Hydrogen atom

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Bohr model
Schrödinger equation
Hydrogen atom

Niels Henrik David Bohr (7 October 1885 – 18 November 1962) was a Danish physicist who made fundamental contributions to understanding atomic structure and quantum mechanics, for which he received the Nobel Prize in Physics in 1922. Bohr mentored and collaborated with many of the top physicists of the century at his institute in Copenhagen. He was part of a team of physicists working on the Manhattan Project. Bohr married Margrethe Nørlund in 1912, and one of their sons, Aage Bohr, grew up to be an important physicist who in 1975 also received the Nobel prize. Bohr has been described as one of the most influential scientists of the 20th century.

http://en.wikipedia.org/wiki/Niels_Bohr

Erwin Rudolf Josef Alexander Schrödinger (12 August 1887– 4 January 1961) was an Austrian theoretical physicist who was one of the fathers of quantum mechanics, and is famed for a number of important contributions to physics, especially the Schrödinger equation, for which he received the Nobel Prize in Physics in 1933. In 1935, after extensive correspondence with personal friend Albert Einstein, he proposed the Schrödinger's cat thought experiment.

http://en.wikipedia.org/wiki/Erwin_Schr%C3%B6dinger

1. Orbital angular momentum in quantum mechanics

The orbital angular momentum is defined as

$$\hat{\mathbf{L}} = \hat{\mathbf{r}} \times \hat{\mathbf{p}} = \begin{vmatrix} \mathbf{e}_x & \mathbf{e}_y & \mathbf{e}_z \\ \hat{x} & \hat{y} & \hat{z} \\ \hat{p}_x & \hat{p}_y & \hat{p}_z \end{vmatrix}$$

$$\hat{L}_x = \hat{y}\hat{p}_z - \hat{z}\hat{p}_y$$

$$\hat{L}_y = \hat{z}\hat{p}_x - \hat{x}\hat{p}_z$$

$$\hat{L}_z = \hat{x}\hat{p}_y - \hat{y}\hat{p}_x$$

$$\begin{aligned}[\hat{L}_x, \hat{L}_y] &= [\hat{y}\hat{p}_z - \hat{z}\hat{p}_y, \hat{z}\hat{p}_x - \hat{x}\hat{p}_z] \\ &= [\hat{y}\hat{p}_z, \hat{z}\hat{p}_x] + [\hat{z}\hat{p}_y, \hat{x}\hat{p}_z] \\ &= \hat{y}[\hat{p}_z, \hat{z}]\hat{p}_x + \hat{p}_y[\hat{z}, \hat{p}_z]\hat{x} \\ &= -\frac{\hbar}{i}(-\hat{y}\hat{p}_x + \hat{x}\hat{p}_y) = i\hbar\hat{L}_z\end{aligned}$$

or

$$[\hat{L}_x, \hat{L}_y] = i\hbar\hat{L}_z,$$

Similarly,

$$[\hat{L}_y, \hat{L}_z] = i\hbar\hat{L}_x, \qquad [\hat{L}_z, \hat{L}_x] = i\hbar\hat{L}_y$$

$\hat{L}^2$ is defined by

$$\hat{L}^2 = \hat{L}_x{}^2 + \hat{L}_y{}^2 + \hat{L}_z{}^2$$

We have

$$[\hat{L}^2, \hat{L}_z] = [\hat{L}_x{}^2 + \hat{L}_y{}^2 + \hat{L}_z{}^2, \hat{L}_z] = [\hat{L}_x{}^2, \hat{L}_z] + [\hat{L}_y{}^2, \hat{L}_z]$$
$$= -[\hat{L}_z, \hat{L}_x{}^2] - [\hat{L}_z, \hat{L}_y{}^2] = \hat{0}$$

using the relations

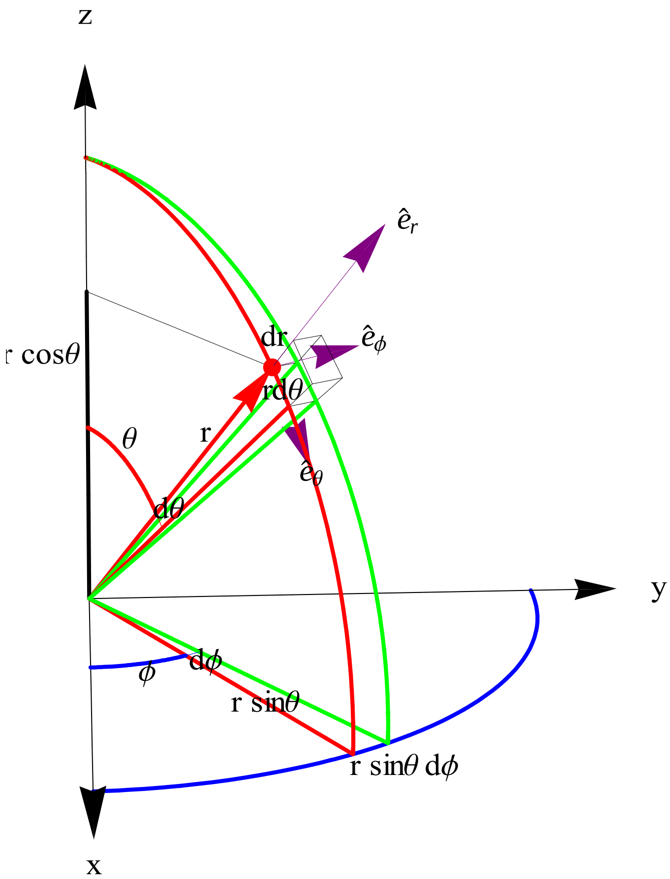
$$[\hat{L}_z, \hat{L}_x{}^2] = [\hat{L}_z, \hat{L}_x]\hat{L}_x + \hat{L}_x[\hat{L}_z, \hat{L}_x] = i\hbar(\hat{L}_y\hat{L}_x + \hat{L}_x\hat{L}_y)$$

$$[\hat{L}_z, \hat{L}_y{}^2] = [\hat{L}_z, \hat{L}_y]\hat{L}_y + \hat{L}_y[\hat{L}_z, \hat{L}_y] = -i\hbar(\hat{L}_y\hat{L}_x + \hat{L}_x\hat{L}_y)$$

Similarly

$$[\hat{L}^2, \hat{L}_x] = \hat{0}, \quad [\hat{L}^2, \hat{L}_y] = \hat{0} \quad [\hat{L}^2, \hat{L}_z] = \hat{0}$$

2. Quantum mechanical orbital angular momentum: spherical coordinates



The orbital angular momentum in the quantum mechanics is defined by

$$\mathbf{L} = \mathbf{r}\times\mathbf{p} = -i\hbar(r\times\nabla)$$

using the expression

$$\nabla = \mathbf{e}_r\frac{\partial}{\partial r} + \mathbf{e}_\theta\frac{1}{r}\frac{\partial}{\partial\theta} + \mathbf{e}_\phi\frac{1}{r\sin\theta}\frac{\partial}{\partial\phi}$$

in the spherical coordinate. Then we have

$$\mathbf{L} = -i\hbar(\mathbf{r}\times\nabla) = -i\hbar\mathbf{e}_r r\times(\mathbf{e}_r\frac{\partial}{\partial r} + \mathbf{e}_\theta\frac{1}{r}\frac{\partial}{\partial\theta} + \mathbf{e}_\phi\frac{1}{r\sin\theta}\frac{\partial}{\partial\phi})$$

$$= i\hbar(-\mathbf{e}_\phi\frac{\partial}{\partial\theta} + \mathbf{e}_\theta\frac{1}{\sin\theta}\frac{\partial}{\partial\phi})$$

.

The angular momentum L_x, L_y, and L_z (Cartesian components) can be described by

$$\mathbf{L} = i\hbar[-(-\sin\phi\mathbf{e}_x + \cos\phi\mathbf{e}_y)\frac{\partial}{\partial\theta} + (\cos\theta\cos\phi\mathbf{e}_x + \cos\theta\sin\phi\mathbf{e}_y - \sin\theta\mathbf{e}_z)\frac{1}{\sin\theta}\frac{\partial}{\partial\phi}].$$

or

$$L_x = i\hbar(\sin\phi\frac{\partial}{\partial\theta} + \cot\theta\cos\phi\frac{\partial}{\partial\phi})$$

$$L_y = i\hbar(-\cos\phi\frac{\partial}{\partial\theta} + \cot\theta\sin\phi\frac{\partial}{\partial\phi})$$

$$L_z = -i\hbar\frac{\partial}{\partial\phi}$$

We define L_+ and L_- as

$$L_+ = L_x + iL_y = -i\hbar e^{i\phi}(i\frac{\partial}{\partial\theta} - \cot\theta\frac{\partial}{\partial\phi})$$

and

$$L_- = L_x - iL_y = -i\hbar e^{-i\phi}(-i\frac{\partial}{\partial\theta} - \cot\theta\frac{\partial}{\partial\phi})$$

We note that the operator ∇ can be expressed using the operator $\boldsymbol{L}$ as

$$\nabla = \mathbf{e}_r\frac{\partial}{\partial r} - \frac{i}{\hbar}\frac{\mathbf{r}\times\mathbf{L}}{r^2}$$

