

12b.57 atomic hydrogen according to wave mechanics in coordinate space -- extended cartesian coordinates

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> **restart**:

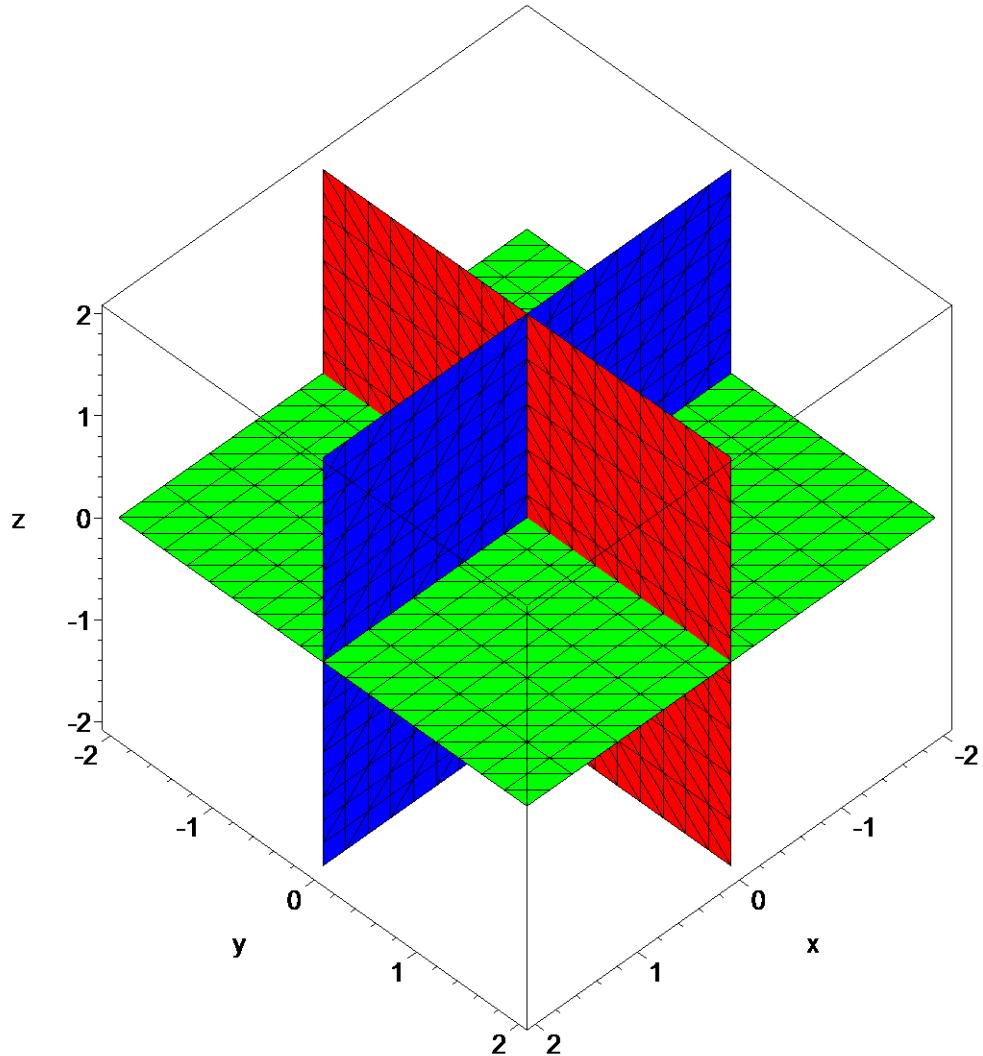
In section 12b.53a we demonstrate that a direct solution of Schroedinger's temporally dependent or independent equation is impractical in cartesian coordinates x, y, z because the

coulonbic potential energy proportional to $\frac{1}{r}$ or $\frac{1}{\sqrt{x^2 + y^2 + z^2}}$ prevents the separation of those

variables. Fowles (*American Journal of Physics* 30 (4) 308, 1962) sought to prove that, with amplitude function $\psi(x, y, z)$ as an extended function $f(x, y, z, r)$ of those four variables and with $r^2 = x^2 + y^2 + z^2$, a separation of variables was practicable. We remind that the surfaces of constant x, y, z are planes perpendicular to the corresponding axes of coordinates.

```
> plots[implicitplot3d]([x=0,y=0,z=0], x=-2..2, y=-2..2, z=-2..2,  
                          title="planes in cartesian coordinates -- x=0 red, y=0  
                          blue, z=0 green",  
                          axes=boxed,  
                          colour=[red,blue,green], titlefont=[TIMES,BOLD,14]);
```

planes in cartesian coordinates – x=0 red, y=0 blue, z=0 green



[>

[As

[> **r** := sqrt(x^2 + y^2 + z^2);

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

[> **Diff(r,x)** = **diff(r,x)**;

$$\frac{\partial}{\partial x} (\sqrt{x^2 + y^2 + z^2}) = \frac{x}{\sqrt{x^2 + y^2 + z^2}}$$

$$\text{so } \frac{\partial}{\partial x} r = \frac{x}{r}$$

[> **psi** := f(x,y,z,r);

$$\Psi := f(x, y, z, \sqrt{x^2 + y^2 + z^2})$$

> **Diff('psi', x) = convert(diff(psi, x), diff);**

$$\frac{\partial}{\partial x} \Psi = \left(\frac{\partial}{\partial x} f(x, y, z, tL) \right) \Big|_{tL=\sqrt{x^2+y^2+z^2}} + \frac{\left(\frac{\partial}{\partial tL} f(x, y, z, tL) \right) \Big|_{tL=\sqrt{x^2+y^2+z^2}} x}{\sqrt{x^2+y^2+z^2}}$$

which we rewrite as

> **Diff('psi', x) = diff(f(x, y, z, 'r'), x) +**
x*diff(f(x, y, z, 'r'), 'r')/r'; # **

$$\frac{\partial}{\partial x} \Psi = \left(\frac{\partial}{\partial x} f(x, y, z, r) \right) + \frac{x \left(\frac{\partial}{\partial r} f(x, y, z, r) \right)}{r}$$

For the second derivative,

> **Diff('psi', x\$2) = expand(convert(diff(psi, x\$2), diff));**

$$\frac{\partial^2}{\partial x^2} \Psi = \left(\frac{\partial^2}{\partial x^2} f(x, y, z, tL) \right) \Big|_{tL=\sqrt{x^2+y^2+z^2}} + \frac{2 \left(\frac{\partial^2}{\partial x \partial tL} f(x, y, z, tL) \right) \Big|_{tL=\sqrt{x^2+y^2+z^2}} x}{\sqrt{x^2+y^2+z^2}}$$

$$+ \frac{x^2 \left(\frac{\partial^2}{\partial tL^2} f(x, y, z, tL) \right) \Big|_{tL=\sqrt{x^2+y^2+z^2}}}{x^2+y^2+z^2} - \frac{\left(\frac{\partial}{\partial tL} f(x, y, z, tL) \right) \Big|_{tL=\sqrt{x^2+y^2+z^2}} x^2}{(x^2+y^2+z^2)^{(3/2)}}$$

$$+ \frac{\left(\frac{\partial}{\partial tL} f(x, y, z, tL) \right) \Big|_{tL=\sqrt{x^2+y^2+z^2}}}{\sqrt{x^2+y^2+z^2}}$$

which we rewrite as

> **dx2 := Diff('psi', x\$2) = Diff(f(x, y, z, 'r'), x\$2) +**
2*x*Diff(f(x, y, z, 'r'), x, 'r')/r'
+ x^2*Diff(f(x, y, z, 'r'), 'r', 'r')/r'^2 +
Diff(f(x, y, z, 'r'), 'r')/r'
- x^2*Diff(f(x, y, z, 'r'), 'r')/r'^3;

$$dx2 := \frac{\partial^2}{\partial x^2} \Psi = \left(\frac{\partial^2}{\partial x^2} f(x, y, z, r) \right) + \frac{2 x \left(\frac{\partial^2}{\partial r \partial x} f(x, y, z, r) \right)}{r} + \frac{x^2 \left(\frac{\partial^2}{\partial r^2} f(x, y, z, r) \right)}{r^2}$$

$$+ \frac{\frac{\partial}{\partial r} f(x, y, z, r)}{r} - \frac{x^2 \left(\frac{\partial}{\partial r} f(x, y, z, r) \right)}{r^3}$$

with nalogous expressions for $\frac{\partial^2}{\partial y^2} \Psi$ and $\frac{\partial^2}{\partial z^2} \Psi$.

