qquad p_y$$
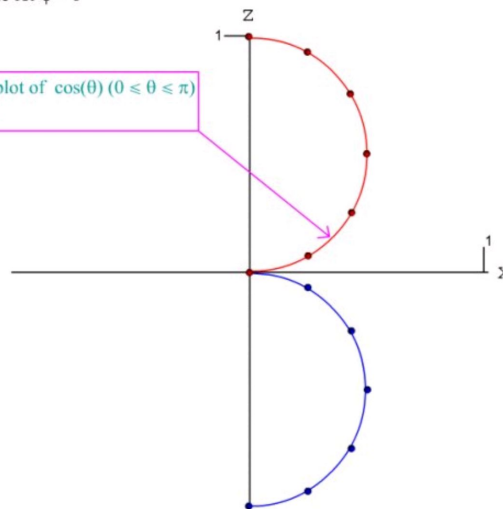
Polar plot of function (sin(θ)sin(φ))

PROCEDURE

1. Vary angle theta made by the vector with **z** axis for values ($0 \leqslant \theta \leqslant \pi$)
2. Draw circle of radius **r = (sin(θ)sin(φ))**. Mark the point of intersection of circle with the vector
3. This plot is made for $\phi = 90$ (or $\sin\phi = 1$)

Polar plot of (sin(θ)sin(φ))
($0 \leqslant \theta \leqslant \pi$); $\phi = 90$ (or sin (φ) = 1)

θ	sin(θ)
0	0
15	0.2588
30	0.5
45	0.7071
60	0.8660
75	0.9659
90	1
105	0.9659
120	0.8660
135	0.7071
150	0.5
165	0.2588
180	0

■ positive value of the function

+ ve
− ve

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$$l = 2, \quad m = 0 \quad Y_2^0(\theta, \phi) \propto \left(3\cos^2\theta - 1\right); \qquad d_{3z^2 - r^2} \quad \text{or often written as} \quad d_{z^2}$$

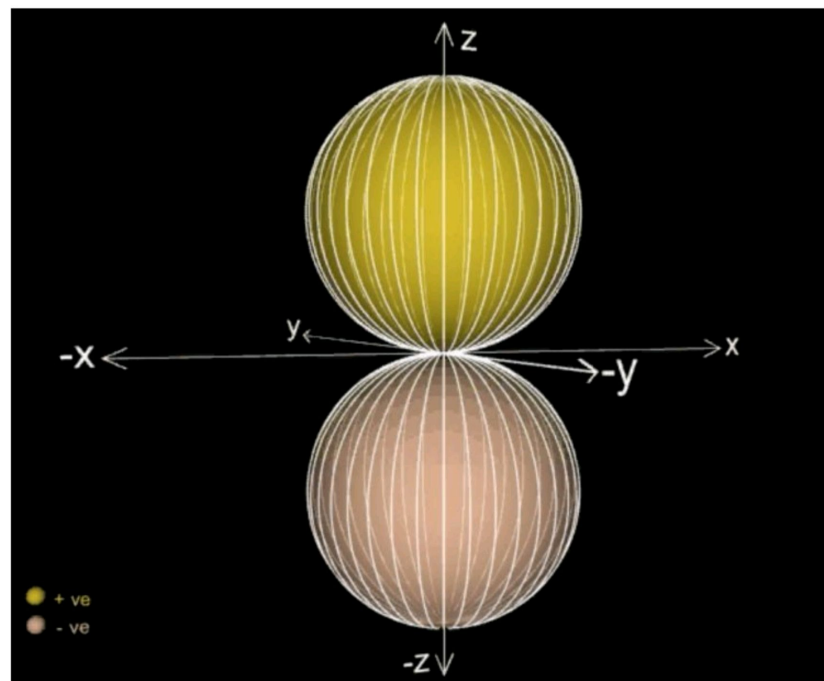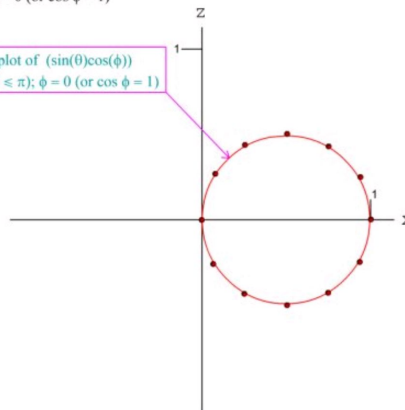Polar plot of function $(3\cos^2(\theta) - 1)$
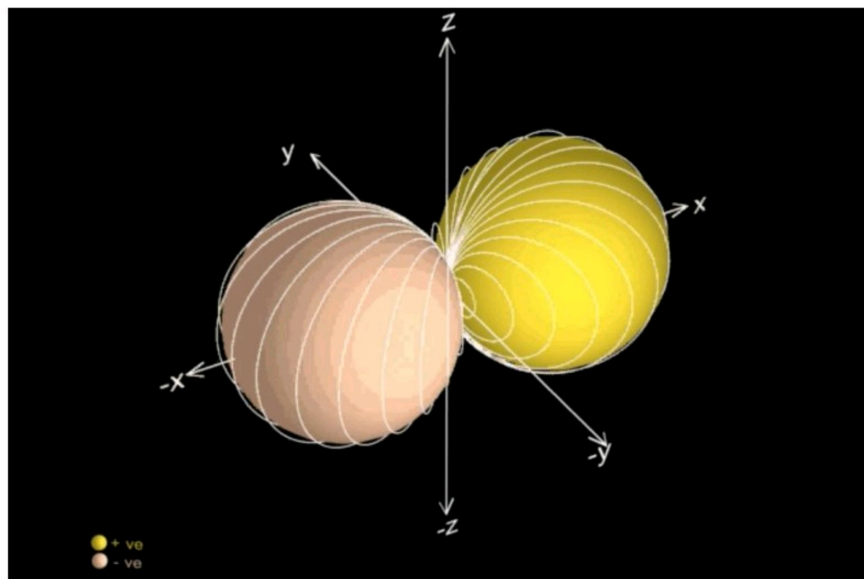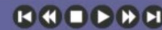
PROCEDURE
1. Vary angle theta made by the vector with **z** axis for values $(0 \leqslant \theta \leqslant \pi)$
2. Draw circle of radius $r = (3\cos^2(\theta) - 1)$. Mark the point of intersection of circle with the vector
3. This plot is made for $\phi = 0$

θ	$3\cos^2(\theta) - 1$
0	2
15	1.799
30	1.25
45	0.5
54.74	0
60	-0.25
75	-0.799
90	-1
105	-0.799
120	-0.25
125.26	0
135	0.5
150	1.25
165	1.799
180	2