The proof of this equation is given as follows.

$$\frac{(\mathbf{r}\times\mathbf{L})}{i\hbar} = r\mathbf{e}_r \times (-\mathbf{e}_\phi\frac{\partial}{\partial\theta} + \mathbf{e}_\theta\frac{1}{\sin\theta}\frac{\partial}{\partial\phi}) = r(\mathbf{e}_\theta\frac{\partial}{\partial\theta} + \mathbf{e}_\phi\frac{1}{\sin\theta}\frac{\partial}{\partial\phi})$$

or

$$\frac{(\mathbf{r}\times\mathbf{L})}{i\hbar r^2} = \frac{1}{r}\mathbf{e}_\theta\frac{\partial}{\partial\theta} + \mathbf{e}_r\frac{1}{r\sin\theta}\frac{\partial}{\partial\phi} = \nabla - \mathbf{e}_r\frac{\partial}{\partial r}$$

or

$$\nabla = \mathbf{e}_r \frac{\partial}{\partial r} - \frac{i(\mathbf{r}\times\mathbf{L})}{\hbar r^2}$$

From $\mathbf{L}^2 = L_x{}^2 + L_y{}^2 + L_z{}^2$, we have

$$\mathbf{L}^2 = -\hbar^2 [\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta\frac{\partial}{\partial\theta})]$$

Using

$$\frac{\mathbf{L}^2}{\hbar^2} = -r^2\nabla^2 + \frac{\partial}{\partial r}(r^2\frac{\partial}{\partial r})$$

we can also prove that

$$r\nabla^2 - \nabla(1 + r\frac{\partial}{\partial r}) = \frac{i}{\hbar}\nabla\times\mathbf{L}$$

((**Note**))

$$\begin{aligned}
\nabla^2 &= -\frac{1}{\hbar^2 r^2}\mathbf{L}^2 + \frac{1}{r^2}\frac{\partial}{\partial r}(r^2\frac{\partial}{\partial r}) \\
&= -\frac{1}{\hbar^2 r^2}\mathbf{L}^2 + \frac{1}{r^2}\frac{\partial}{\partial r}(r^2\frac{\partial}{\partial r}) \\
&= -\frac{1}{\hbar^2 r^2}\mathbf{L}^2 + \frac{1}{r}\frac{\partial^2}{\partial r^2}(r) \\
&= -\frac{1}{\hbar^2 r^2}\mathbf{L}^2 - \frac{p_r{}^2}{\hbar^2}
\end{aligned}$$

where the definition of pr is given below. This expression can be rewritten as

$$-\frac{\hbar^2}{2\mu}\nabla^2 = \frac{p_r{}^2}{2\mu} + \frac{\mathbf{L}^2}{2\mu r^2}$$

3. Radial momentum operator p_r in the quantum mechanics

(a) In classical mechanics, the radial momentum of the radius *r* is defined by

$$p_{rc} = \frac{1}{r}(\mathbf{r}\cdot\mathbf{p})$$

(b) In quantum mechanics, this definition becomes ambiguous since the component of *p* and r do not commute. Since pr should be Hermitian operator, we need to define as the radial momentum of the radius *r* is defined by

$$p_{rq} = \frac{1}{2}(\frac{\mathbf{r}}{r}\cdot\mathbf{p} + \mathbf{p}\cdot\frac{\mathbf{r}}{r})$$

This symmetric expression is indeed the canonical conjugate of *r*.

$$p_{rq}r - rp_{rq} = \frac{\hbar}{i}$$

Note that

$$p_{rq} = (-i\hbar)(\frac{\partial}{\partial r} + \frac{1}{r}) = (-i\hbar)\frac{1}{r}\frac{\partial}{\partial r}r$$

This can be proved as follows.

$$\begin{aligned}
p_{rq}\psi(r,\theta,\phi) &= \frac{1}{2}(-i\hbar)\{\mathbf{e}_r.\nabla\psi(r,\theta,\phi) + \nabla\cdot[\mathbf{e}_r\psi(r,\theta,\phi)]\} \\
&= \frac{1}{2}(-i\hbar)[\frac{\partial\psi}{\partial r} + \frac{1}{r^2}\frac{\partial}{\partial r}(r^2\psi)] \\
&= \frac{1}{2}(-i\hbar)(2\frac{\partial\psi}{\partial r} + \frac{2}{r}\frac{\partial}{\partial r}\psi) \\
&= -i\hbar(\frac{\partial\psi}{\partial r} + \frac{1}{r}\frac{\partial}{\partial r}\psi) \\
&= (-i\hbar\frac{1}{r}\frac{\partial}{\partial r}r)\psi
\end{aligned}$$

where

$$\nabla\psi = \mathbf{e}_r\frac{\partial\psi}{\partial r} + \mathbf{e}_\theta\frac{1}{r}\frac{\partial\psi}{\partial\theta} + \mathbf{e}_\phi\frac{1}{r\sin\theta}\frac{\partial\psi}{\partial\phi}$$

$$\nabla\cdot\mathbf{A} = \frac{1}{r^2}\frac{\partial}{\partial r}(r^2A_r) + \frac{1}{r\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta A_\theta) + \frac{1}{r\sin\theta}\frac{\partial}{\partial\phi}A_\phi$$

For convenience we use

$$p_{eq} = p_r$$

then we have

$$p_r^{\ 2} = (-i\hbar\frac{1}{r}\frac{\partial}{\partial r}r)(-i\hbar\frac{1}{r}\frac{\partial}{\partial r}r) = -\hbar^2\frac{1}{r}\frac{\partial^2}{\partial r^2}r$$

4. Central field problem

Free particle wave function ψ satisfies the Schrödinger equation

$$[-\frac{\hbar^2}{2\mu}\nabla^2 + V(r)]\psi = E\psi\ ,$$

where μ is the reduced mass of particle, E is the energy eigenvalue of the system. The wavefunction can be expressed by

$$\psi = \varphi_{k\ell m}(r,\theta,\phi)$$

$$\frac{1}{2\mu}[p_r^{\ 2} + \frac{\mathbf{L}^2}{r^2} + V(r)]\varphi_{n\ell m}(r,\theta,\phi) = E\varphi_{n\ell m}(r,\theta,\phi)$$

(separation variables),

$$\varphi_{n\ell m}(r,\theta,\phi) = R_{n\ell}(r)Y_{\ell m}(\theta,\phi)$$

with

$$\mathbf{L}^2 Y_{\ell m}(\theta,\phi) = \hbar^2\ell(\ell+1)Y_{\ell m}(\theta,\phi)$$

$$L_z Y_{\ell m}(\theta,\phi) = \hbar m Y_{\ell m}(\theta,\phi)$$

Note that $Y_{\ell m}(\theta,\phi)$ is the spherical harmonics.

$$\frac{1}{2\mu}[p_r^{\ 2} + \frac{\hbar^2 l(l+1)}{r^2}]R_{n\ell}(r) + V(r)R_{n\ell}(r) = ER_{n\ell}(r)$$

Since $p_r = \frac{\hbar}{i}\frac{1}{r}\frac{\partial}{\partial r}r$, we have

$$p_r^{\ 2}R_{n\ell}(r) = \frac{\hbar}{i}\frac{1}{r}\frac{\partial}{\partial r}r(\frac{\hbar}{i}\frac{1}{r}\frac{\partial}{\partial r}r)R_{n\ell}(r) = -\hbar^2\frac{1}{r}\frac{\partial^2}{\partial r^2}[rR_{n\ell}(r)]$$

or

$$-\frac{1}{r}\frac{\partial^2}{\partial r^2}[rR_{n\ell}(r)]+[\frac{2\mu}{\hbar^2}V(r)+\frac{1}{r^2}\ell(\ell+1)]R_{n\ell}(r)=\frac{2\mu}{\hbar^2}ER_{n\ell}(r)$$

or

$$\frac{1}{r}\frac{\partial^2}{\partial r^2}[rR_{n\ell}(r)]+[\frac{2\mu}{\hbar^2}(E-V(r))-\frac{1}{r^2}\ell(\ell+1)]R_{n\ell}(r)=0\,.$$

Note that for a fixed *l*, the energy eigenvalue is independent of *m*, and is at least (2*l*+1)-fold degenerate.