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> dy2 := Diff('psi',y$2) = Diff(f(x,y,z,'r'),y$2) +
2*y*Diff(f(x,y,z,'r'),y,'r')/'r'
+ y^2*Diff(f(x,y,z,'r'),'r','r')/'r'^2 +
Diff(f(x,y,z,'r'),'r')/'r'
- y^2*Diff(f(x,y,z,'r'),'r')/'r'^3;

```

$$dy2 := \frac{\partial^2}{\partial y^2} \Psi = \left(\frac{\partial^2}{\partial y^2} f(x, y, z, r) \right) + \frac{2y \left(\frac{\partial^2}{\partial r \partial y} f(x, y, z, r) \right)}{r} + \frac{y^2 \left(\frac{\partial^2}{\partial r^2} f(x, y, z, r) \right)}{r^2}$$

$$+ \frac{\frac{\partial}{\partial r} f(x, y, z, r)}{r} - \frac{y^2 \left(\frac{\partial}{\partial r} f(x, y, z, r) \right)}{r^3}$$


```

> dz2 := Diff('psi',z$2) = Diff(f(x,y,z,'r'),z$2) +
2*z*Diff(f(x,y,z,'r'),z,'r')/'r'
+ z^2*Diff(f(x,y,z,'r'),'r','r')/'r'^2 +
Diff(f(x,y,z,'r'),'r')/'r'
- z^2*Diff(f(x,y,z,'r'),'r')/'r'^3;

```

$$dz2 := \frac{\partial^2}{\partial z^2} \Psi = \left(\frac{\partial^2}{\partial z^2} f(x, y, z, r) \right) + \frac{2z \left(\frac{\partial^2}{\partial r \partial z} f(x, y, z, r) \right)}{r} + \frac{z^2 \left(\frac{\partial^2}{\partial r^2} f(x, y, z, r) \right)}{r^2}$$

$$+ \frac{\frac{\partial}{\partial r} f(x, y, z, r)}{r} - \frac{z^2 \left(\frac{\partial}{\partial r} f(x, y, z, r) \right)}{r^3}$$

To form the laplacian operator as the sum of the three second derivatives, we add the right sides of the above three equations and collect the terms to obtain

```

> Diff('psi',x$2) + Diff('psi',y$2) + Diff('psi',z$2) =
Diff(f(x,y,z,'r'),'x','x')
+ Diff(f(x,y,z,'r'),'y','y') +
Diff(f(x,y,z,'r'),'z','z')
+ (2/'r')*(x*Diff(f(x,y,z,'r'),'x','r')
+ y*Diff(f(x,y,z,'r'),'y','r')
+ z*Diff(f(x,y,z,'r'),'z','r')) +
3*Diff(f(x,y,z,'r'),'r')/'r'
- Diff(f(x,y,z,'r'),'r')/'r';

```

$$\left(\frac{\partial^2}{\partial x^2} \Psi \right) + \left(\frac{\partial^2}{\partial y^2} \Psi \right) + \left(\frac{\partial^2}{\partial z^2} \Psi \right) = \left(\frac{\partial^2}{\partial x^2} f(x, y, z, r) \right) + \left(\frac{\partial^2}{\partial y^2} f(x, y, z, r) \right) + \left(\frac{\partial^2}{\partial z^2} f(x, y, z, r) \right)$$

$$+ \frac{2 \left(x \left(\frac{\partial^2}{\partial r \partial x} f(x, y, z, r) \right) + y \left(\frac{\partial^2}{\partial r \partial y} f(x, y, z, r) \right) + z \left(\frac{\partial^2}{\partial r \partial z} f(x, y, z, r) \right) \right)}{r}$$

$$+ \frac{2 \left(\frac{\partial}{\partial r} f(x, y, z, r) \right)}{r}$$

For the hydrogen atom as a central field for which potential energy V depends on only r , we assume that the part of $f(x, y, z, r)$ dependent on r is separable, so that $f(x, y, z, r) = F(x, y, z) R(r)$. The laplacian operator becomes accordingly,

$$\begin{aligned} > & \mathbf{R('r')} * (\mathbf{Diff(F(x, y, z), x\$2)} + \mathbf{Diff(F(x, y, z), y\$2)} + \\ & \mathbf{Diff(F(x, y, z), z\$2)}) \\ & + (2 / 'r') * \mathbf{Diff(R('r'), 'r')} * (\mathbf{x} * \mathbf{Diff(F(x, y, z), x)} + \\ & \mathbf{y} * \mathbf{Diff(F(x, y, z), y)} + \mathbf{z} * \mathbf{Diff(F(x, y, z), z)}) \\ & + \mathbf{F(x, y, z)} * \mathbf{Diff(R('r'), 'r', 'r')} + \\ & 2 * \mathbf{F(x, y, z)} * \mathbf{Diff(R('r'), 'r')} / 'r'; \\ & \mathbf{R(r)} \left(\left(\frac{\partial^2}{\partial x^2} F(x, y, z) \right) + \left(\frac{\partial^2}{\partial y^2} F(x, y, z) \right) + \left(\frac{\partial^2}{\partial z^2} F(x, y, z) \right) \right) \\ & + \frac{2 \left(\frac{d}{dr} R(r) \right) \left(x \left(\frac{\partial}{\partial x} F(x, y, z) \right) + y \left(\frac{\partial}{\partial y} F(x, y, z) \right) + z \left(\frac{\partial}{\partial z} F(x, y, z) \right) \right)}{r} \\ & + F(x, y, z) \left(\frac{d^2}{dr^2} R(r) \right) + \frac{2 F(x, y, z) \left(\frac{d}{dr} R(r) \right)}{r} \end{aligned}$$

and Schroedinger's temporally independent equation incorporating a term for the electrostatic potential energy, after division through by $F(x, y, z)$, becomes

$$\begin{aligned} > & \mathbf{R('r')} * (\mathbf{Diff(F(x, y, z), x\$2)} + \mathbf{Diff(F(x, y, z), y\$2)} + \\ & \mathbf{Diff(F(x, y, z), z\$2)}) \\ & + (2 / 'r') * \mathbf{Diff(R('r'), 'r')} * (\mathbf{x} * \mathbf{Diff(F(x, y, z), x)} + \\ & \mathbf{y} * \mathbf{Diff(F(x, y, z), y)} + \mathbf{z} * \mathbf{Diff(F(x, y, z), z)}) \\ & + \mathbf{F(x, y, z)} * \mathbf{Diff(R('r'), 'r', 'r')} + \\ & 2 * \mathbf{F(x, y, z)} * \mathbf{Diff(R('r'), 'r')} / 'r' + \\ & 8 * \mathbf{Pi}^2 * \mathbf{mu/h^2} * (\mathbf{E - V('r')}) * \mathbf{R('r')} = 0; \\ & \mathbf{R(r)} \left(\left(\frac{\partial^2}{\partial x^2} F(x, y, z) \right) + \left(\frac{\partial^2}{\partial y^2} F(x, y, z) \right) + \left(\frac{\partial^2}{\partial z^2} F(x, y, z) \right) \right) \\ & + \frac{2 \left(\frac{d}{dr} R(r) \right) \left(x \left(\frac{\partial}{\partial x} F(x, y, z) \right) + y \left(\frac{\partial}{\partial y} F(x, y, z) \right) + z \left(\frac{\partial}{\partial z} F(x, y, z) \right) \right)}{r} \\ & + F(x, y, z) \left(\frac{d^2}{dr^2} R(r) \right) + \frac{2 F(x, y, z) \left(\frac{d}{dr} R(r) \right)}{r} + \frac{8 \pi^2 \mu (E - V(r)) R(r)}{h^2} = 0 \end{aligned}$$

We seek solutions for which $F(x, y, z)$ satisfies Laplace's equation in three spatial dimensions.

$$\left(\frac{\partial^2}{\partial x^2} F(x, y, z) \right) + \left(\frac{\partial^2}{\partial y^2} F(x, y, z) \right) + \left(\frac{\partial^2}{\partial z^2} F(x, y, z) \right) = 0$$

In section 7.401 we show that $F_l(x, y, z) = (a x + b y + c z)^l$ is a solution of Laplace's equation providing that $a^2 + b^2 + c^2 = 0$, which implies that at least one coefficient a, b, c must be complex, and that l must be an integer for F_l to be singly valued. In section 7.401 we derive further that

$$x \left(\frac{\partial}{\partial x} F_l(x, y, z) \right) + y \left(\frac{\partial}{\partial y} F_l(x, y, z) \right) + z \left(\frac{\partial}{\partial z} F_l(x, y, z) \right) = l F_l(x, y, z)$$

The Schrödinger equation above consequently reduces to this radial equation,

```
> Diff(R('r'), 'r', 'r') + 2*(l+1)/'r'*Diff(R('r'), 'r') +  
  8*Pi^2*mu/h^2*(E-V('r'))*R('r') = 0;
```

$$\left(\frac{d^2}{dr^2} R(r) \right) + \frac{2(l+1) \left(\frac{d}{dr} R(r) \right)}{r} + \frac{8\pi^2 \mu (E - V(r)) R(r)}{h^2} = 0$$

For an atom of atomic number Z with one electron, $V(r) = -\frac{Z e^2}{4\pi\epsilon_0 r}$. Following Fowles, we

introduce dimensionless variable $\rho = \frac{r}{a_\mu}$ and parameter $\lambda = \frac{2\pi Z e^2 \sqrt{\mu}}{h \sqrt{-2 E}}$ for eigenvalues in which

Bohr radius $a_\mu = \frac{h^2 \lambda}{8\pi^2 Z \mu e^2}$ with $a_\mu = \frac{m_e a_0}{\mu}$ for effective reduced mass μ of the atomic system;

setting $R(\rho) = e^{\left(-\frac{\rho}{2}\right)} L(\rho)$, the preceding equation becomes

```
> rho*Diff(L(rho), rho$2) + (2*(l+1)-rho)*Diff(L(rho), rho) + (lambda-l-1)*L(rho)=0;
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$$\rho \left(\frac{d^2}{d\rho^2} L(\rho) \right) + (2l + 2 - \rho) \left(\frac{d}{d\rho} L(\rho) \right) + (\lambda - l - 1) L(\rho) = 0$$

This equation has well behaved solutions in the form of associated Laguerre polynomials

$(L_k^{(2l+1)})(\rho)$ which $\lambda = n = k + l + 1$, a positive integer. The eigenvalues E are thus given by

$E_n = -\frac{2\pi^2 Z^2 \mu e^4}{h^2 n^2}$, as derived in section 12b.53. The corresponding eigenfunctions are expressed as

```
> psi[n,l](x,y,z,'r') := F[l](x,y,z)*R[n,l]('r');
```

$$\Psi_{n,l}(x, y, z, r) := F_l(x, y, z) R_{n,l}(r)$$

expanded into this formula containing only cartesian coordinates as variables, with several parameters or constants. As $R_{n,l}(r)$ is essentially the same here as in spherical polar coordinates, we include the normalizing factor for that radial part from section 12b.53a.

```
> psi[k,l](x,y,z) :=  
  (1/a[mu]/k!* (k+2*l+2)! * (k+2*l+2))^(1/2) / ((k+l+1)*(2+2*l)!) * (a*x
```