Polar plot of $3\cos^2(\theta) - 1$
$(0 \leqslant \theta \leqslant \pi); \phi = 0$
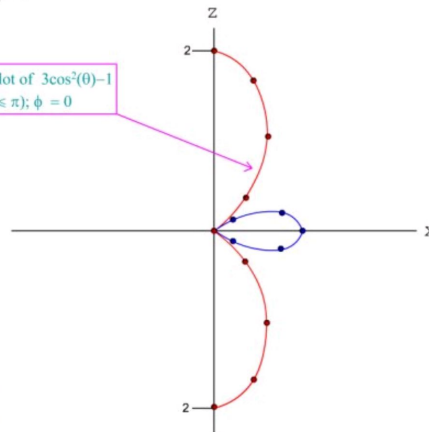
positive value of the function
negative value of the function

Title of PDF Document
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$l=2, \quad m=1 \quad \mathrm{Re}\left[Y_2^1(\theta,\phi)\right] \propto \cos\theta\sin\theta\cos\phi; \qquad d_{xz}$

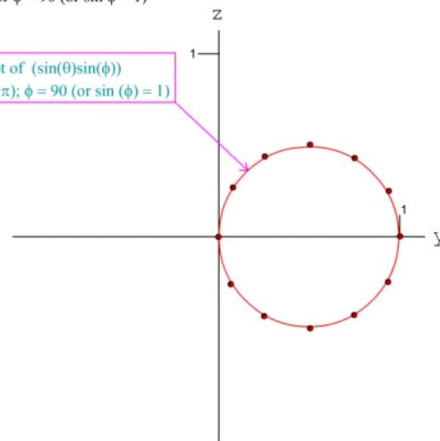Polar plot of function $(\sin(\theta)\cos(\theta)\cos(\phi))$

PROCEDURE
1. Vary angle theta made by the vector with **z** axis for values $(0 \le \theta \le \pi)$
2. Draw circle of radius $\mathbf{r} = (\sin(\theta)\cos(\theta)\cos(\phi))$. Mark the point of intersection of circle with the vector
3. This plot is made for $\phi = 0$ (or $\cos\phi = 1$)

Polar plot of $(\sin(\theta)\cos(\theta)\cos(\phi))$ $(0 \le \theta \le \pi); \phi = 0$ (or $\cos(\phi) = 1$)

θ	$\sin(\theta)\cos(\theta)$
0	0
15	0.25
30	0.433
45	0.5
60	0.433
75	0.25
90	0
105	-0.25
120	-0.433
135	-0.5
150	-0.433
165	-0.25
180	0

positive value of the function
negative value of the function

+ ve
- ve

28

Title of PDF Document
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$$l = 2, \quad m = 1 \quad \mathrm{Im}\left[Y_2^1(\theta,\phi)\right] \propto \cos\theta \sin\theta \sin\phi; \qquad d_{yz}$$

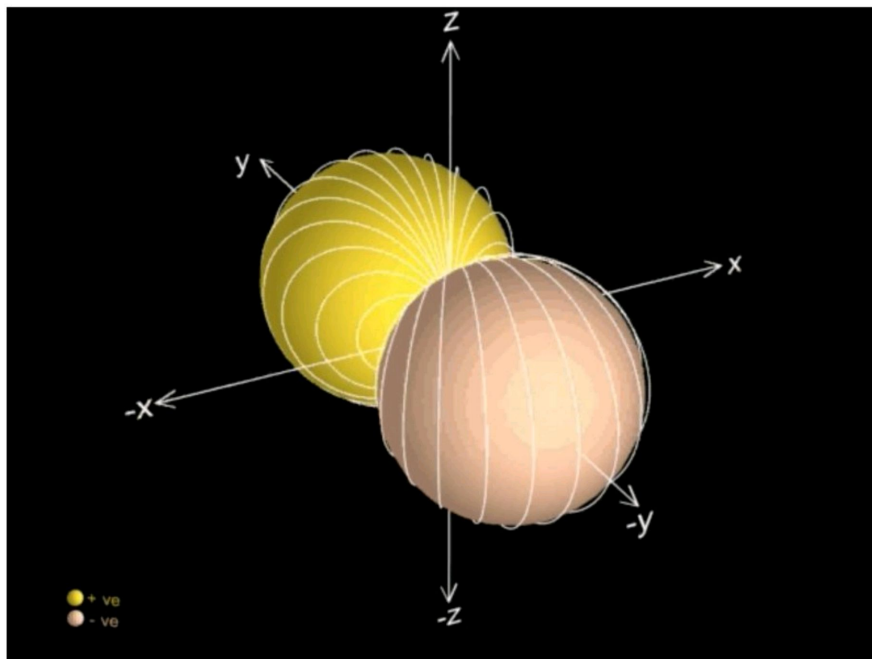**Polar plot of function $(\sin(\theta)\cos(\theta)\sin(\phi))$** ⏮ ⏪ ⏹ ▶ ⏩ ⏭

PROCEDURE
1. Vary angle theta made by the vector with **z** axis for values ($0 \leq \theta \leq \pi$)
2. Draw circle of radius $\mathbf{r} = (\mathbf{sin(\theta)cos(\theta)sin(\phi)})$. Mark the point of intersection of circle with the vector
3. This plot is made for $\phi = 90$ (or $\sin \phi = 1$)

Polar plot of $(\sin(\theta)\cos(\theta)\sin(\phi)\,)$
$(0 \leq \theta \leq \pi)$; $\phi = 90$ (or $\sin (\phi) = 1$)

| θ	$\sin(\theta)\cos(\theta)$
0	0
15	0.25
30	0.433
45	0.5
60	0.433
75	0.25
90	0
105	-0.25
120	-0.433
135	-0.5
150	-0.433
165	-0.25
180	0

+ ve
- ve

29

Title of PDF Document
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$$l = 2, \quad m = 2 \quad \mathrm{Re}\left[Y_2^2(\theta, \phi)\right] \quad \propto \sin^2\theta \cos 2\phi; \ (\sin^2\theta\cos^2\phi - \sin^2\theta\sin^2\phi) \qquad d_{x^2-y^2}$$

Polar plot of function $(\sin^2(\theta)\cos(2\phi))$	

PROCEDURE

last frame
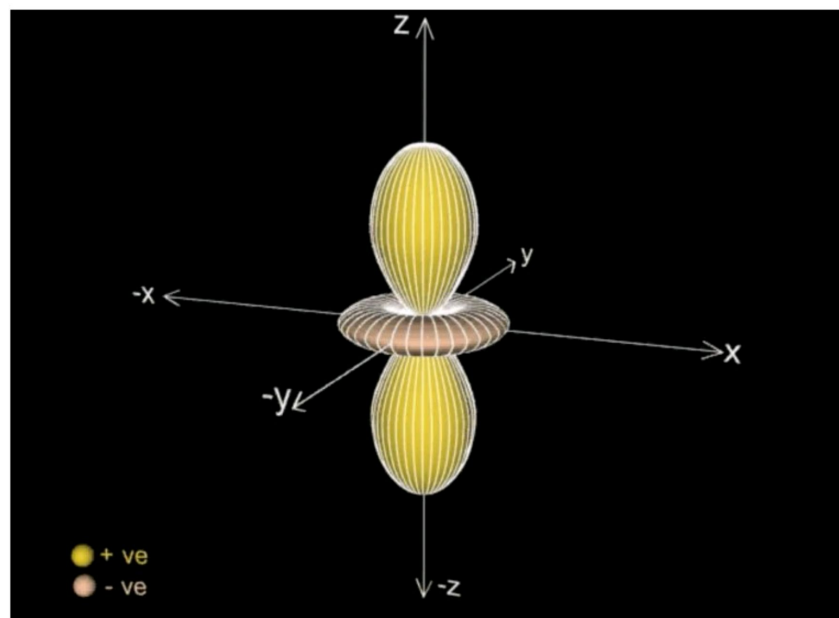
1. Vary angle theta made by the vector with **z** axis for values $(0 \leq \theta \leq \pi)$
2. Draw circle of radius $r = (\sin^2(\theta)\cos(2\phi))$. Mark the point of intersection of circle with the vector
3. This plot is made for $\phi = 0$ (or $\cos 2\phi = 1$)