We assume that

$$R_{nl}(r)=\frac{u(r)}{r}, \qquad E=-\varepsilon_1$$

$$u''(r)-[\frac{l(l+1)}{r^2}+\frac{2\mu(\varepsilon_1+V(r))}{\hbar^2}]u(r)=0$$

We further assume a Coulomb potential given by

$$V(r)=-k\frac{Ze^2}{r}$$

with

$$k=\frac{1}{4\pi\varepsilon_0}$$

Then

$$u''(r)-[\frac{l(l+1)}{r^2}+\frac{2\mu(\varepsilon_1-k\frac{Ze^2}{r})}{\hbar^2}]u(r)=0$$

We now introduce a new variable

$$r=\frac{\hbar\rho}{\sqrt{8\mu\varepsilon_1}}=\frac{\hbar\rho}{\sqrt{8\mu k^2\frac{Z^2\mu e^4}{2\hbar^2n^2}}}=\frac{\hbar^2n\rho}{2\mu kZe^2}=\frac{an}{2Z}\rho=\frac{\rho}{2\kappa}$$

where

$$\varepsilon_1 = k^2 \frac{Z^2 \mu e^4}{2\hbar^2 n^2} = \frac{ke^2}{2a}\frac{Z^2}{n^2}, \qquad E_n = -\varepsilon_1$$

$$a = \frac{\hbar^2}{k\mu e^2} \qquad (a = a_0\text{: Bohr radius when } \mu = m \text{ (electron mass)})$$

$$\frac{ke^2}{2a} \qquad (\text{Rydberg energy when } a = a_0)$$

$$\kappa = \frac{Z}{na}$$

Since

$$\rho = \frac{2rZ}{na} = 2\kappa r$$

we get

$$\frac{d}{dr} = \frac{d\rho}{dr}\frac{d}{d\rho} = 2\kappa \frac{d}{d\rho}$$

$$\frac{d^2}{dr^2} = 2\kappa \frac{d}{d\rho}(2\kappa \frac{d}{d\rho}) = 4\kappa^2 \frac{d^2}{d\rho^2}$$

$$4\kappa^2 u''(\rho) - [4\kappa^2 \frac{l(l+1)}{\rho^2} + \kappa^2 (1 - \frac{4n}{\rho})]u(\rho) = 0$$

where

$$\frac{2\mu}{\hbar^2}(\varepsilon_1 - k\frac{Ze^2}{r}) = \kappa^2 (1 - \frac{4n}{\rho})$$

Then we have

$$u''(\rho) - [\frac{l(l+1)}{\rho^2} + (\frac{1}{4} - \frac{n}{\rho})]u(\rho) = 0$$

or

$$[\frac{d^2}{d\rho^2} - \frac{l(l+1)}{\rho^2} + \frac{n}{\rho} - \frac{1}{4}]u(\rho) = 0 \qquad (1)$$

5. Series expansion method

Solution of radial part of the hydrogen atom (we need to show that $\lambda = n$; positive integer)

$$[\frac{d^2}{d\rho^2} - \frac{l(l+1)}{\rho^2} + \frac{\lambda}{\rho} - \frac{1}{4}]u(\rho) = 0 \qquad (1)$$

with

$$\lambda = \frac{kZe^2}{\hbar}\sqrt{\frac{\mu}{2\varepsilon_1}}$$, which corresponds to the eigenvalue.

Note that according to the Bohr model, $\lambda = n$ (positive integer) since

$$\varepsilon_1 = k^2 \frac{Z^2 \mu e^4}{2\hbar^2 n^2} = \frac{ke^2}{2a}\frac{Z^2}{n^2}$$

We solve the differential equation to determine the eigenvalue and eigenfunction. In the limit of $\rho \rightarrow 0$, we assume that it behaves at the origin like

$$u \approx \rho^s$$

$$[s(s-1) - l(l+1)]\rho^{s-2} + \lambda\rho^{s-1} - \frac{1}{4}\rho^s = 0$$

Note that the ρ^{s-2} term dominates for small ρ.

$$s(s-1) - l(l+1) = 0,$$

or

$$(s - \ell - 1)(s + l) = 0$$

$$s = l + 1 \text{ or } s = -l.$$

We must discard those solutions that behave as ρ^{-l}. So we get the form around $\rho = 0$:

$$u(\rho) \approx \rho^{l+1}$$

In the limit of $\rho \rightarrow \infty$,

$$(\frac{d^2}{d\rho^2} - \frac{1}{4})u(\rho) = 0$$

The solution for this equation is

$$u(\rho) \approx Ae^{-\rho/2} + Be^{\rho/2}$$

The constant B should be equal to zero ($\rho \to \infty$):

$$u(\rho) \approx e^{-\rho/2}$$

Thus we can attempt to find a solution of the form

$$u(\rho) = \rho^{l+1} e^{-\rho/2} F(\rho)$$

With this substitution, the differential equation (1) becomes

$$\frac{d^2 F(\rho)}{d\rho^2} + (\frac{2l+2}{\rho} - 1)\frac{dF(\rho)}{d\rho} + (\frac{\lambda}{\rho} - \frac{l+1}{\rho})F(\rho) = 0$$

We assume that

$$F(\rho) = \sum_{k=0}^{\infty} C_k \rho^k$$

with $C_0 \neq 0$.

$$\sum_{k=2}^{\infty} k(k-1)C_k\}\rho^{k-2} + \sum_{k=1}^{\infty}(2l+2)kC_k\rho^{k-2} + \sum_{k=0}^{\infty}[-k+\lambda-(l+1)]C_k\}\rho^{k-1} = 0$$

or

$$\sum_{k=0}^{\infty}\{k(k+1) + (2l+2)(k+1)]C_{k+1} + [-k+\lambda-(l+1)]C_k\}\rho^{k-1} = 0$$

leading to

$$\frac{C_{k+1}}{C_k} = \frac{k+l+1-\lambda}{(k+1)(k+2l+2)}$$

((Note))

Coefficient of ρ^0

$$(-1-l+\lambda)C_0+(2+2l)C_1=0$$

Coefficient of ρ^1

$$(-2-l+\lambda)C_1+2(3+2l)C_2=0$$

Coefficient of ρ^2

$$(-3-l+\lambda)C_2+3(4+2l)C_3=0$$

Coefficient of ρ^3

$$(-4-l+\lambda)C_3+4(5+2l)C_4=0$$

Coefficient of ρ^4

$$(-5-l+\lambda)C_4+5(6+2l)C_5=0$$

Coefficient of ρ^5

$$(-6-l+\lambda)C_5+6(7+2l)C_6=0$$

....

Note that

$$\frac{C_{k+1}}{C_k}\to\frac{1}{k}$$

which is the same asymptotic behavior as e^{ρ}. Thus, unless the series terminate, $u(\rho)$ will grow exponentially like $e^{\rho/2}$.

To avoid this, we must have

For $k = n_r$,

$$n_r+l+1-\lambda=0$$

or

$$\lambda = n_r + l + 1$$

Then we have

$$C_{n_r+1} = C_{n_r+2} = \ldots = 0$$

For $n_r = 0$, $\lambda = l + 1$

$$F(\rho) = C_0$$

For $n_r = 1$, $\lambda = l + 2$

$$F(\rho) = C_0 + C_1\rho$$

For $n_r = 2$, $\lambda = l + 3$

$$F(\rho) = C_0 + C_1\rho + C_2\rho^2$$

The function F will thus be a polynomial of degree of n_r, known as an associated Laguerre polynomial.

$$\lambda = k\frac{Ze^2}{\hbar}\sqrt{\frac{\mu}{2|E|}} = l + 1 + n_r$$

or

$$E = -\frac{k^2 Z^2 \mu e^4}{2\hbar^2 (l + 1 + n_r)^2}$$

Since $l = 0, 1, 2, 3, \ldots$, $n_r = 0, 1, 2, \ldots$, we introduced a principal quantum number n, defined by

$$n = l + 1 + n_r$$

with $n = 1, 2, 3, \ldots$. Thus, in terms of n,

$$E_n = -\frac{k^2 Z^2 \mu e^4}{2\hbar^2 n^2} = -\frac{ke^2 Z^2}{2an^2}$$

$n = 1$, $n_r = 0$, $l = 0$	(1s)
$n = 2$, $n_r = 0$, $l = 1$	(2p)

$n = 2$, $n_r = 1$, $l = 0$	(2s)
$n = 3$, $n_r = 0$, $l = 2$	(3d)
$n = 3$, $n_r = 1$, $l = 1$	(3p)
$n = 3$, $n_r = 2$, $l = 0$	(3s)
$n = 4$, $n_r = 0$, $l = 3$	(4f)
$n = 4$, $n_r = 1$, $l = 2$	(4d)
$n = 4$, $n_r = 2$, $l = 1$	(4p)
$n = 4$, $n_r = 3$, $l = 0$	(4s)
$n = 5$, $n_r = 0$, $l = 4$	(5g)
$n = 5$, $n_r = 1$, $l = 3$	(5f)
$n = 5$, $n_r = 2$, $l = 2$	(5d)
$n = 5$, $n_r = 3$, $l = 1$	(5p)
$n = 5$, $n_r = 4$, $l = 0$	(5s)

These $|nlm\rangle$ states have the same energy which is only dependent on *n*.