$+b*y+c*z)^l$

$*exp(-sqrt(x^2+y^2+z^2)/(2*a[mu]*(k+l+1)))*LaguerreL(k, 2*l+1, sqrt(x^2+y^2+z^2)/a[mu])/((k+l)!*(-1)^(2*l+1));$

$$\Psi_{k,l}(x, y, z) := \sqrt{\frac{(k+2l+2)!}{a_\mu k!}} \frac{(ax + by + cz)^l}{\text{LaguerreL}\left(k, 2l+1, \frac{\sqrt{x^2+y^2+z^2}}{a_\mu}\right)} e^{\left(-\frac{1}{2} \frac{\sqrt{x^2+y^2+z^2}}{a_\mu^{(k+l+1)}}\right)}$$

Proceeding to consider angular momentum M , we have, with $I = \sqrt{-1}$,

> $M[z]*psi = -I*h*(x*Diff(psi, y)-y*Diff(psi, x));$

$$M_z \psi = -I h \left(x \left(\frac{\partial}{\partial y} \psi \right) - y \left(\frac{\partial}{\partial x} \psi \right) \right)$$

> $M[x]*psi = -I*h*(y*Diff(psi, z)-z*Diff(psi, y));$

$$M_x \psi = -I h \left(y \left(\frac{\partial}{\partial z} \psi \right) - z \left(\frac{\partial}{\partial y} \psi \right) \right)$$

> $M[y]*psi = -I*h*(z*Diff(psi, x)-x*Diff(psi, z));$

$$M_y \psi = -I h \left(z \left(\frac{\partial}{\partial x} \psi \right) - x \left(\frac{\partial}{\partial z} \psi \right) \right)$$

Taking $\Psi_{n,l}(x, y, z, r) := F_l(x, y, z) R_{n,l}(r)$ as above and making use of the derivative relation marked with ** above, we obtain

> $M[z]*F[1](x, y, z) = -I*(h/(2*Pi))*(x*Diff(F[1](x, y, z), y)-y*Diff(F[1](x, y, z), y));$

$$M_z F_l(x, y, z) = \frac{-\frac{1}{2} I h \left(x \left(\frac{\partial}{\partial y} F_l(x, y, z) \right) - y \left(\frac{\partial}{\partial y} F_l(x, y, z) \right) \right)}{\pi}$$

from which $R(r)$ has cancelled out because $R(r)$ commutes with angular momentum M . As $R(r)$ commutes also with $M^2 = M_x^2 + M_y^2 + M_z^2$, from the above formulae we obtain, subject to $a^2 + b^2 + c^2 = 0$,

> $M^2*F[1](x, y, z) = -(h/(2*Pi))^2 * ((x*Diff(F[1](x, y, z), y)-y*Diff(F[1](x, y, z), x))^2$

$$\begin{aligned} &+ \\ &(y*Diff(F[1](x, y, z), z)-z*Diff(F[1](x, y, z), y))^2 \\ &+ \\ &(z*Diff(F[1](x, y, z), x)-x*Diff(F[1](x, y, z), z))^2; \end{aligned}$$

$$M^2 F_l(x, y, z) = -\frac{1}{4} h^2 \left(\left(x \left(\frac{\partial}{\partial y} F_l(x, y, z) \right) - y \left(\frac{\partial}{\partial x} F_l(x, y, z) \right) \right)^2 \right)$$

$$+ \left(y \left(\frac{\partial}{\partial z} F_l(x, y, z) \right) - z \left(\frac{\partial}{\partial y} F_l(x, y, z) \right) \right)^2 + \left(z \left(\frac{\partial}{\partial x} F_l(x, y, z) \right) - x \left(\frac{\partial}{\partial z} F_l(x, y, z) \right) \right)^2 \Bigg) / \pi^2$$

which becomes

$$> M^2 * F[l](x, y, z) = (h / (2 * Pi))^2 * l * (l + 1) * F[l](x, y, z);$$

$$M^2 F_l(x, y, z) = \frac{1}{4} \frac{h^2 l(l+1) F_l(x, y, z)}{\pi^2}$$

so that the eigenvalues of M^2 are $\left(\frac{h}{2\pi}\right)^2 l(l+1)$, with no preferred axis. From the formula for

$M_z \psi$ above, we obtain

$$> M[z] * F[l](x, y, z) =$$

$$-I * (h / (2 * Pi)) * l * ((b * x - a * y) / (a * x + b * y + c * z)) * F[l](x, y, z);$$

$$M_z F_l(x, y, z) = \frac{-\frac{1}{2} I h l (-a y + b x) F_l(x, y, z)}{\pi (a x + b y + c z)}$$

which implies that $F_l(x, y, z)$ lacks a definite value of M_z . When we consider that $a^2 + b^2 + c^2 = 0$, this condition is satisfied on defining a, b, c in terms of two arbitrary complex numbers u, v as follows.

$$\begin{aligned} &> a = u^2 - v^2; \\ &\quad b = -I * (u^2 + v^2); \\ &\quad c = -2 * u * v; \end{aligned}$$

$$a = u^2 - v^2$$

$$b = -I(u^2 + v^2)$$

$$c = -2 u v$$

With these definitions,

$$> F[l](x, y, z) = ((u^2 - v^2) * x - I * (u^2 + v^2) * y - 2 * u * v * z)^l;$$

$$F_l(x, y, z) = ((u^2 - v^2) x - (u^2 + v^2) y I - 2 u v z)^l$$

$$> lhs(%) = expand(rhs(%));$$

$$F_l(x, y, z) = (u^2 x - v^2 x - y u^2 I - y v^2 I - 2 u v z)^l$$

which on rearrangement becomes

$$> F[l](x, y, z) = (u^2 * (x - I * y) - v^2 * (x + I * y) - 2 * u * v * z)^l;$$

$$F_l(x, y, z) = (u^2 (x - y I) - v^2 (x + y I) - 2 u v z)^l$$

Expressed in this way, which is intended to produce amplitude functions of which the plots of their surfaces at selected values of ψ maximally resemble the corresponding surfaces of $\Psi_{k,l,m}(r, \theta, \phi)$ in spherical polar coordinates, $F_l(x, y, z)$ is an homogeneous polynomial of degree $2l$ in u and v that contains $2l+1$ terms; their coefficients are polynomials Q of degree l in x, y, z :

$$> F[l](x, y, z) = Sum(u^(l-m) * v^(l+m) * Q[l, m](x, y, z), m=-l..l);$$

$$F_l(x, y, z) = \sum_{m=-l}^l u^{(l-m)} v^{(l+m)} Q_{l,m}(x, y, z)$$

[For example, for $l = 0$ we have

$$> F[0](x, y, z) = (u^2 * (x - I*y) - v^2 * (x + I*y) - 2*u*v*z)^0;$$

$$F_0(x, y, z) = 1$$

[which is a trivial case,

$$> Q[0, 0](x, y, z) := 1;$$

$$Q_{0,0}(x, y, z) := 1$$

[leaving only the radial part of the amplitude function. For $l = 1$,

$$> F[1](x, y, z) = (u^2 * (x - I*y) - v^2 * (x + I*y) - 2*u*v*z)^1;$$

$$F_1(x, y, z) = u^2(x - yI) - v^2(x + yI) - 2uvz$$

$$> F[1](x, y, z) := \text{collect}(\text{expand}((u^2 * (x - I*y) - v^2 * (x + I*y) - 2*u*v*z)^1), [u, v]);$$

$$F_1(x, y, z) := u^2(x - yI) - 2uvz + (-yI - x)v^2$$

[the coefficient of uv is real but the coefficients of u^2 and v^2 are complex.

$$> Q[1, -1](x, y, z) := \text{factor}(\text{coeff}(F[1](x, y, z), u^2));$$

$$Q[1, 0](x, y, z) := \text{factor}(\text{coeff}(F[1](x, y, z)/u, v));$$

$$Q[1, 1](x, y, z) := \text{factor}(\text{coeff}(F[1](x, y, z), v^2));$$

$$Q_{1,-1}(x, y, z) := x - yI$$

$$Q_{1,0}(x, y, z) := -2z$$

$$Q_{1,1}(x, y, z) := -yI - x$$

[For $l = 2$, we have

$$> F[2](x, y, z) = (u^2 * (x - I*y) - v^2 * (x + I*y) - 2*u*v*z)^2;$$

$$F_2(x, y, z) = (u^2(x - yI) - v^2(x + yI) - 2uvz)^2$$

$$> F[2](x, y, z) := \text{collect}(\text{expand}(\text{rhs}(%)), [u, v]);$$

$$F_2(x, y, z) := (-2Ixy + x^2 - y^2)u^4 + (4Iyz - 4xz)v^4 + (-2x^2 - 2y^2 + 4z^2)v^2u^2$$

$$+ (4Iyz + 4xz)v^3u + (2Ixy + x^2 - y^2)v^4$$

[according to which

$$> Q[2, -2](x, y, z) := \text{factor}(\text{coeff}(F[2](x, y, z), u^4));$$

$$Q[2, -1](x, y, z) := \text{factor}(\text{coeff}(F[2](x, y, z)/v, u^3));$$

$$Q[2, 0](x, y, z) := \text{factor}(\text{coeff}(F[2](x, y, z)/v^2, u^2));$$

$$Q[2, 1](x, y, z) := \text{factor}(\text{coeff}(F[2](x, y, z)/u, v^3));$$

$$Q[2, 2](x, y, z) := \text{factor}(\text{coeff}(F[2](x, y, z), v^4));$$

$$Q_{2,-2}(x, y, z) := (yI - x)^2$$

$$Q_{2,-1}(x, y, z) := 4(yI - x)z$$

$$Q_{2,0}(x, y, z) := -2x^2 - 2y^2 + 4z^2$$

$$Q_{2,1}(x, y, z) := 4(x + yI)z$$

$$Q_{2,2}(x, y, z) := (x + yI)^2$$

For $l = 3$, we have

$$> \mathbf{F[3](x,y,z)} = (\mathbf{u}^2 * (\mathbf{x}-\mathbf{I}*y) - \mathbf{v}^2 * (\mathbf{x}+\mathbf{I}*y) - 2*\mathbf{u}*\mathbf{v}*\mathbf{z})^3;$$