Polar plot of $(\sin^2(\theta)\cos(2\phi))$
$(0 \leq \theta \leq \pi)$; $\phi = 0$ (or $\cos(2\phi) = 1$)

θ	$\sin^2(\theta)$
0	0
15	0.0669
30	0.25
45	0.5
60	0.75
75	0.933
90	1
105	0.933
120	0.75
135	0.5
150	0.25
165	0.0669
180	0

positive value of the function

+ ve
- ve

30
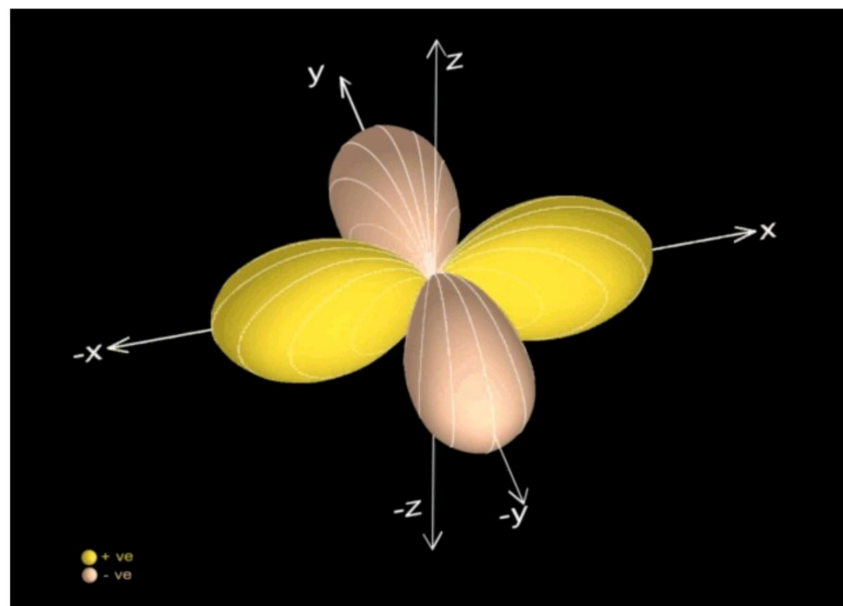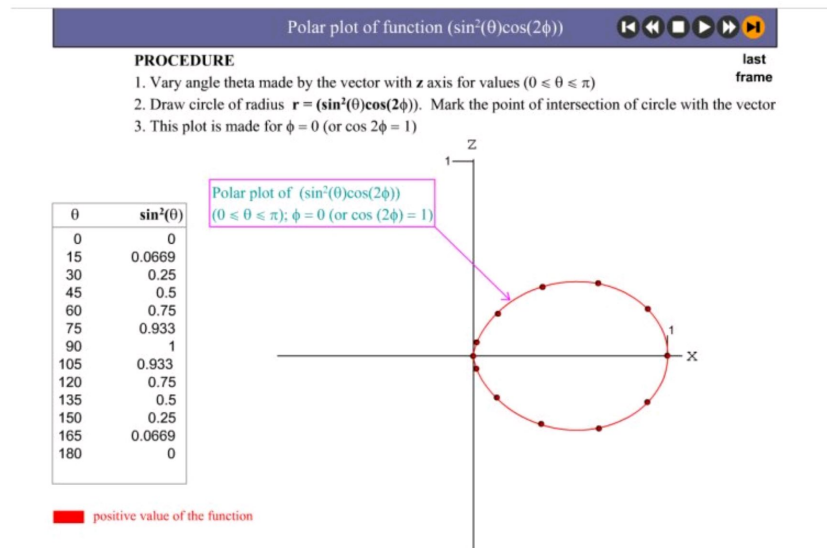
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$$l = 2, \quad m = 2 \quad \text{Im}\left[Y_2^2(\theta,\phi)\right] \propto \sin^2\theta \sin 2\phi; \quad (\sin\theta\cos\phi\sin\theta\sin\phi) \quad d_{xy}$$
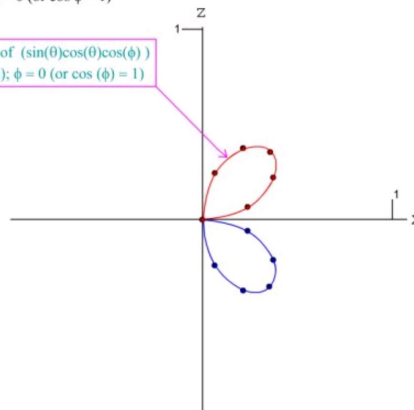
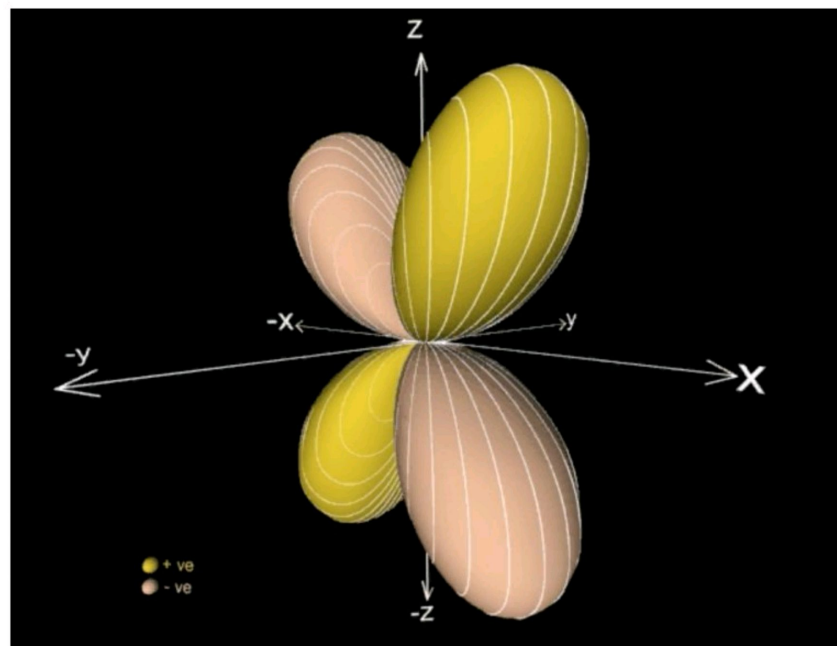Polar plot of function $(\sin^2(\theta)\sin(2\phi))$