6. Spherical harmonics $Y_{lm}(\theta,\phi)$

$$L_z Y_{lm}(\theta,\phi) = \frac{\hbar}{i}\frac{\partial}{\partial\phi} Y_{lm}(\theta,\phi) = m\hbar Y_{lm}(\theta,\phi) \qquad (1)$$

The θ and ϕ dependence of $Y_l^m(\theta,\phi)$ is given by

$$\begin{aligned}\mathbf{L}^2 Y_l^m(\theta,\phi) &= -\hbar^2[\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta\frac{\partial}{\partial\theta})]Y_l^m(\theta,\phi) \\ &= \hbar^2 l(l+1) Y_l^m(\theta,\phi)\end{aligned} \qquad (2)$$

Equation (1) shows that

$$Y_l^m(\theta,\phi) = \Theta_l^m(\theta)e^{im\phi}$$

where $Y_l^m(\theta,\phi)$ is normalized as

$$\delta_{l,l'}\delta_{m,m'} = \int d\Omega Y_{l'}^{m'^*}(\theta,\phi)Y_l^m(\theta,\phi) = \iint \sin\theta d\theta d\phi Y_{l'}^{m'^*}(\theta,\phi)Y_l^m(\theta,\phi)$$

where Ω is a solid angle and $d\Omega = \sin\theta d\theta d\phi$. We must require that the eigenfunction be single valued

$$e^{im\phi} = e^{im(\phi+2\pi)}$$

which means that $m = 0, \pm1, \pm2,$ (integers). Equation (2) can be rewritten as

$$[\frac{1}{\sin\theta}\frac{d}{d\theta}(\sin\theta\frac{d}{d\theta}) - \frac{m^2}{\sin^2\theta} + l(l+1)]\Theta_l^m(\theta) = 0$$

The result for $m \geq 0$ is

$$Y_l^m(\theta,\phi) = \frac{(-1)^l}{2^l l!}\sqrt{\frac{(2l+1)}{4\pi}\frac{(l+m)!}{(l-m)!}}e^{im\phi}\frac{1}{\sin^m\theta}\frac{d^{l-m}}{d(\cos\theta)^{l-m}}(\sin\theta)^{2l}$$

and we define $Y_l^{-m}(\theta,\phi)$ by

$$Y_l^{-m}(\theta,\phi) = (-1)^m[Y_l^m(\theta,\phi)]^*$$

or

$$[Y_l^m(\theta,\phi)]^* = (-1)^m Y_l^{-m}(\theta,\phi)$$

7. Quantum numbers

n: the principal quantum number.
l: the azimuthal quantum number
m: the magnetic quantum number

For the fixed n (=1, 2, 3, 4, ...),

$l = n$-1, n-2,......., 1, and 0.

$l = 0$ sharp (s)
$m = 0$

$l = 1$ principal (p)
$m = 1, 0, -1$

$l = 2$ diffuse (d)
$m = 2, 1, 0, -1, -2$

$l = 3$ fundamental (f)
$m = 3, 2, 1, 0, -1, -2, -3$

$l = 4$ (g)
$m = 4, 3, 2, 1, 0, -1, -2, -3, -4$

There are $(2l+1)$ solutions to the Schrodinger equation corresponding to the same energy eigenvalue E_n.

$$\text{Degeneracy of } E_n = \sum_{l=0}^{n-1}(2l+1) = 2\frac{n(n-1)}{2} + n = n^2 .$$

((Note)) Including spin degeneracy of states is $2n^2$.

	n	l	m	m_s
1s	1	0	0	$\pm 1/2$
2s	2	0	0	$\pm 1/2$
2p	2	1	0, ±1	$\pm 1/2$
3s	3	0	0	$\pm 1/2$
3p	3	1	0, ±1	$\pm 1/2$
3d	3	2	0, ±1, , ±2	$\pm 1/2$
4s	4	0	0	$\pm 1/2$
4p	4	1	0, ±1	$\pm 1/2$
4d	4	2	0, ±1, , ±2	$\pm 1/2$
4f	4	3	0, ±1, , ±2, ±3	$\pm 1/2$

8. Vector model of the orbital angular momentum

We consider a case which l is some fixed number (l = 1, 2, 3,...). Then the total angular momentum may be represented by a vector of length

$$\hbar\sqrt{l(l+1)}$$

The component m in the z direction is

$$m = l, l - 1, l - 2, \ldots\ldots, -l + 1, -l$$

The vector $\boldsymbol{J}$ should be thought of as covering a cone, with vector angle given by

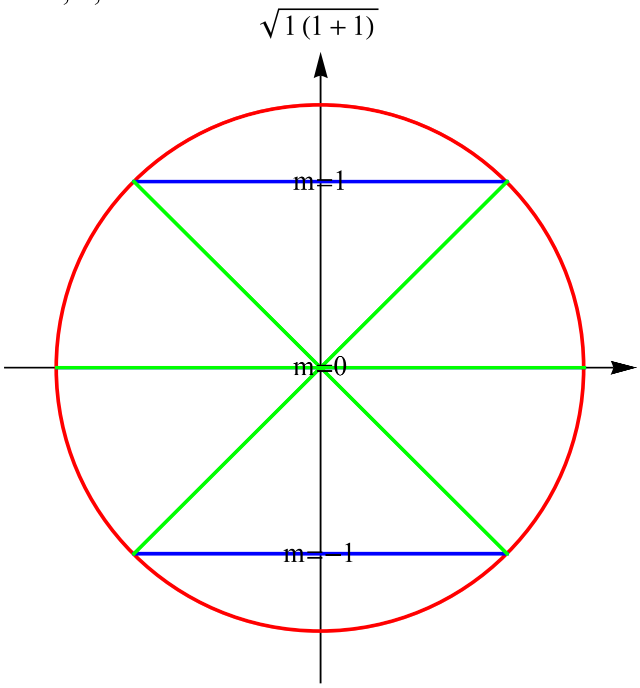
$$\cos\theta_m = \frac{m}{\sqrt{l(l+1)}}$$

where θ_m is the angle between the *z* axis and ***L***.

(a)

$l = 1$

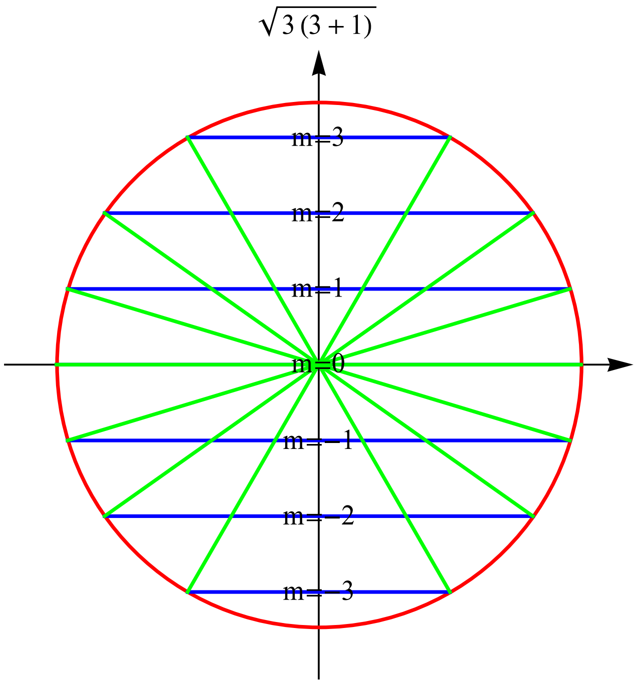
$m = 1, 0, -1$



(b)

$l = 3$

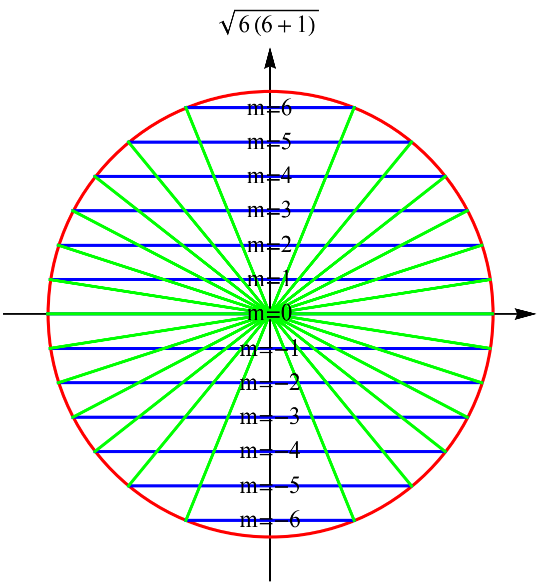
$m = 3, 2, 1, 0, -1, -2, -3$



(c)

$l = 6$

$m = 6, 5, 4, 3, 2, 1, 0, -1, -2, -3, -4, -5, -6$



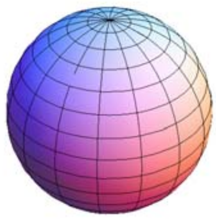
9. SphericalPlot3D of $\left|Y_l^m(\theta,\phi)\right|^2$

We make a SphericalPlot3D of the spherical harmonics.