$$F_3(x, y, z) = (u^2(x - yI) - v^2(x + yI) - 2uvz)^3$$

$$> \mathbf{F[3](x,y,z)} := \mathbf{collect(expand(rhs(%)), [u,v])};$$

$$\begin{aligned} F_3(x, y, z) := & (-3Ix^2y + y^3I + x^3 - 3xy^2)u^6 + (12Ix y z - 6x^2z + 6y^2z)v u^5 \\ & + (3Ix^2y + 3Iy^3 - 12Iyz^2 - 3x^3 - 3xy^2 + 12xz^2)v^2 u^4 + (12x^2z + 12y^2z - 8z^3)v^3 u^3 \\ & + (3Ix^2y + 3Iy^3 - 12Iyz^2 + 3x^3 + 3xy^2 - 12xz^2)v^4 u^2 \\ & + (-12Ix y z - 6x^2z + 6y^2z)v^5 u + (-3Ix^2y + y^3I - x^3 + 3xy^2)v^6 \end{aligned}$$

according to which

$$\begin{aligned} > \mathbf{Q[3,-3](x,y,z)} &:= \mathbf{factor(coeff(F[3](x,y,z), u^6))}; \\ \mathbf{Q[3,-2](x,y,z)} &:= \mathbf{factor(coeff(F[3](x,y,z)/v, u^5))}; \\ \mathbf{Q[3,-1](x,y,z)} &:= \mathbf{factor(coeff(F[3](x,y,z)/v^2, u^4))}; \\ \mathbf{Q[3,0](x,y,z)} &:= \mathbf{factor(coeff(F[3](x,y,z)/v^3, u^3))}; \\ \mathbf{Q[3,1](x,y,z)} &:= \mathbf{factor(coeff(F[3](x,y,z)/u^2, v^4))}; \\ \mathbf{Q[3,2](x,y,z)} &:= \mathbf{factor(coeff(F[3](x,y,z)/u, v^5))}; \\ \mathbf{Q[3,-3](x,y,z)} &:= \mathbf{factor(coeff(F[3](x,y,z), v^6))}; \end{aligned}$$

$$Q_{3,-3}(x, y, z) := -(yI - x)^3$$

$$Q_{3,-2}(x, y, z) := -6z(yI - x)^2$$

$$Q_{3,-1}(x, y, z) := 3(x^2 + y^2 - 4z^2)(yI - x)$$

$$Q_{3,0}(x, y, z) := 4z(3x^2 + 3y^2 - 2z^2)$$

$$Q_{3,1}(x, y, z) := 3(x^2 + y^2 - 4z^2)(x + yI)$$

$$Q_{3,2}(x, y, z) := -6z(x + yI)^2$$

$$Q_{3,-3}(x, y, z) := -(x + yI)^3$$

Because u and v are arbitrary complex numbers, each $Q_{l,m}$ is a solution of Laplace's equation and, according to the assumptions above, are hence suitable eigenfunctions for the solution of the hydrogen atom in wave mechanics in cartesian coordinates. In general,

$$> -\mathbf{I} * (\mathbf{x} * \mathbf{Diff(Q[1,m],y)} - \mathbf{y} * \mathbf{Diff(Q[1,m],x)}) = \mathbf{m} * \mathbf{Q[1,m]};$$

$$-I\left(x\left(\frac{\partial}{\partial y} Q_{l,m}\right) - y\left(\frac{\partial}{\partial x} Q_{l,m}\right)\right) = m Q_{l,m}$$

in which m takes values of integers from $-l$ to l . In this representation in terms of $Q_{l,m}$ according to the choice of conditions above, component z of angular momentum, i.e. M_z , has eigenvalue $\frac{m\ h}{2\pi}$

. The total amplitude function, unnormalized, is thus

```
> psi := (k,l,m) ->
  (1/a[mu]/k!* (k+2*l+2)! * (k+2*l+2))^^(1/2) / ((k+l+1)*(2+2*l)!) * Q[l,
m] (x,y,z)
  *exp(-sqrt(x^2+y^2+z^2)/(2*a[mu]*(k+l+1)))
```

*LaguerreL(**k**, 2*l+1, (**x**^2+**y**^2+**z**^2)^(1/2)/a[**mu**]) / ((k+l)!*(-1)^l);

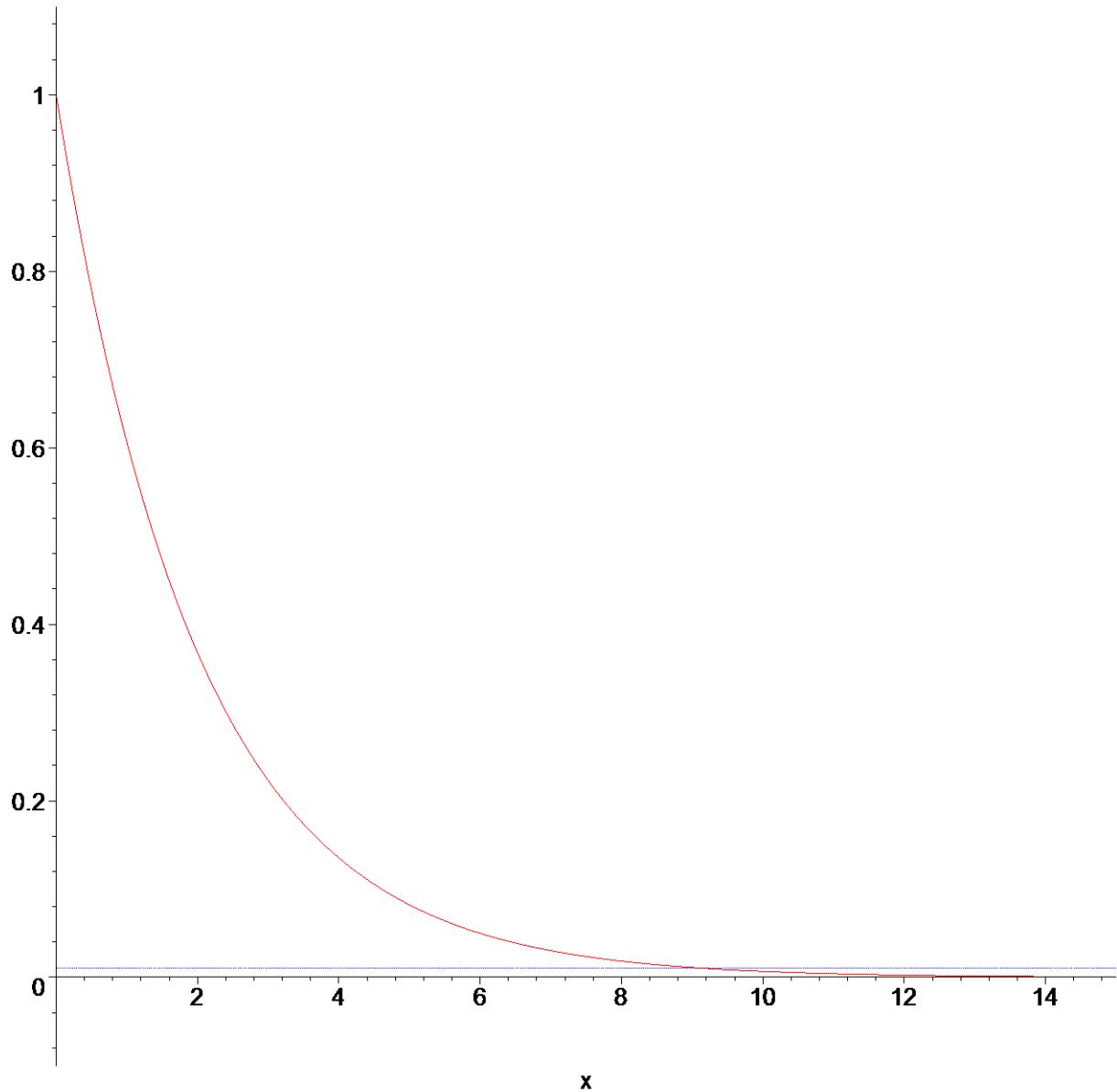
$$\psi := (k, l, m) \rightarrow \sqrt{\frac{(k + 2l + 2)! (k + 2l + 2)}{a_{\mu} k!}} Q_{l,m}(x, y, z) e^{-\frac{\sqrt{x^2 + y^2 + z^2}}{a_{\mu} (k + l + 1)}}$$

$$\text{LaguerreL}\left(k, 2l + 1, \frac{\sqrt{x^2 + y^2 + z^2}}{a_{\mu}}\right) / ((k + l + 1)(2 + 2l)!(k + l)!(-1)^l)$$

We plot a few surfaces, according to the same criteria as in section 12b.53a, of amplitude functions directly in these cartesian coordinates according to the above formula that is modified from Fowles, first $\psi_{0,0,0}(x, y, z)$. The scale of length in these plots is Bohr radius $a_{\mu} \sim a_0$.