PROCEDURE

1. Vary angle theta made by the vector with **z** axis for values ($0 \le \theta \le \pi$)
2. Draw circle of radius $\mathbf{r = (sin^2(\theta)sin(2\phi))}$. Mark the point of intersection of circle with the vector
3. This plot is made for $\phi = 45$ (or $\sin 2\phi = 1$)

θ	$\sin^2(\theta)\sin(2\phi)$
0	0
15	0.066987
30	0.25
45	0.5
60	0.75
75	0.933013
90	1
105	0.933013
120	0.75
135	0.5
150	0.25
165	0.066987
180	0

Polar plot of $(\sin^2(\theta)\sin(2\phi))$
$(0 \le \theta \le \pi)$; $\phi = 45$ (or $\sin(2\phi) = 1$)
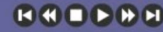
$\phi = 45°$

positive value of the function

+ ve
- ve

Title of PDF Document

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$$l = 3, \quad m = 0 \quad \left[Y_3^0(\theta, \phi) \right] \propto (5\cos^3\theta - 3\cos\theta) \quad f_{5z^3 - 3zr^2}$$

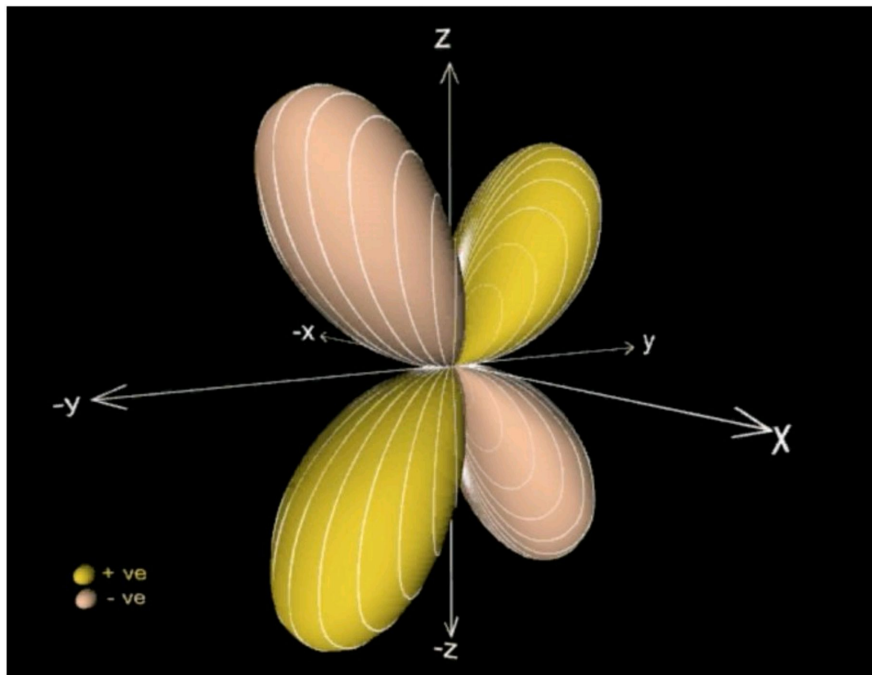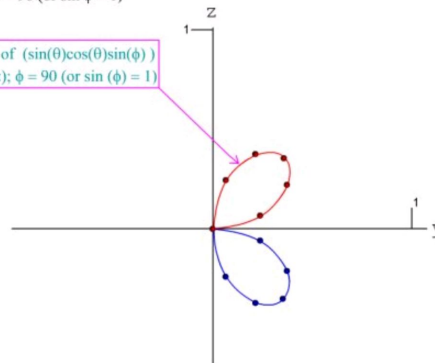Polar plot of function $((5\cos^3(\theta) - 3\cos(\theta))$ ⏮ ⏪ ⏹ ▶ ⏩ ⏭
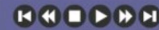
PROCEDURE
1. Vary angle theta made by the vector with **z** axis for values ($0 \le \theta \le \pi$)
2. Draw circle of radius **r** = **(5cos³(θ)–3cos(θ))**. Mark the point of intersection of circle with the vector
3. This plot is made for $\phi = 0$

Polar plot of $(5\cos^3(\theta) - 3\cos(\theta))$
$(0 \le \theta \le \pi)\varpi$

θ	5cos³(θ)–3cos(θ)
0	2
15	1.608328
30	0.649519
39.2	0
45	-0.35355
60	-0.875
75	-0.68977
90	0
105	0.689769
120	0.875
135	0.353553
140.8	0
150	-0.64952
165	-1.60833
180	-2

▮ positive value of the function
▮ negative value of the function

Title of PDF Document

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$$l = 3, \quad m = 1 \quad \mathrm{Re}\left[Y_3^1(\theta, \phi)\right] \propto (5\cos^2\theta - 1)\sin\theta\cos\phi \quad f_{x(5z^2 - r^2)}$$

Polar plot of function $((5\cos^2(\theta)-1)\sin(\theta)\cos(\phi))$

PROCEDURE

1. Vary angle theta made by the vector with **z** axis for values $(0 \leq \theta \leq \pi)$
2. Draw circle of radius $\mathbf{r = (5cos^2(\theta)-1)sin(\theta)cos(\phi)}$. Mark the point of intersection of circle with the vector
3. This plot is made for $\phi = 0$ (or $\cos \phi = 1$)

Polar plot of $(5\cos^2(\theta)-1)\sin(\theta)\cos(\phi)$
$(0 \leq \theta \leq \pi); \phi = 0$ (or cos $(\phi) = 1$)

θ	$(5\cos^2(\theta)-1)\sin(\theta)$
0	0
15	0.948588
30	1.375
45	1.06066
60	0.216506
71.05	0
75	-0.6424
90	-1
105	-0.6424
108.95	0
120	0.216506
135	1.06066
150	1.375
165	0.948588
180	0