(i)

l=0 m=0 $Y_{l=0}^{0}(\theta,\phi)$

0 0 $\frac{1}{2\sqrt{\pi}}$



$l = 0, m = 0$

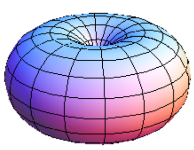
(ii) $m = -1, 0, 1$

l=1 m $Y_{l=1}^{m}(\theta,\phi)$

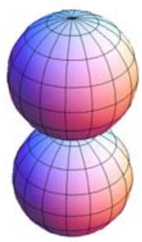
1 -1 $\frac{1}{2} e^{-i\phi} \sqrt{\frac{3}{2\pi}}$ Sin[θ]

1 0 $\frac{1}{2} \sqrt{\frac{3}{\pi}}$ Cos[θ]

1 1 $-\frac{1}{2} e^{i\phi} \sqrt{\frac{3}{2\pi}}$ Sin[θ]



$l = 1, m = \pm 1$



$l = 1, m = 0$

(ii) $m = -2, -1, 0, 1, 2$

l=2 m $Y_{l=2}^{m}(\theta,\phi)$

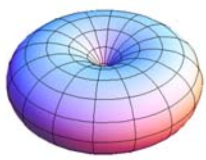
2 -2 $\frac{1}{4} e^{-2 i \phi} \sqrt{\frac{15}{2 \pi}} \text{Sin}[\theta]^2$

2 -1 $\frac{1}{2} e^{-i \phi} \sqrt{\frac{15}{2 \pi}} \text{Cos}[\theta] \text{Sin}[\theta]$

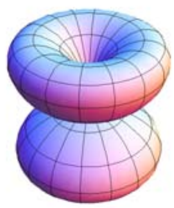
2 0 $\frac{1}{8} \sqrt{\frac{5}{\pi}} (1 + 3 \text{Cos}[2 \theta])$

2 1 $-\frac{1}{2} e^{i \phi} \sqrt{\frac{15}{2 \pi}} \text{Cos}[\theta] \text{Sin}[\theta]$

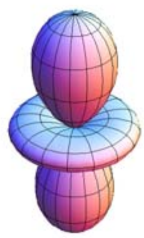
2 2 $\frac{1}{4} e^{2 i \phi} \sqrt{\frac{15}{2 \pi}} \text{Sin}[\theta]^2$



$l = 2, m = \pm 2$



$l = 2, m = \pm 1$

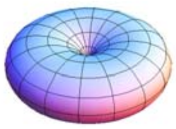


$l = 2, m = 0$

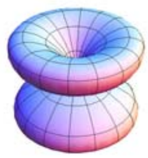
(iv) m = -3, -2, -1, 0, 1, 2, 3

l=3 m $Y_{l=3}^{m}(\theta,\phi)$

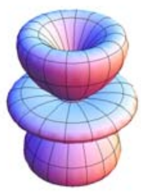
3	-3	$\frac{1}{8} e^{-3 i \phi} \sqrt{\frac{35}{\pi}}$ Sin[θ]^3
3	-2	$\frac{1}{4} e^{-2 i \phi} \sqrt{\frac{105}{2\pi}}$ Cos[θ] Sin[θ]^2
3	-1	$\frac{1}{16} e^{-i \phi} \sqrt{\frac{21}{\pi}}$ (3 + 5 Cos[2 θ]) Sin[θ]
3	0	$\frac{1}{16} \sqrt{\frac{7}{\pi}}$ (3 Cos[θ] + 5 Cos[3 θ])
3	1	$-\frac{1}{16} e^{i \phi} \sqrt{\frac{21}{\pi}}$ (3 + 5 Cos[2 θ]) Sin[θ]
3	2	$\frac{1}{4} e^{2 i \phi} \sqrt{\frac{105}{2\pi}}$ Cos[θ] Sin[θ]^2
3	3	$-\frac{1}{8} e^{3 i \phi} \sqrt{\frac{35}{\pi}}$ Sin[θ]^3



$l = 3, m = \pm 3$



$l = 3, m = \pm 2$



$l = 3, m = \pm 1$

$l = 3, m = 0$

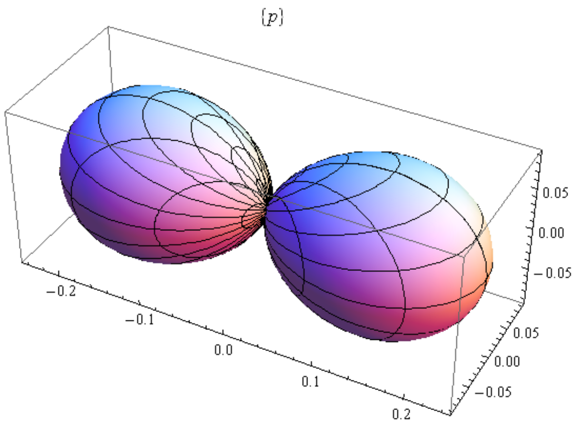
10. SphericalPlot of 2*p* orbitals

p-orbitals

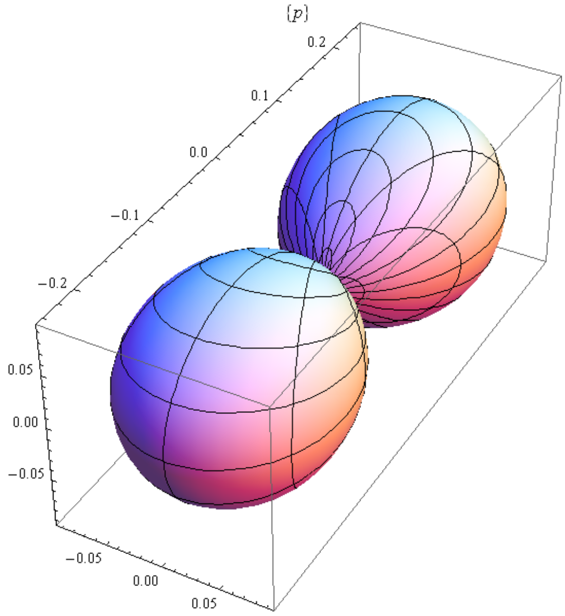
$$\psi_{px}=\frac{1}{\sqrt{2}}\left[-Y_1^1(\theta,\phi)+Y_1^{-1}(\theta,\phi)\right]$$

$$\psi_{py}=i\frac{1}{\sqrt{2}}\left[Y_1^1(\theta,\phi)+Y_1^{-1}(\theta,\phi)\right]$$

$$\psi_{pz}=Y_1^0(\theta,\phi)$$

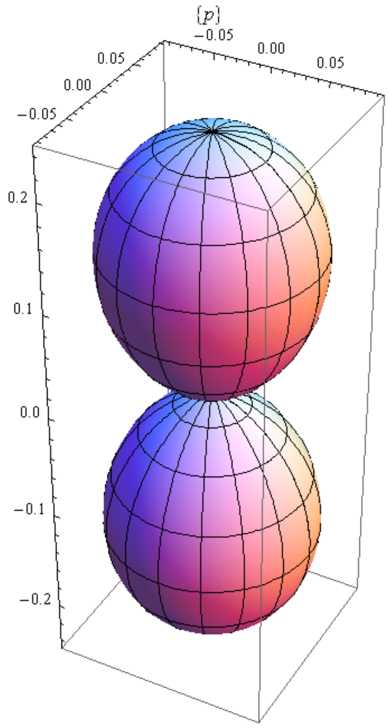


p_x orbit



p_y orbit

Out[53]=



p_z orbit

11. SphericalPlot of 3*d* orbitals

dϵ-orbitals

ψ_{xy}=-$i\frac{1}{\sqrt{2}}$ $[Y_2^2(\theta,\phi)$- $Y_2^{-2}(\theta,\phi)]$

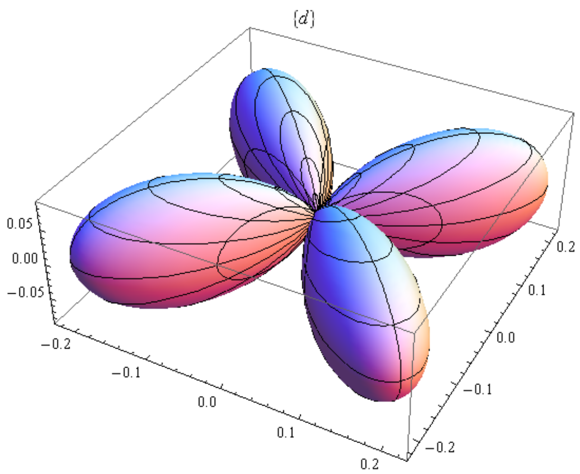
ψ_{yz}=-$i\frac{1}{\sqrt{2}}$ $[Y_2^2(\theta,\phi)+ Y_2^{-2}(\theta,\phi)]$

ψ_{zx}=-$\frac{1}{\sqrt{2}}$ $[Y_2^1(\theta,\phi)$- $Y_2^{-1}(\theta,\phi)]$

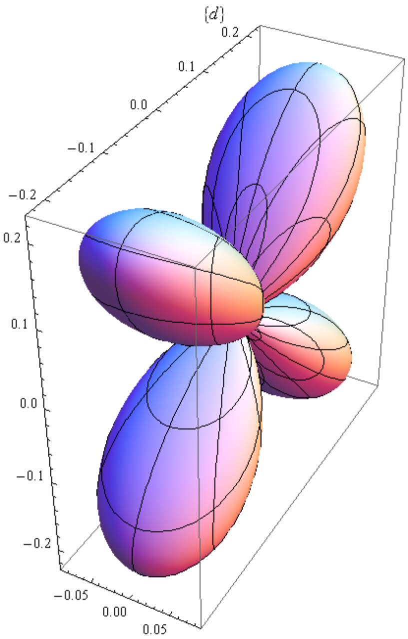
dγ-orbitals

$\psi_{x^2-y^2}$=$\frac{1}{\sqrt{2}}$ $[Y_2^2(\theta,\phi)+Y_2^{-2}(\theta,\phi)]$