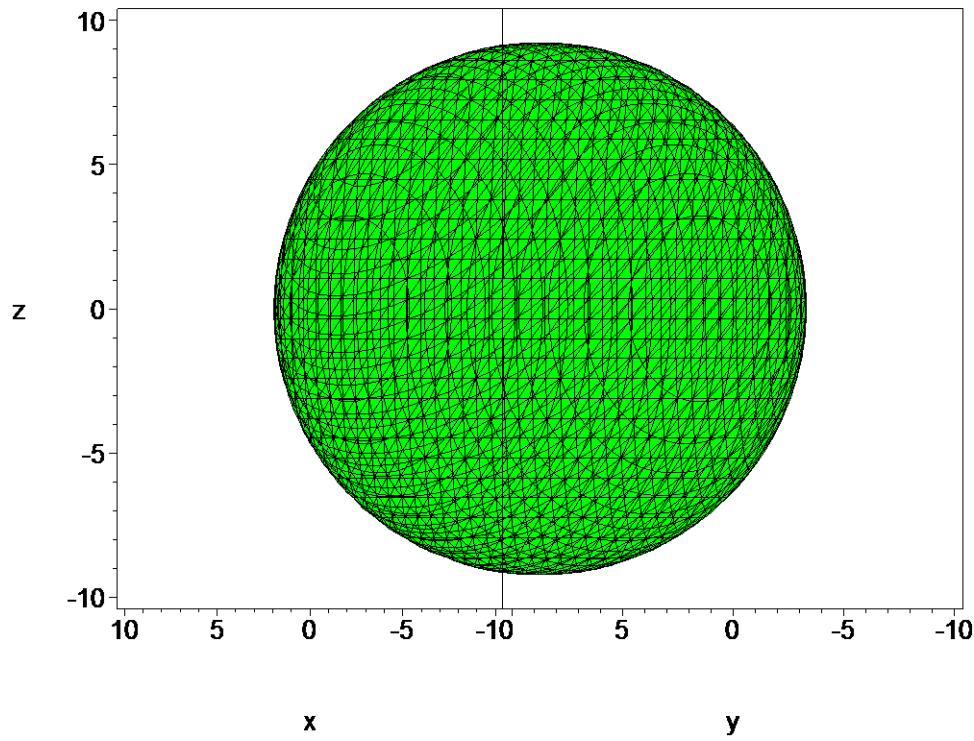
```
> 'psi[0,0,0] (x,y,z)' = simplify(psi(0,0,0));
   $\psi_{0,0,0}(x, y, z) = \sqrt{\frac{1}{a_{\mu}}} e^{-\frac{\sqrt{x^2 + y^2 + z^2}}{a_{\mu}}}$ 
> plot([simplify(eval(psi(0,0,0), [a[mu]=1, y=0, z=0])), 0.01], x=0..15, -0.1..1.1,
  colour=[red,blue], linestyle=[1,2],
  titlefont=[TIMES,BOLD,14],
  title="amplitude function psi(0,0,0) in direction x",
  titlefont=[TIMES,BOLD,14]);
```

amplitude function $\psi(0,0,0)$ in direction x



```
>  
> plots[implicitplot3d](eval(simplify(psi(0,0,0))), a[mu]=1)=0.01,  
                 x=-10..10, y=-10..10, z=-10..10, colour=green,  
grid=[30,30,30],  
      axes=boxed, labels=["x","y","z"], title="amplitude function  
psi(0,0,0)",  
      scaling=constrained, titlefont=[TIMES,BOLD,14],  
orientation=[140,90]);
```

amplitude function $\psi(0,0,0)$

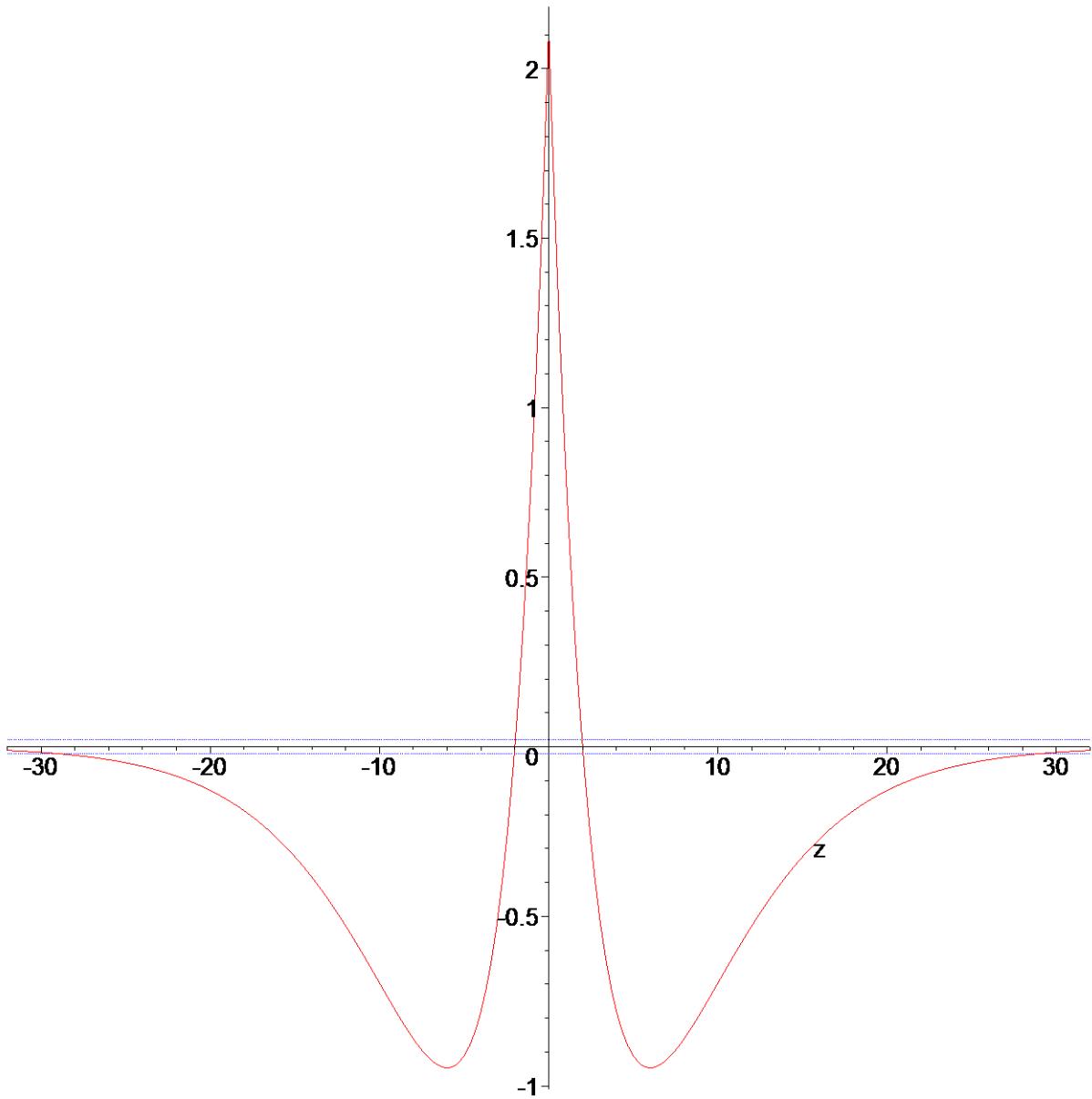


```
>
> 'psi[1,0,0](x,y,z)' = simplify(psi(1,0,0));

$$\psi_{1,0,0}(x, y, z) = -\frac{3}{4} \sqrt{\frac{1}{a_\mu}} e^{\left(-\frac{1}{4} \frac{\sqrt{x^2 + y^2 + z^2}}{a_\mu}\right)} (-2 a_\mu + \sqrt{x^2 + y^2 + z^2})$$

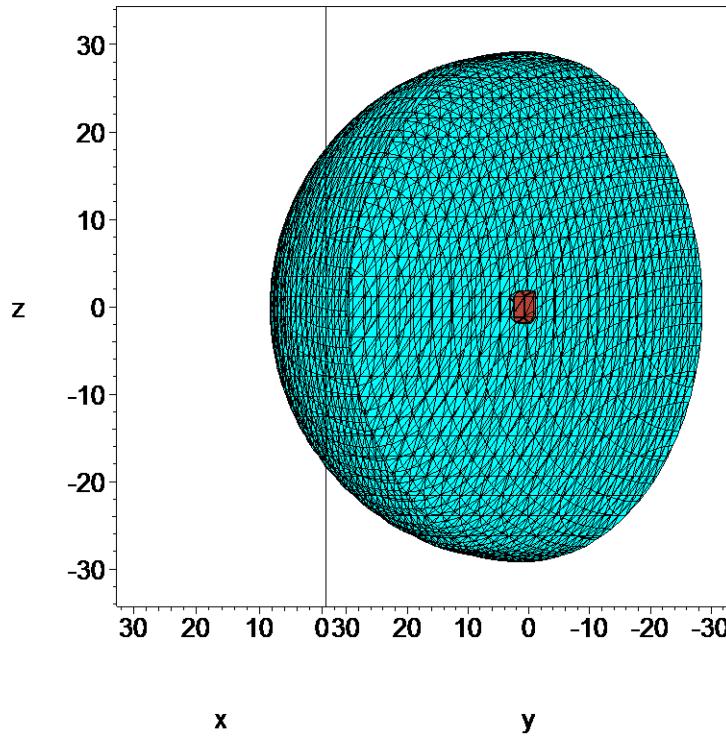
> plot([simplify(eval(psi(1,0,0), [a[mu]=1, x=0, y=0])), 0.02,
-0.02], z=-32..32,
colour=[red, blue, blue], linestyle=[1,2,2],
titlefont=[TIMES,BOLD,14],
title="amplitude function psi(1,0,0) in direction z");
```

amplitude function $\psi(1,0,0)$ in direction z



```
>
> plots[implicitplot3d]([eval(simplify(psi(1,0,0))),a[mu]=1)=0.02,
  eval(simplify(psi(1,0,0)),a[mu]=1)=-0.02], x=-0..32,
  y=-32..32,
  z=-33..33, colour=[red,blue], grid=[30,30,30],
  scaling=constrained,
  axes=boxed, labels=["x","y","z"], title="amplitude function
psi(1,0,0)",
  titlefont=[TIMES,BOLD,14], orientation=[134,90],
  colour=[brown,cyan]);
```

amplitude function psi(1,0,0)