positive value of the function

negative value of the function

+ ve
- ve
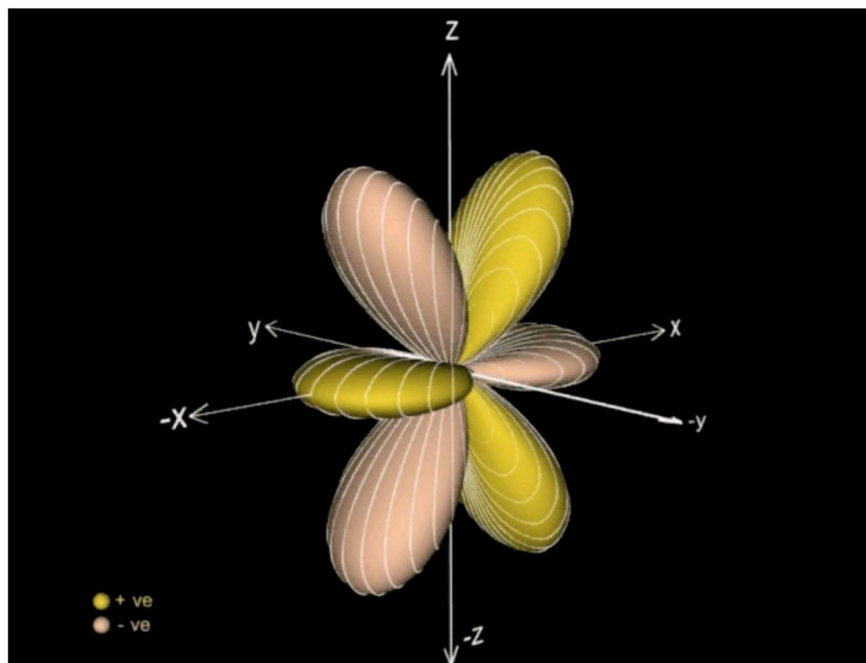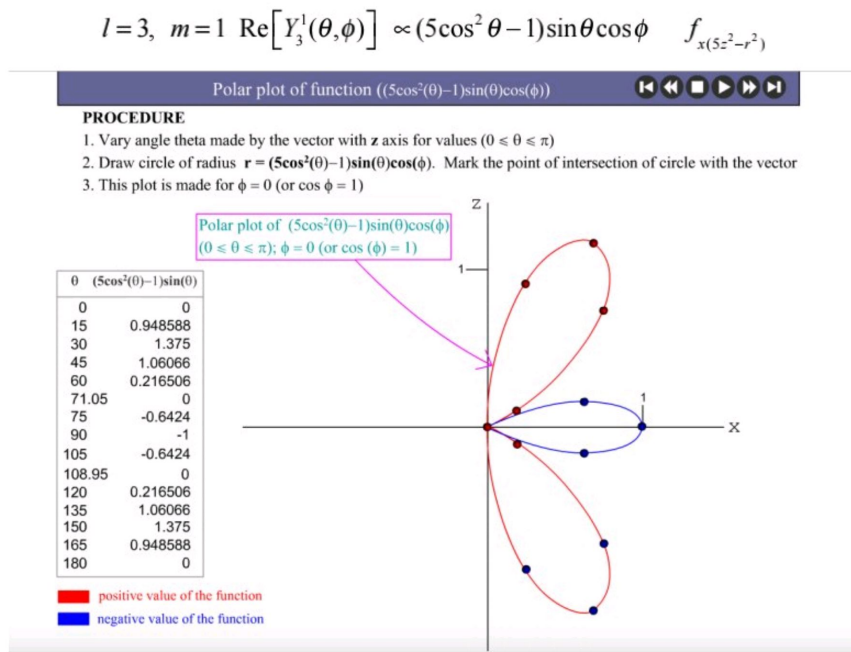
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$$l = 3, \quad m = 1 \quad \text{Im}\left[Y_3^1(\theta,\phi)\right] \propto (5\cos^2\theta - 1)\sin\theta\sin\phi \qquad f_{y(5z^2-r^2)}$$

Polar plot of function $((5\cos^2(\theta)-1)\sin(\theta)\sin(\phi))$ ⏮ ⏪ ⏹ ▶ ⏩ ⏭
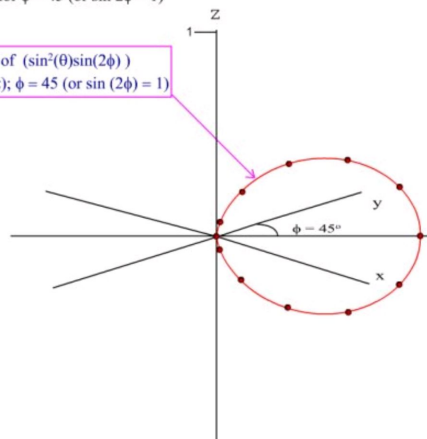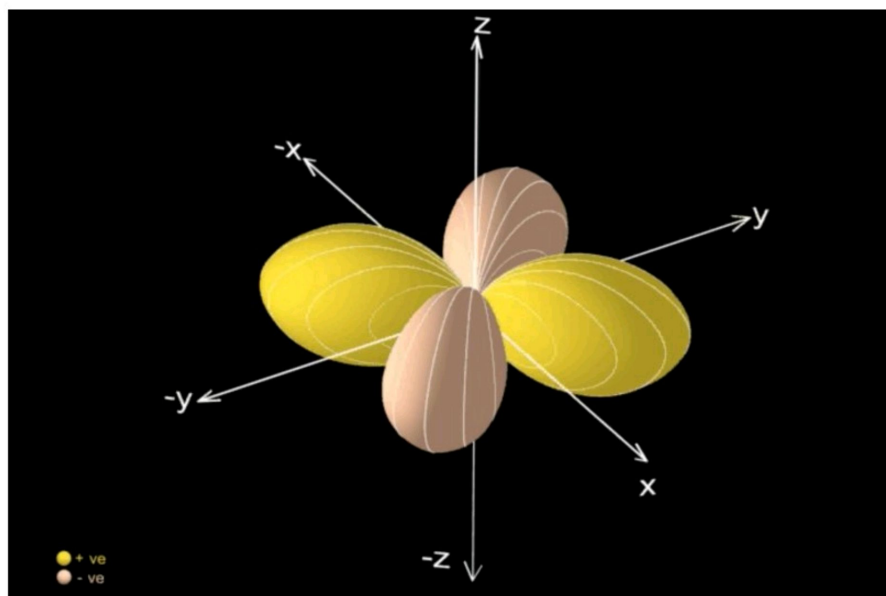
PROCEDURE

1. Vary angle theta made by the vector with **z** axis for values $(0 \leqslant \theta \leqslant \pi)$
2. Draw circle of radius $r = (5\cos^2(\theta)-1)\sin(\theta)\sin(\phi))$. Mark the point of intersection of circle with the vector
3. This plot is made for $\phi = 90$ (or $\sin\phi = 1$)

Polar plot of $(5\cos^2(\theta)-1)\sin(\theta)\sin(\phi)$
$(0 \leqslant \theta \leqslant \pi)$; $\phi = 90$ (or $\sin(\phi) = 1$)

θ	$(5\cos^2(\theta)-1)\sin(\theta)$
0	0
15	0.948588
30	1.375
45	1.06066
60	0.216506
71.05	0
75	-0.6424
90	-1
105	-0.6424
108.95	0
120	0.216506
135	1.06066
150	1.375
165	0.948588
180	0