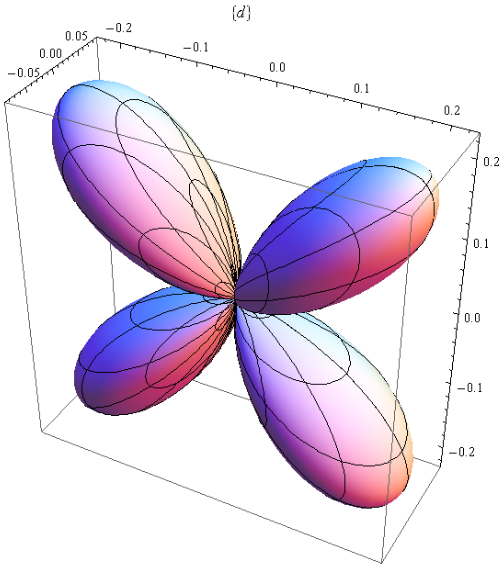
$\psi_{3z^2-r^2}$=$Y_2^0(\theta,\phi)$



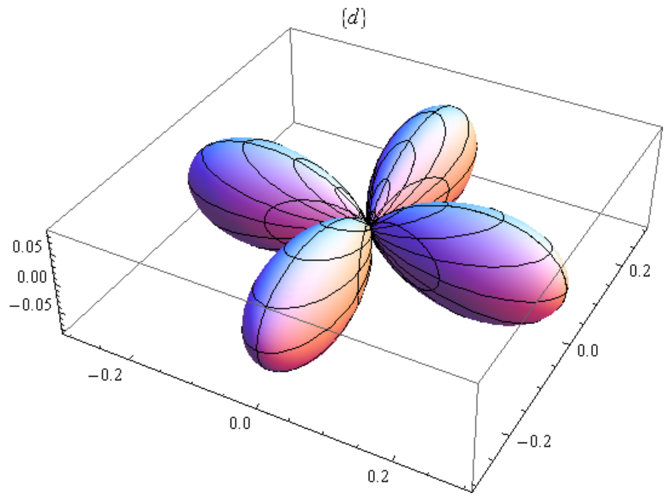
dγ(*xy*) orbit



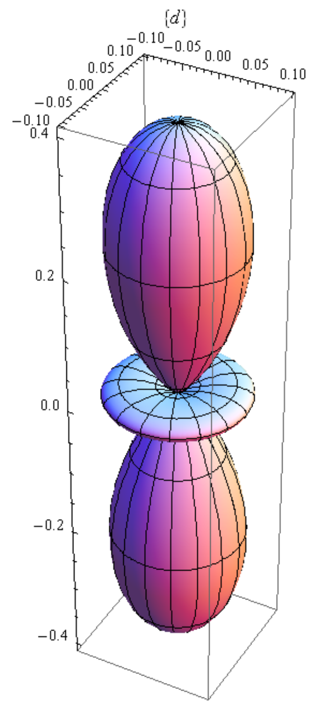
dγ (*yz*) orbit



dγ (*zx*) orbit



dε(x^2-y^2) orbit



dε(3z^2-r^2) orbit

12. The form of radial wave function $R_{nl}(r)$

The radial wave function $R_{nl}(r)$ is given by

$$rR_{nl}(r) = u_{nl}(r) = Ae^{-\rho/2}\rho^{l+1}L_{n-l-1}^{2l+1}(\rho),$$

where

$$\rho = 2\kappa r \,.$$

Then we have

$$R_{nl}(r) = \frac{u_{nl}(r)}{r} = \frac{A}{r} e^{-\rho/2} \rho^{l+1} L_{n-l-1}^{2l+1}(\rho) = 2A\kappa e^{-\rho/2} \rho^{l} L_{n-l-1}^{2l+1}(\rho)$$

A is determined from the condition of normalization.

$$1 = \int_0^\infty [R_{nl}(r)]^2 r^2 dr = \frac{A^2}{2\kappa} \int_0^\infty e^{-\rho} \rho^{2l+2} [L_{n-l-1}^{2l+1}(\rho)]^2 d\rho, \qquad (2)$$

Here we use the formula:

$$\int_0^\infty e^{-\rho} \rho^{q+1} L_p^q(\rho) L_p^q(\rho) d\rho = \frac{(p+q)!}{p!} (2p+q+1)$$

Note that

$p = n - l - 1$, $q = 2l + 1$, $p + q = n + l$, and $2p + q + 1 = 2n$

Then we have

$$\int_0^\infty e^{-\rho} \rho^{2l+2} [L_{n-l-1}^{2l+1}(\rho)]^2 d\rho = \frac{(n+l)!}{(n-l-1)!} (2n)$$

Using this formula, Eq.(2) can be rewritten as

$$1 = \frac{A^2}{2\kappa} \frac{(n+l)!}{(n-l-1)!} (2n)$$

or

$$A = \frac{Z^{1/2}}{n a^{1/2}} \sqrt{\frac{(n-l-1)!}{(n+l)!}}$$

Thus we get

$$R_{nl}(r) = R_{nl}(\rho) = A_{nl} e^{-\rho/2} \rho^{l} L_{n-l-1}^{2l+1}(\rho)$$

with

$$A_{nl}=\frac{2Z^{3/2}}{n^2a^{3/2}}\sqrt{\frac{(n-l-1)!}{(n+l)!}}$$

((Note)) The final form of $R_{nl}(r)$ is as follows.

$$R_{nl}(r)=\frac{2Z^{3/2}}{n^2a^{3/2}}\sqrt{\frac{(n-l-1)!}{(n+l)!}}\exp(-\frac{Zr}{na})\left(\frac{2Z}{na}r\right)^l L_{n-l-1}^{2l+1}(\rho=\frac{2Z}{na}r)$$
$$=\sqrt{\frac{(n-l-1)!}{(n+l)!}}2^{l+1}a^{-l-3/2}Z^{l+3/2}n^{-l-2}r^l\exp(-\frac{Zr}{na})L_{n-l-1}^{2l+1}(\rho=\frac{2Z}{na}r)$$

since

$$\rho=\frac{2Z}{na}r$$

This function satisfies the differential equation

$$[\frac{d^2}{d\rho^2}+\frac{2}{\rho}\frac{d}{d\rho}+(-\frac{1}{4}+\frac{n}{\rho}-\frac{l(l+1)}{\rho^2})]R_{nl}(\rho)=0\,.$$

We also have

$$u_{nl}(r)=u_{nl}(\rho)=\frac{Z^{1/2}}{na^{1/2}}\sqrt{\frac{(n-l-1)!}{(n+l)!}}e^{-\rho/2}\rho^{l+1}L_{n-l-1}^{2l+1}(\rho)$$

13. Radial probability

The wave function $\psi_{nlm}(\mathbf{r})$ is normalized as

$$1=\int|\psi_{nlm}(\mathbf{r})|d\Omega r^2dr$$

where Ω is the solid angle and $d\Omega=\sin\theta d\theta d\phi$

$$\psi_{nlm}(\mathbf{r})=R_{nl}(r)Y_l^m(\theta,\phi)$$

and

$$1=\int drr^2|R_{nl}(r)|^2\int d\Omega|Y_l^m(\theta,\phi)|^2=\int drr^2|R_{nl}(r)|^2$$

where

$$\int d\Omega \left| Y_l^m(\theta,\phi) \right|^2 = 1$$

We define $P_r dr$ as

$$P_r dr = r^2 \mid R_{nl}(r) \mid^2 dr$$

Then the average $\langle r^s \rangle$ is defined by

$$< r^s >= \int_0^\infty dr r^2 [R_{nl}(r)]^2 r^s = \int_0^\infty dr r^{s+2} [R_{nl}(r)]^2$$

where

$$a = \frac{\hbar^2}{k\mu e^2}$$

$$E_n = -\frac{kZe^2}{2n^2 a}$$

The average $\langle r^s \rangle$ is obtained as

$$\langle r^{-4} \rangle = \frac{Z^4[3n^2 - l(l+1)]}{n^5 a^4 l(l+1/2)(l+1)[2l(l+1) - 3/2]}$$

$$\langle r^{-3} \rangle = \frac{Z^3}{n^4 a l(l+1/2)(l+1)}$$

$$\langle r^{-2} \rangle = \frac{Z^2}{n^3 a^2 (l+1/2)}$$

$$\langle r^{-1} \rangle = \frac{Z}{n^2 a}$$

$$\langle r^0 \rangle = 1$$

$$\langle r \rangle = \frac{a}{2Z}[3n^2 - l(l+1)]$$

$$\langle r^2 \rangle = \frac{a^2}{2Z^2} n^2 [5n^2 + 1 - 3l(l+1)]$$

$$\langle r^3 \rangle = \frac{a^3}{8Z^3} n^2 [35n^4 + 3(l-1)l(l+1)(l+2) - 5n^2(6l(l+1) - 5)]$$