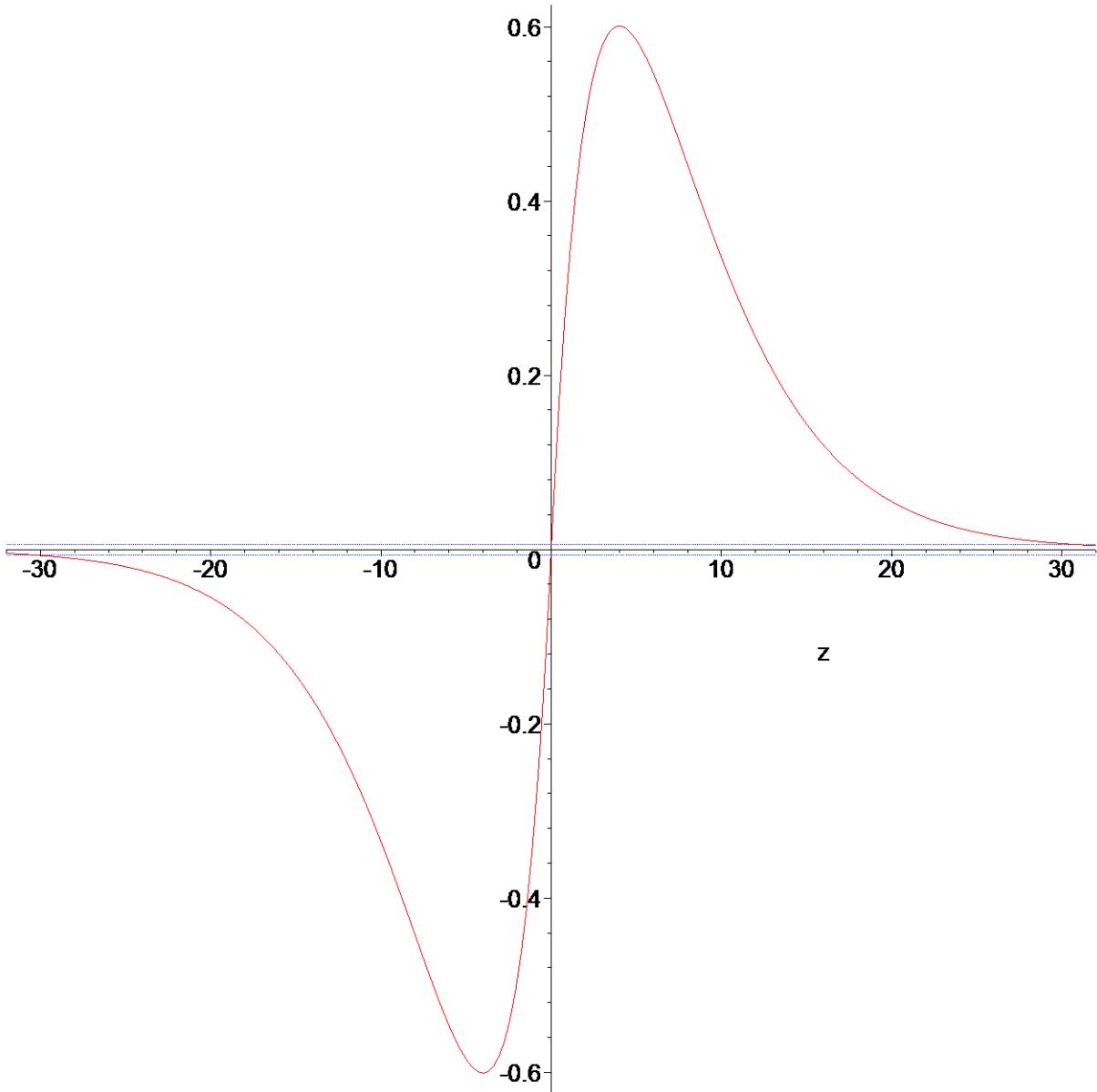


```
>
> 'psi[0,1,0](x,y,z)' = simplify(psi(0,1,0));

$$\Psi_{0,1,0}(x,y,z) = \frac{1}{6} \sqrt{6} \sqrt{\frac{1}{a_\mu}} z e^{\left(-\frac{1}{4} \frac{\sqrt{x^2 + y^2 + z^2}}{a_\mu}\right)}$$

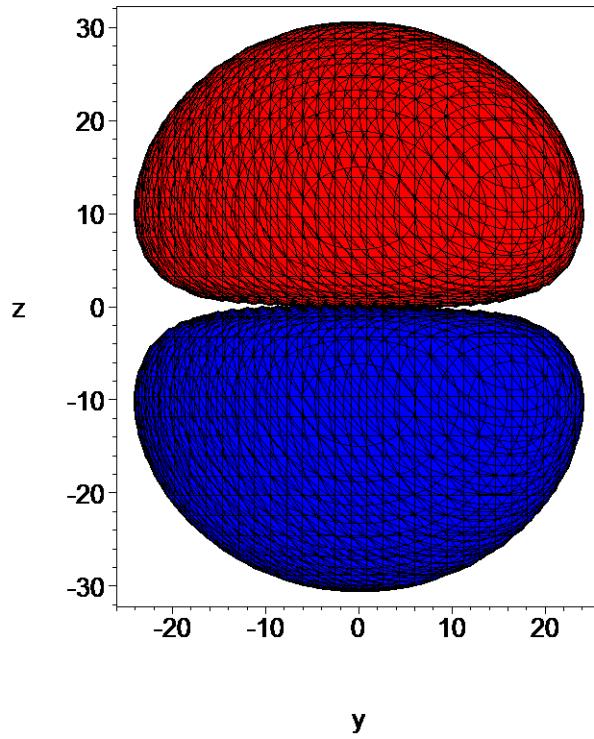
> plot([simplify(eval(psi(0,1,0), [a[mu]=1, x=0, y=0])), 0.006,
-0.006], z=-32..32,
colour=[red, blue, blue], linestyle=[1,2,2],
titlefont=[TIMES,BOLD,14],
title="amplitude function psi(0,1,0) in direction z");
```

amplitude function $\psi(0,1,0)$ in direction z



```
>  
> plots[implicitplot3d]([eval(simplify(psi(0,1,0))),a[mu]=1)=0.006  
'  
    eval(simplify(psi(0,1,0)),a[mu]=1)=-0.006], x=-25..25,  
y=-25..25,  
    z=-31..31, colour=[red,blue], grid=[30,30,30],  
scaling=constrained,  
    axes=boxed, labels=["x","y","z"], title="amplitude function  
psi(0,1,0)",  
    titlefont=[TIMES,BOLD,14], orientation=[0,90],  
colour=[red,blue]);
```

amplitude function psi(0,1,0)

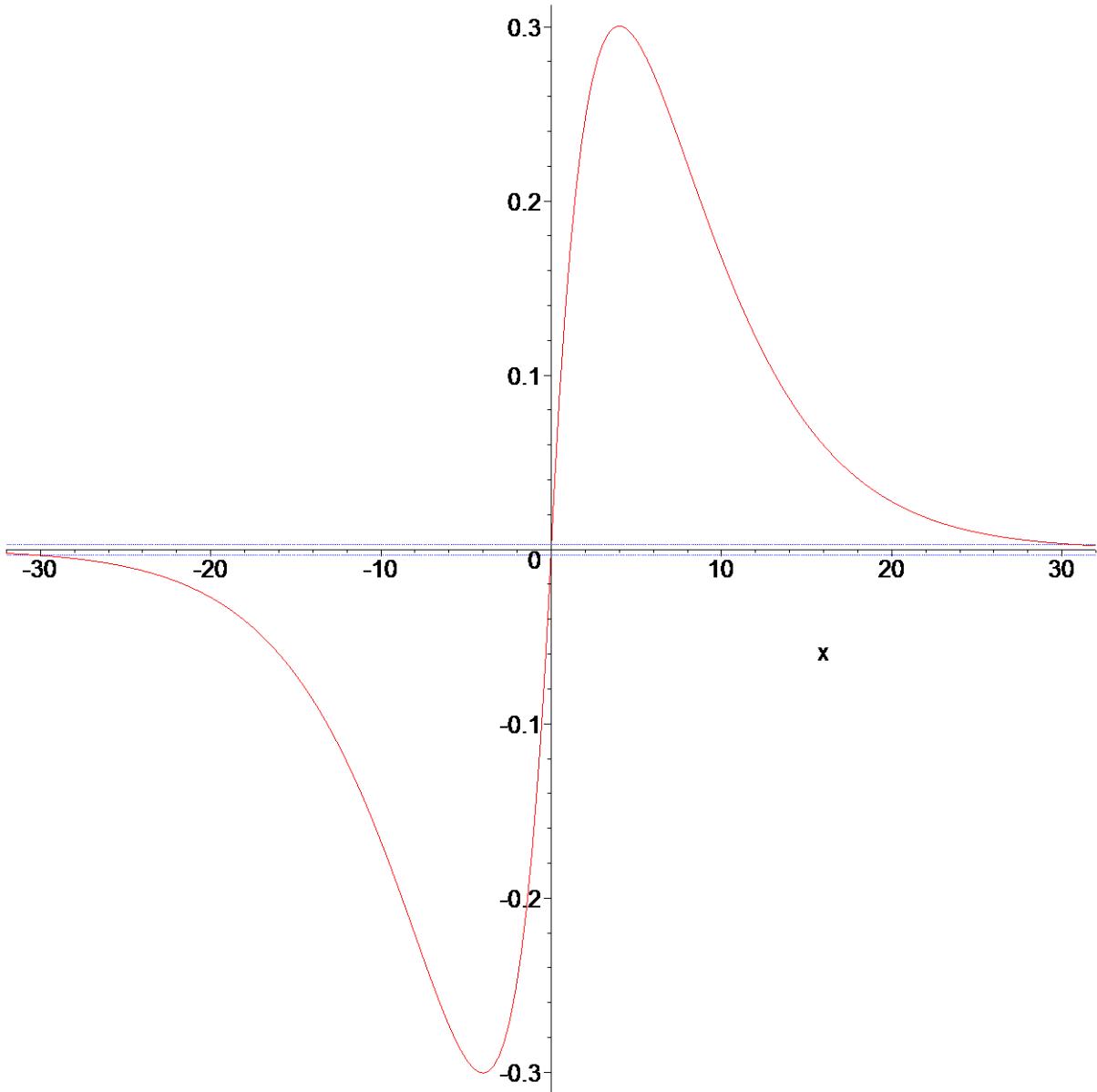


```
>
> 'psi[0,1,1](x,y,z)' = simplify(psi(0,1,1));

$$\Psi_{0,1,1}(x, y, z) = \frac{1}{12} \sqrt{6} \sqrt{\frac{1}{a_\mu}} (x + y I) e^{\left(-\frac{1}{4} \frac{\sqrt{x^2 + y^2 + z^2}}{a_\mu}\right)}$$

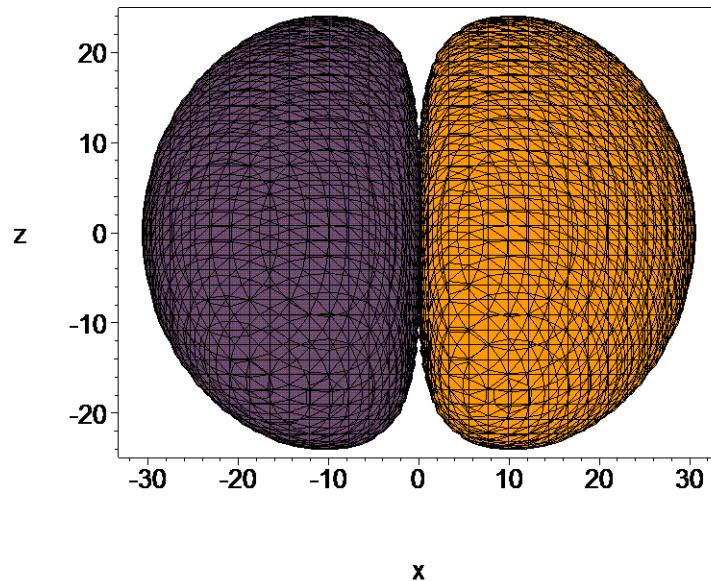
> plot([simplify(eval(Re(psi(0,1,1))), [a[mu]=1, y=0, z=0])), 0.003, -0.003], x=-32..32,
       colour=[red, blue, blue], linestyle=[1,2,2],
       titlefont=[TIMES,BOLD,14],
       title="amplitude function psi(0,1,1) in direction x");
```