■ positive value of the function
■ negative value of the function

+ ve
- ve

Title of PDF Document
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$$l = 3, \quad m = 2 \quad \text{Re}\left[Y_3^2(\theta,\phi)\right] \propto \sin^2\theta\cos\theta\cos 2\phi \quad \sim \cos\theta(\sin^2\theta\cos^2\phi - \sin^2\theta\sin^2\phi)$$

$$f_{z(x^2-y^2)}$$

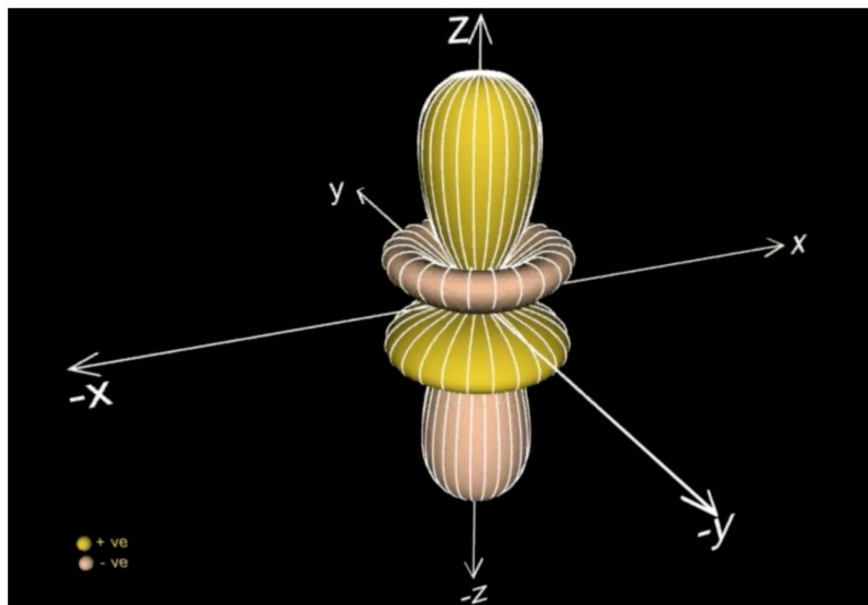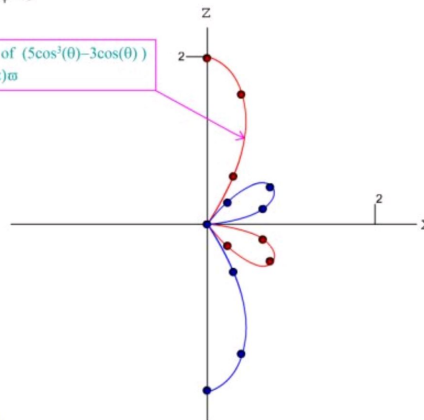Polar plot of function $(\sin^2(\theta)\cos(\theta)\cos(2\phi))$

PROCEDURE
1. Vary angle theta made by the vector with **z** axis for values $(0 \le \theta \le \pi)$
2. Draw circle of radius $r = (\sin^2(\theta)\cos(\theta)\cos(2\phi))$. Mark the point of intersection of circle with the vector
3. This plot is made for $\phi = 0$ (or $\cos 2\phi = 1$)

Polar plot of $(\sin^2(\theta)\cos(\theta)\cos(2\phi))$
$(0 \le \theta \le \pi)$; $\phi = 0$ (or $\cos(2\phi) = 1$)

θ	$\sin^2(\theta)\cos(\theta)$
0	0
15	0.064705
30	0.216506
45	0.353553
60	0.375
75	0.241481
90	0
105	-0.24148
120	-0.375
135	-0.35355
150	-0.21651
165	-0.0647
180	0

■ positive value of the function
■ negative value of the function

● + ve
● - ve

35
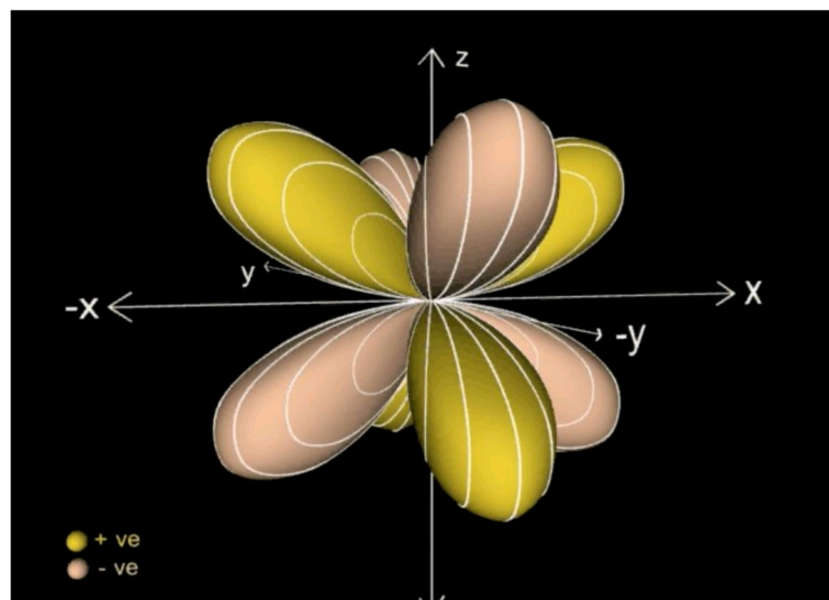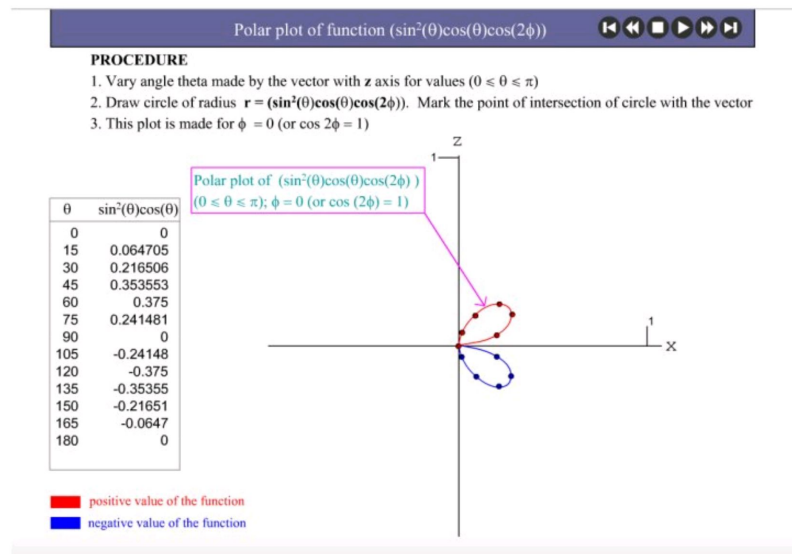
Title of PDF Document
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$$l = 3, \quad m = 2 \quad \mathrm{Im}\left[Y_3^2(\theta,\phi)\right] \quad \propto \sin^2\theta\cos\theta\sin 2\phi \quad \sim \cos\theta\sin\theta\cos\phi\sin\theta\sin\phi$$