14. Form of the wave function

We use the radial wave function as

$$R_{nl}(r) = R_{nl}(\rho) == \frac{2Z^{3/2}}{n^2 a^{3/2}} \sqrt{\frac{(n-l-1)!}{(n+l)!}} e^{-\rho/2} \rho^l L_{n-l-1}^{2l+1}(\rho)$$

where

$$\rho = 2\kappa r == \frac{2Zr}{na}$$

(a) Expression of $R_{nl}(r)$

n =1

$$R_{10}(r) = 2\left(\frac{Z}{a}\right)^{3/2} \exp(-\frac{Zr}{a})$$

n = 2

$$R_{20}(r) = \frac{1}{\sqrt{2}}\left(\frac{Z}{a}\right)^{3/2} (1 - \frac{Zr}{2a}) \exp(-\frac{Zr}{2a})$$

$$R_{21}(r) = \frac{1}{2\sqrt{6}}\left(\frac{Z}{a}\right)^{3/2} \frac{Zr}{a} \exp(-\frac{Zr}{2a})$$

n=3

$$R_{30}(r) = \frac{2}{3\sqrt{3}}\left(\frac{Z}{a}\right)^{3/2} (1 - \frac{2Zr}{3a} + \frac{2Z^2r^2}{27a^2}) \exp(-\frac{Zr}{3a})$$

$$R_{31}(r) = \frac{8}{27\sqrt{6}}\left(\frac{Z}{a}\right)^{3/2} \frac{Zr}{a}(1 - \frac{Zr}{6a}) \exp(-\frac{Zr}{3a})$$

$$R_{32}(r) = \frac{4}{81\sqrt{30}}\left(\frac{Z}{a}\right)^{3/2} \frac{Z^2r^2}{a^2} \exp(-\frac{Zr}{3a})$$

(b) Expression of $R_{nl}(\rho)$

n =1

$$R_{10}(\rho) = 2\left(\frac{Z}{a}\right)^{3/2} \exp(-\frac{\rho}{2})$$

$n = 2$

$$R_{20}(\rho) = \frac{1}{2\sqrt{2}}\left(\frac{Z}{a}\right)^{3/2} (2-\rho)\exp(-\frac{\rho}{2})$$

$$R_{21}(r) = \frac{1}{2\sqrt{6}}\left(\frac{Z}{a}\right)^{3/2} \rho\exp(-\frac{\rho}{2})$$

n=3

$$R_{30}(r) = \frac{1}{9\sqrt{3}}\left(\frac{Z}{a}\right)^{3/2} (6-6\rho+\rho^2)\exp(-\frac{\rho}{2})$$

$$R_{31}(r) = \frac{1}{9\sqrt{6}}\left(\frac{Z}{a}\right)^{3/2} \rho(4-\rho)\exp(-\frac{\rho}{2})$$

$$R_{32}(r) = \frac{1}{9\sqrt{30}}\left(\frac{Z}{a}\right)^{3/2} \rho^2\exp(-\frac{\rho}{2})$$

---

15. Plot of the probability of the wave function and the average radius

(i) $r^2[R_{nl}(r)]^2$ vs r/a, where a = 1 and Z =1.

(ii) $<r>= \frac{a}{2Z}[3n^2 - l(l+1)]$, where a = 1 and Z = 1.

For the 1s state,

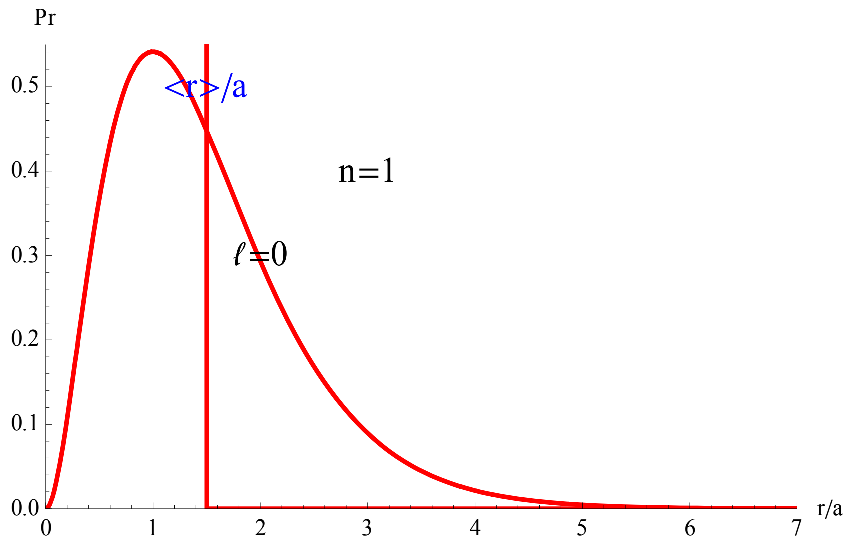


Fig. 1*s* (*n* = 1, *l* = 0). The straight line denotes the average value (<r>/a).

For the 2s, 2p states

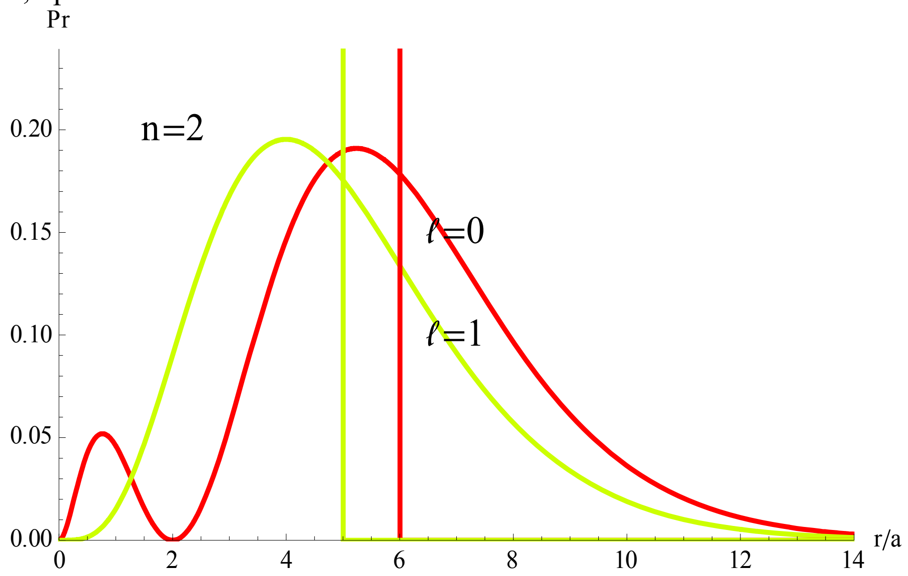


Fig. 2*s* (*n* = 2, *l* = 0). 2*p* (*n* = 2, *l* = 1). The straight lines denote the average value (<*r*>/a).

For the 3s, sp, and 3d states,

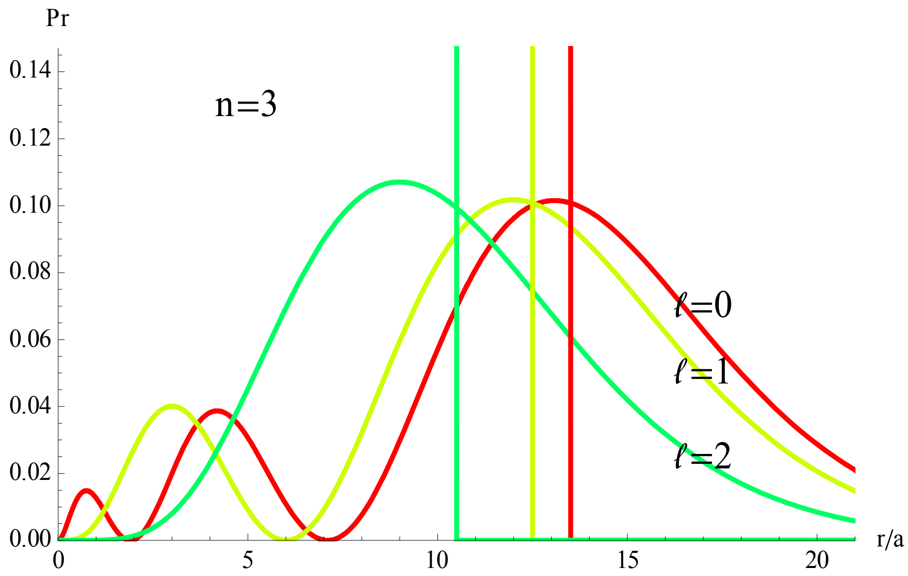


Fig. 3*s* (n = 3, l = 0). 3*p* (n = 3, l = 1). 3*d* (n = 3, l = 2). The straight lines denote the average value (<*r*>/a).