amplitude function $\psi(0,1,1)$ in direction x



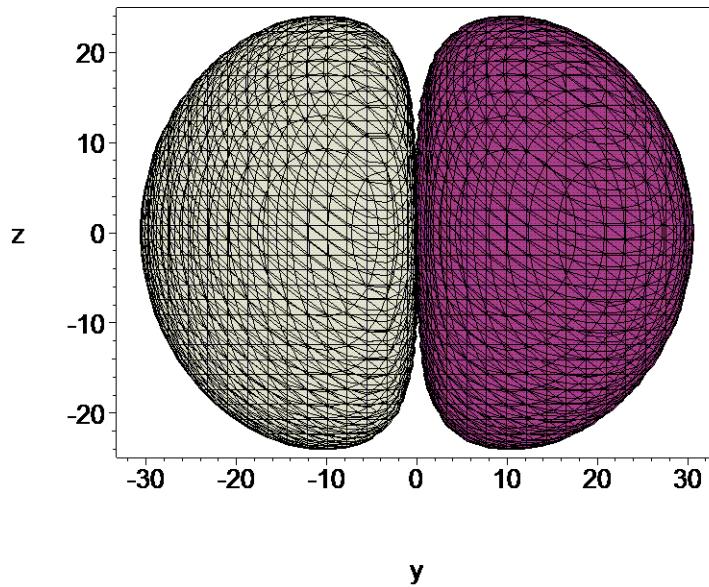
```
>  
> plots[implicitplot3d]([eval(simplify(Re(psi(0,1,1)))), a[mu]=1)=0  
.003,  
eval(simplify(Re(psi(0,1,1)))), a[mu]=1)=-0.003], x=-32..32,  
y=-28..28,  
z=-24..24, colour=[red,blue], grid=[30,30,30],  
scaling=constrained,  
axes=boxed, labels=["x","y","z"], title="real part of  
amplitude function psi(0,1,1)",  
titlefont=[TIMES,BOLD,14], orientation=[-90,90],  
colour=[coral,violet]);
```

real part of amplitude function $\psi(0,1,1)$



```
>  
> plots[implicitplot3d]([eval(simplify(Im(psi(0,1,1)))), a[mu]=1)=0  
.003,  
eval(simplify(Im(psi(0,1,1)))), a[mu]=1)=-0.003], x=-28..28,  
y=-32..32,  
z=-24..24, colour=[red,blue], grid=[30,30,30],  
scaling=constrained,  
axes=boxed, labels=["x","y","z"], title="imaginary part of  
amplitude function psi(0,1,1)",  
titlefont=[TIMES,BOLD,14], orientation=[0,90],  
colour=[maroon,wheat]);
```

imaginary part of amplitude function $\psi(0,1,1)$



```

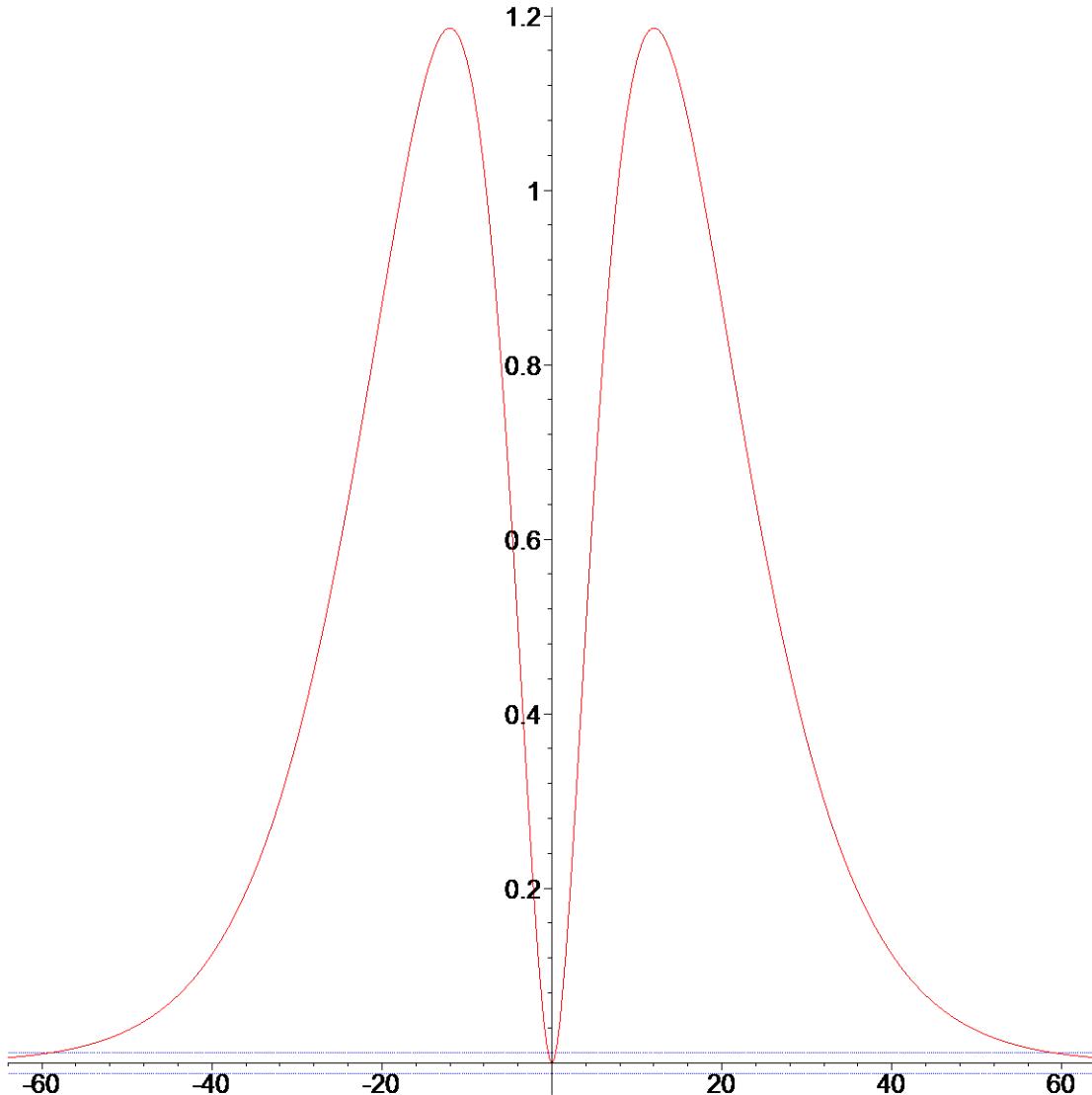
>
> 'psi[0,2,0](x,y,z)' = simplify(psi(0,2,0));

$$\Psi_{0,2,0}(x,y,z) = -\frac{1}{180}\sqrt{30}\sqrt{\frac{1}{a_\mu}}(x^2+y^2-2z^2)e^{-\frac{\sqrt{x^2+y^2+z^2}}{a_\mu}}$$

> plot([simplify(eval(psi(0,2,0), [a[mu]=1, x=0, y=0])), 0.012,
-0.012], z=-64..64,
    colour=[red, blue, blue], linestyle=[1,2,2],
    titlefont=[TIMES,BOLD,14],
    title="amplitude function psi(0,2,0) in direction z");