$$f_{zxy}$$

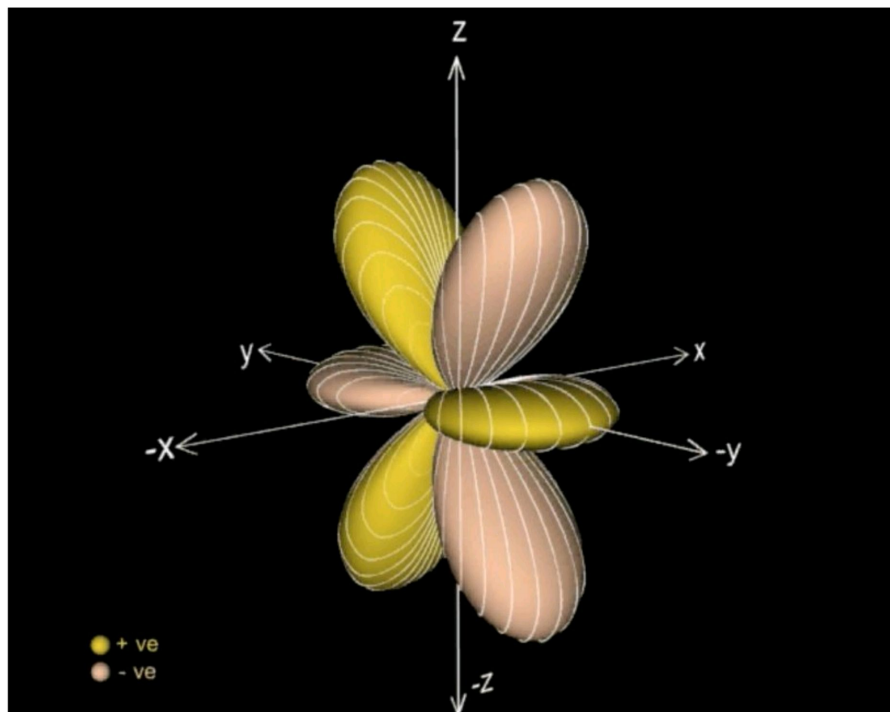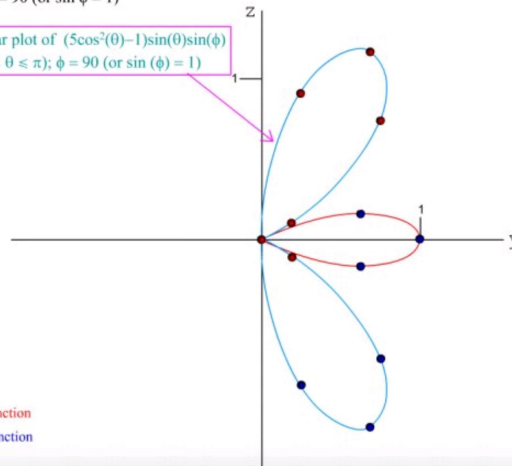Polar plot of function $(\sin^2(\theta)\cos(\theta)\sin(2\phi))$

PROCEDURE
1. Vary angle theta made by the vector with **z** axis for values $(0 \leq \theta \leq \pi)$
2. Draw circle of radius $\mathbf{r} = (\sin^2(\theta)\cos(\theta)\sin(2\phi))$. Mark the point of intersection of circle with the vector
3. This plot is made for $\phi = 45$ (or $\sin 2\phi = 1$)

Polar plot of $(\sin^2(\theta)\cos(\theta)\sin(2\phi))$
$(0 \leq \theta \leq \pi); \phi = 45$ (or $\sin(2\phi) = 1$)

θ	$\sin^2(\theta)\cos(\theta)$
0	0
15	0.064705
30	0.216506
45	0.353553
60	0.375
75	0.241481
90	0
105	-0.24148
120	-0.375
135	-0.35355
150	-0.21651
165	-0.0647
180	0

$\phi = 45°$

positive value of the function
negative value of the function

+ ve
- ve

Title of PDF Document
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$$l = 3, \quad m = 3 \quad \mathrm{Re}\left[Y_3^3(\theta, \phi)\right] \quad \propto \sin^3\theta \cos 3\phi \quad \sim \left(\sin\theta\cos\phi\right)^3 - 3\left(\sin\theta\sin\phi\right)^2 \sin\theta\cos\phi$$

$$f_{x(x^2-3y^2)}$$

Polar plot of function $(\sin^3(\theta)\cos(3\phi))$

PROCEDURE
1. Vary angle theta made by the vector with **z** axis for values ($0 \leqslant \theta \leqslant \pi$)
2. Draw circle of radius **r = ($\sin^3(\theta)\cos(3\phi)$)**. Mark the point of intersection of circle with the vector
3. This plot is made for $\phi = 0$ (or $\cos 3\phi = 1$)

θ	$\sin^3(\theta)$
0	0
15	0.01733
30	0.125
45	0.3535
60	0.6495
75	0.9012
90	1
105	0.9012
120	0.6495
135	0.3535
150	0.125
165	0.01733
180	0

Polar plot of $(\sin^3(\theta)\cos(3\phi))$
($0 \leqslant \theta \leqslant \pi$); $\phi = 0$ (or $\cos (3\phi) = 1$)

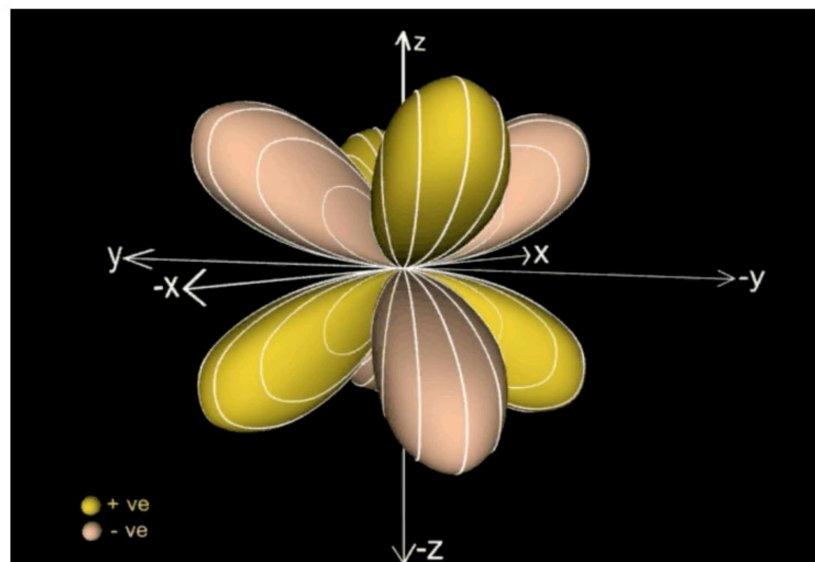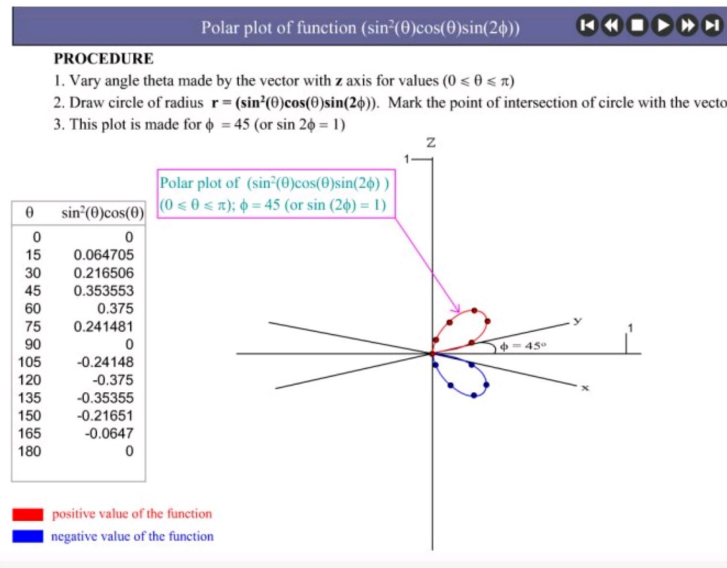positive value of the function