For the 4*s*, 4p, 4d, and 4f states,

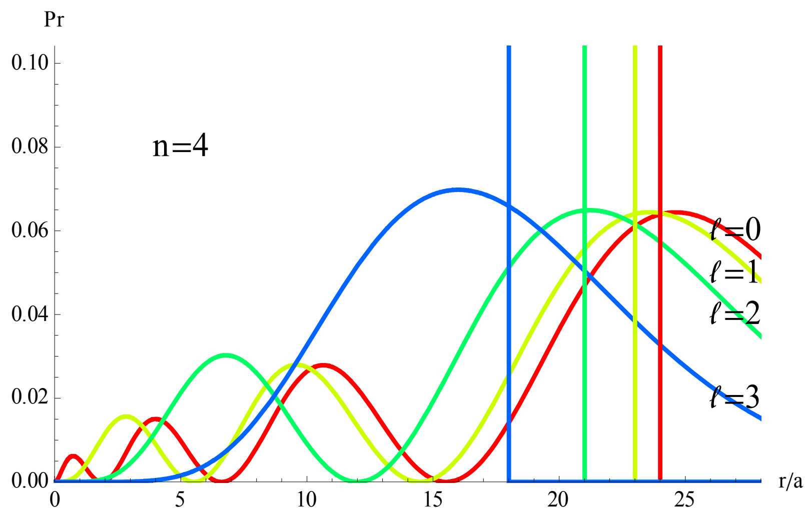


Fig. 4*s* (n = 4, l = 0). 4*p* (n = 4, l = 1). 4*d* (n = 4, l = 2). 4*f* (n = 4, l = 3). The straight lines denote the average value (<*r*>/a).

16. ContourPlot of the wavefunctions (Mathematica)

The probability function $|\psi_{nlm}(r,\theta,\phi)|^2$ is expressed using the spherical co-ordinate (r, θ, ϕ).

$$|\psi_{nlm}(r,\theta,\phi)|^2 = |R_{nl}(r)Y_l^m(\theta,\phi)|^2$$

where

$$R_{nl}(r) = \sqrt{\frac{(n-l-1)!}{(n+l)!}}2^{l+1}a^{-l-3/2}Z^{l+3/2}n^{-l-2}r^l \exp(-\frac{Zr}{na})L_{n-l-1}^{2l+1}(\rho = \frac{2Z}{na}r)$$

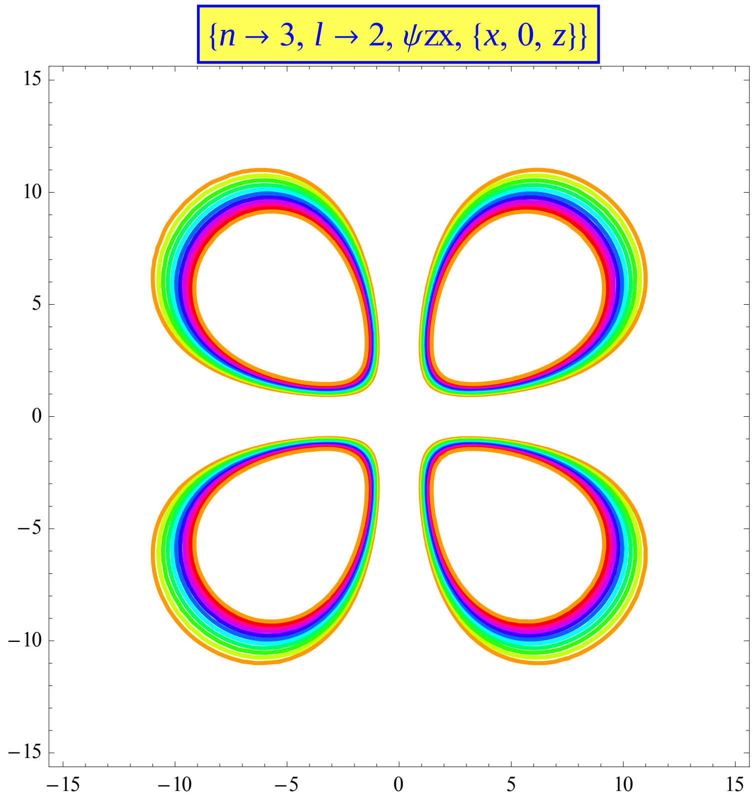
Using the relations

$$r = \sqrt{x^2+y^2+z^2}, \qquad \theta = \arccos\left(\frac{z}{\sqrt{x^2+y^2+z^2}}\right), \qquad \phi = \arctan(\frac{y}{x})$$

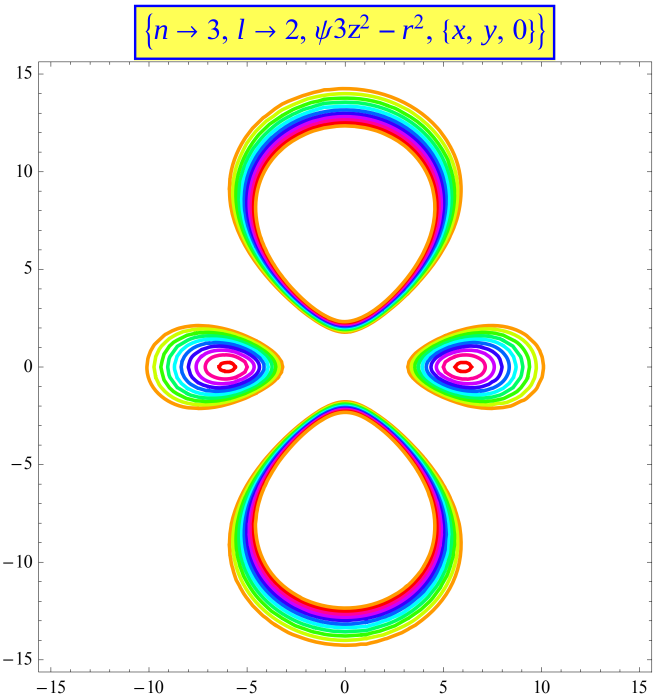
the function can be expressed by the Cartesian co-ordinate. Here we assume that

$Z = 1$, $\mu = m$ (mass of electron), and $a = a_0$ (Bohr radius).

(a) $d\gamma$ (*zx*) orbit



(b) $d\varepsilon\,(3z^2\text{-}r^2)$ orbit



APPENDIX

Vector analysis in the Spherical co-ordinates:

(a) $\nabla \psi$

The gradient is given by

$$\nabla \psi = \mathbf{e}_r \frac{\partial \psi}{\partial r} + \mathbf{e}_\theta \frac{1}{r}\frac{\partial \psi}{\partial \theta} + \mathbf{e}_\phi \frac{1}{r \sin\theta}\frac{\partial \psi}{\partial \phi}$$

where ψ is a scalar function of r, θ, and ϕ.

(b) $\nabla \cdot \mathbf{A}$

The divergence is given by

$$\nabla \cdot \mathbf{A} = \frac{1}{r^2}\frac{\partial}{\partial r}(r^2 A_r) + \frac{1}{r \sin\theta}\frac{\partial}{\partial \theta}(\sin\theta A_\theta) + \frac{1}{r\sin\theta}\frac{\partial}{\partial \phi}A_\phi$$

(c) $\nabla \times \mathbf{A}$

$\nabla \times \mathbf{A}$ is given by

$$\nabla \times \mathbf{A} = \frac{1}{h_r h_\theta h_\phi}\begin{vmatrix} h_r\mathbf{e}_r & h_\theta\mathbf{e}_\theta & h_\phi\mathbf{e}_\phi \\ \frac{\partial}{\partial r} & \frac{\partial}{\partial \theta} & \frac{\partial}{\partial \phi} \\ h_r A_r & h_\theta A_\theta & h_\phi A_\phi \end{vmatrix} = \frac{1}{r^2 \sin\theta}\begin{vmatrix} \mathbf{e}_r & r\mathbf{e}_\theta & r\sin\theta\mathbf{e}_\phi \\ \frac{\partial}{\partial r} & \frac{\partial}{\partial \theta} & \frac{\partial}{\partial \phi} \\ A_r & rA_\theta & r\sin\theta A_\phi \end{vmatrix}$$

(d) Laplacian

$$\nabla^2\psi = \frac{1}{h_r h_\theta h_\phi}[\frac{\partial}{\partial r}(\frac{h_\theta h_\phi}{h_r}\frac{\partial\psi}{\partial r}) + \frac{\partial}{\partial\theta}(\frac{h_\phi h_r}{h_\theta}\frac{\partial\psi}{\partial\theta}) + \frac{\partial}{\partial\phi}(\frac{h_r h_\theta}{h_\phi}\frac{\partial\psi}{\partial\phi})]$$
$$= \frac{1}{r^2\sin\theta}[\frac{\partial}{\partial r}(r^2\sin\theta\frac{\partial\psi}{\partial r}) + \frac{\partial}{\partial\theta}(\sin\theta\frac{\partial\psi}{\partial\theta}) + \frac{\partial}{\partial\phi}(\frac{1}{\sin\theta}\frac{\partial\psi}{\partial\phi})]$$

or

$$\nabla^2\psi = \frac{1}{r^2}\frac{\partial}{\partial r}(r^2\frac{\partial\psi}{\partial r}) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta\frac{\partial\psi}{\partial\theta}) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}$$

We can rewrite the first term of the right hand side as

$$\frac{1}{r^2}\frac{\partial}{\partial r}(r^2\frac{\partial\psi}{\partial r}) = \frac{1}{r}\frac{\partial}{\partial r^2}(r)$$

which can be useful in shortening calculations.

Note that we also use the expression for the operator

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}(r^2\frac{\partial}{\partial r}) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta\frac{\partial}{\partial\theta}) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2} =$$
$$= \frac{1}{r^2}\frac{\partial}{\partial r}(r^2\frac{\partial}{\partial r}) + \frac{1}{r^2}\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta\frac{\partial}{\partial\theta}) + \frac{1}{{}^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\}$$