```

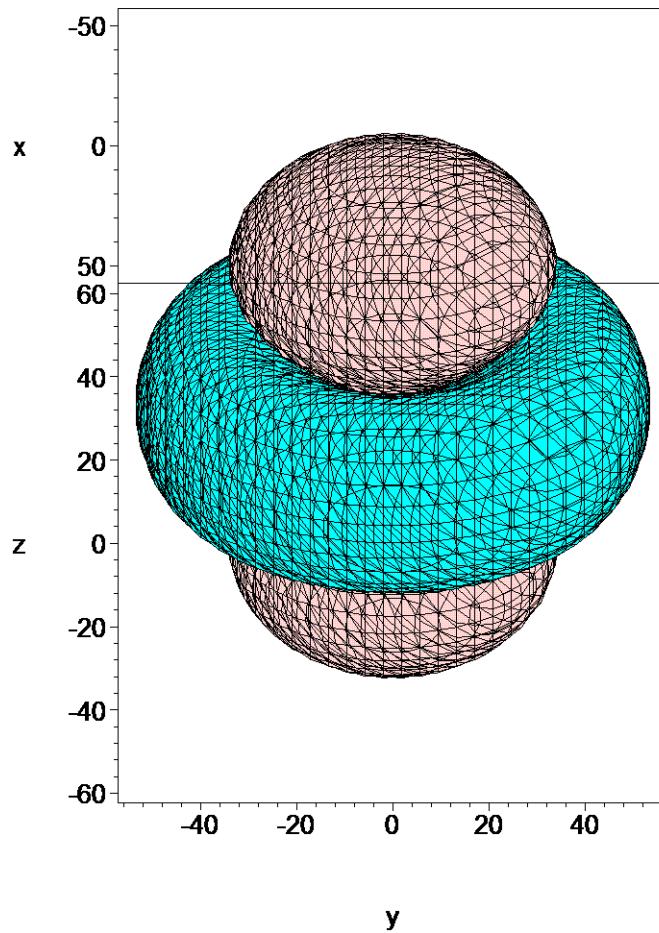
amplitude function $\psi(0,2,0)$ in direction z



z

```
>  
> plots[implicitplot3d]([eval(simplify(psi(0,2,0))),a[mu]=1)=0.012  
'  
    eval(simplify(psi(0,2,0)),a[mu]=1)=-0.012], x=-55..55,  
y=-55..55,  
z=-60..60, colour=[red,blue], grid=[30,30,30],  
scaling=constrained,  
axes=boxed, labels=["x","y","z"], title="amplitude function  
psi(0,2,0)",  
titlefont=[TIMES,BOLD,14], orientation=[0,60],  
colour=[pink,cyan]);
```

amplitude function psi(0,2,0)



```

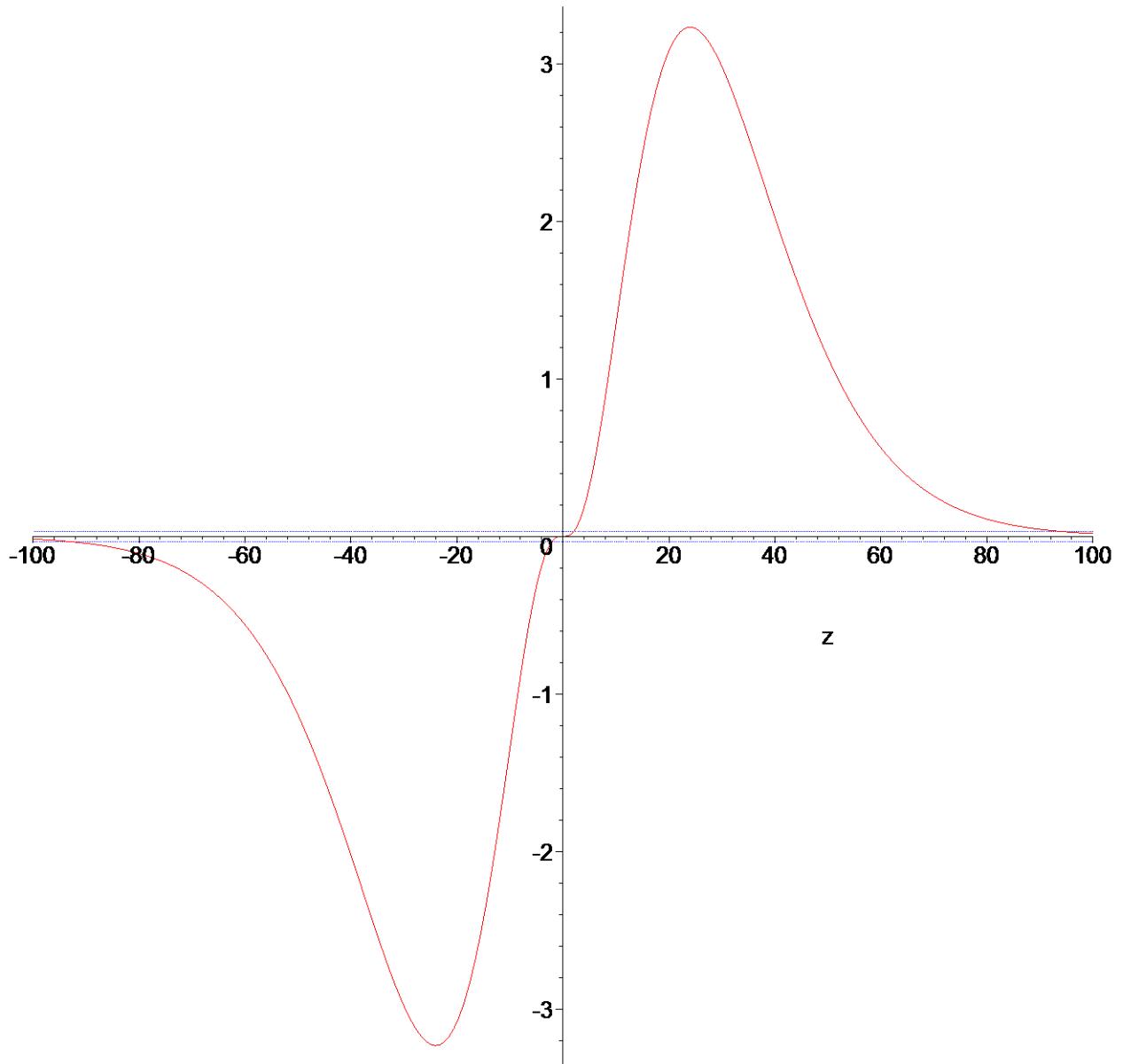
>
> 'psi[0,3,0](x,y,z)' = simplify(psi(0,3,0));

$$\Psi_{0,3,0}(x,y,z) = -\frac{1}{840} \sqrt{35} \sqrt{\frac{1}{a_\mu}} \left( x^2 + y^2 - \frac{2z^2}{3} \right) z e^{\left( -\frac{\sqrt{x^2 + y^2 + z^2}}{a_\mu} \right)}$$

> plot([simplify(eval(psi(0,3,0), [a[mu]=1, x=0, y=0])), 0.033,
       -0.033], z=-100..100,
       colour=[red, blue, blue], linestyle=[1,2,2],
       titlefont=[TIMES,BOLD,14],
       title="amplitude function psi(0,3,0) in direction z");

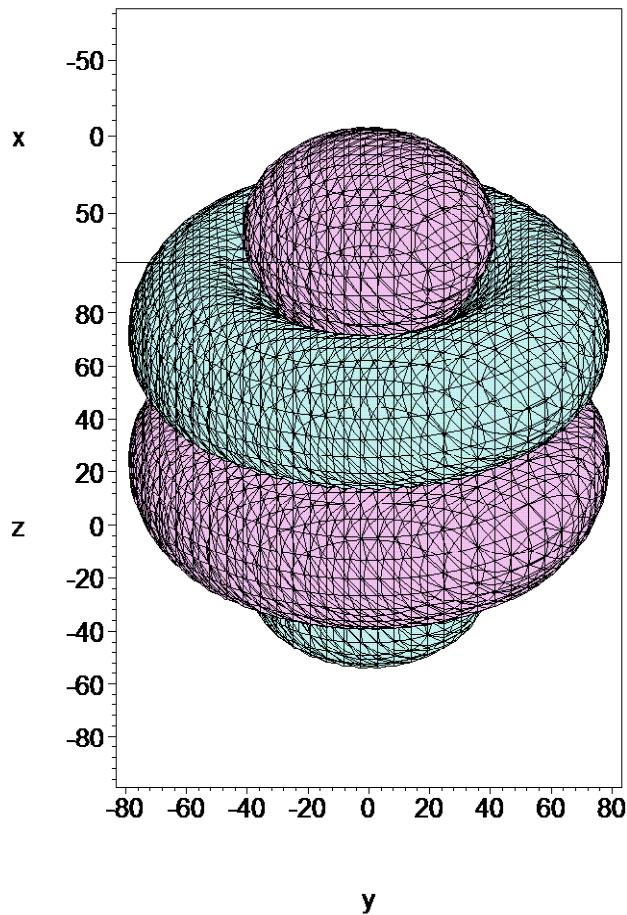
```

amplitude function $\psi(0,3,0)$ in direction z



```
>  
> plots[implicitplot3d]([eval(simplify(psi(0,3,0))), a[mu]=1)=0.033  
'  
    eval(simplify(psi(0,3,0)), a[mu]=1)=-0.033], x=-80..80,  
y=-80..80,  
z=-95..95, colour=[red,blue], grid=[30,30,30],  
scaling=constrained,  
axes=boxed, labels=["x","y","z"], title="amplitude function  
psi(0,3,0)",  
titlefont=[TIMES,BOLD,14], orientation=[0,60],  
colour=[plum,turquoise]);
```

amplitude function $\psi(0,3,0)$



>

The surfaces of other amplitude functions or their real and imaginary parts can be analogously plotted.

This derivation, following Fowles, includes some assumptions and questionable arguments, for instance, the assumption that the terms in x, y, z , in $F(x, y, z)$ satisfy Laplace's equation, which in general has multiple solutions; cf section 7.41, although the method was clearly designed to yield results analogous to those in the system of spherical polar coordinates. The plots above show a satisfactory correlation with the plots for the amplitude functions in spherical polar coordinates in section 12b.53b; the results are hence of interest in the context of multiple coordinates systems for the hydrogen atom according to Schroedinger's equations. Another choice of solution of Laplace's equation might yield amplitude functions in cartesian coordinates that simulate amplitude functions as solutions of Schrödinger's temporally independent equation in paraboloidal,

[] ellipsoidal or spherconical coordinates.
[>