+ ve
- ve

37
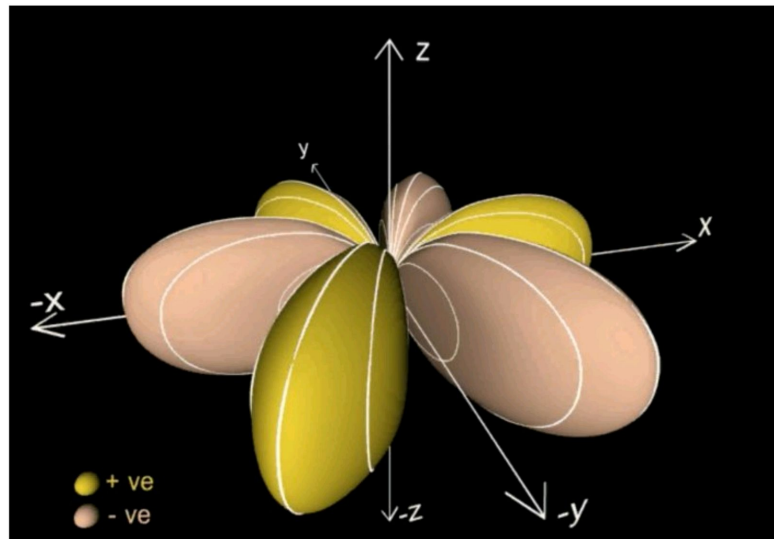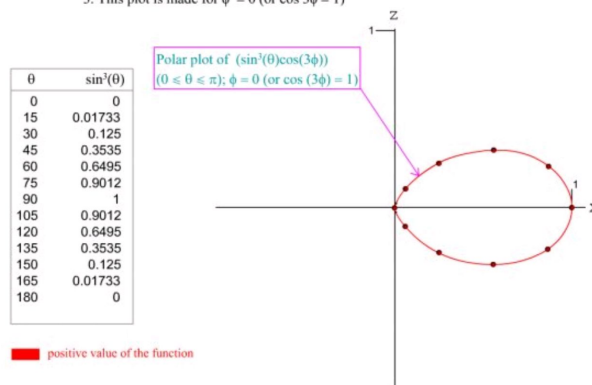
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$$l = 3, \quad m = 3 \quad \mathrm{Im}\left[Y_3^3(\theta,\phi)\right] \propto \sin^3\theta\sin 3\phi \quad \sim 3\left(\sin\theta\cos\phi\right)^2\sin\theta\sin\phi - \left(\sin\theta\sin\phi\right)^3$$

$$f_{y(3x^2-y^2)}$$

/IITPalakkadJanApril2016/HydrogenAtomAnimations/Y3-3/y3-3.swf

Polar plot of function (sin³(θ)sin(3φ))

PROCEDURE   last frame
1. Vary angle theta made by the vector with **z** axis for values ($0 \le \theta \le \pi$)
2. Draw circle of radius **r = (sin³(θ)sin(3φ))**. Mark the point of intersection of circle with the vector
3. This plot is made for φ = 30 (or sin 3φ = 1)

Polar plot of (sin³(θ)sin(3φ))
($0 \le \theta \le \pi$); φ = 0 (or sin(3φ) = 1)

θ	sin³(θ)
0	0
15	0.017338
30	0.125
45	0.353553
60	0.649519
75	0.901221
90	1
105	0.901221
120	0.649519
135	0.353553
150	0.125
165	0.017338
180	0

φ = 30°

■ positive value of the function

+ ve
- ve

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Title of PDF Document
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Radial Functions and the Radial distribution function plots for various values of n and l

n=1, l=0, 1s	radial function for the hydrogen atom (n=1) R(r) vs r varies from 0 to 5, Z/ao =1	radial probability for the hydrogen atom (n=1) radial probability vs r varies from 0 to 5, Z/ao =1
n=2, l=0, 2s	radial function for the hydrogen atom (n=2) R(r) vs r varies from 0 to 15, Z/ao =1	radial probability for the hydrogen atom (n=2) Radial probability density vs r varies from 0 to 15, Z/ao =1
n=2, l=1, 2p	radial function for the hydrogen atom (n=2) R(r) vs r varies from 0 to 15, Z/ao =1	radial probability for the hydrogen atom (n=2) Radial probability density vs r varies from 0 to 15, Z/ao =1
n=2, l=0 and l=1 together	radial functions for the hydrogen atom (n=2) R(r) vs r varies from 0 to 15, Z/ao =1	radial probabilities for the hydrogen atom (n=2) Radial probability density vs r varies from 0 to 15, Z/ao =1

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Title of PDF Document
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n=3, l=0, 3s	radial function for the hydrogen atom (n=3)	radial function for the hydrogen atom (n=3)
n=3, l=1, 3p	radial function for the hydrogen atom (n=3)	radial probability for the hydrogen atom (n=3)
n=3, l=2, 3d	radial function for the hydrogen atom (n=3)	radial probability for the hydrogen atom (n=3)
n=3, l=0, l=1 and l=2 together	radial functions for the hydrogen atom (n=3)	radial probabilities for the hydrogen atom (n=3)

40

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n=4, l=0 4s	Radial wavefunction plot 4s	Probability plot of 4s orbital
n=4, l=1 4p	Radial wavefunction plot 4p	Probability plot of 4p orbital
n=4, l=2, 4d	Radial wavefunction plot 4d	Probability plot of 4d orbital
n=4, l=3, 4f	Radial wavefunction plot 4f	Probability plot of 4f orbital
n=4, l=0, l=1, l=2 and l=3 together	Radial wavefunction plots of 4s,4p,4d and 4f orbitals	Probability plots of 4s,4p,4d and 4f orbitals

Additional sample calculations are provided by a separate handwritten notes in your website. If you find mistakes in these please let me know. Thank you very much. Mangala Sunder