p-orbitals and d-orbitals

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1. *p*-electrons: quenching of the orbital angular momentum;

Frequently, the lowest orbital level, when split by a crystal field, is a singlet. Because of the large splitting, this is usually the only level populated. The orbital momentum is then said to be quenched, since it will make no contribution to the magnetic moment when a field is applied.

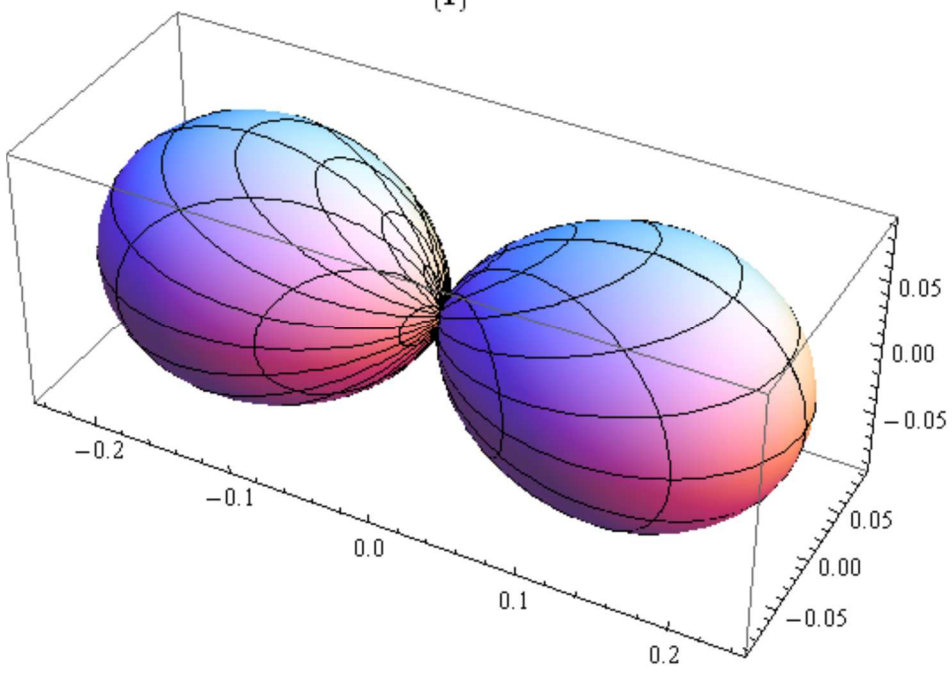
We now a simple model of quenching of the orbital angular momentum due to the crystal field. The electron configuration is given by $1s^2 2s^2 2p^1$ ($1s^2 2s^2$ has a closed shell). According to the Hund's law, we have $L = 1$ (degeneracy = $2L+1 = 3$), $S = 1/2$ (degeneracy = $2S + 1 = 2$). Then the total degeneracy is $(2L+1)(2S+1) = 2 \times 3 = 6$. There is one *p*-electron. Suppose that this ion is surrounded by 6 negative ions located at $(\pm a,0,0)$, $(0,\pm b,0)$, and $(0,0,\pm c)$ with $a>b>c>$. There are three wave functions: $|p_x\rangle$, $|p_y\rangle$, and $|p_z\rangle$ given by

$$\langle \mathbf{r}|p_x\rangle = xf(r), \quad \langle \mathbf{r}|p_y\rangle = yf(r), \quad \langle \mathbf{r}|p_z\rangle = zf(r), \tag{1}$$

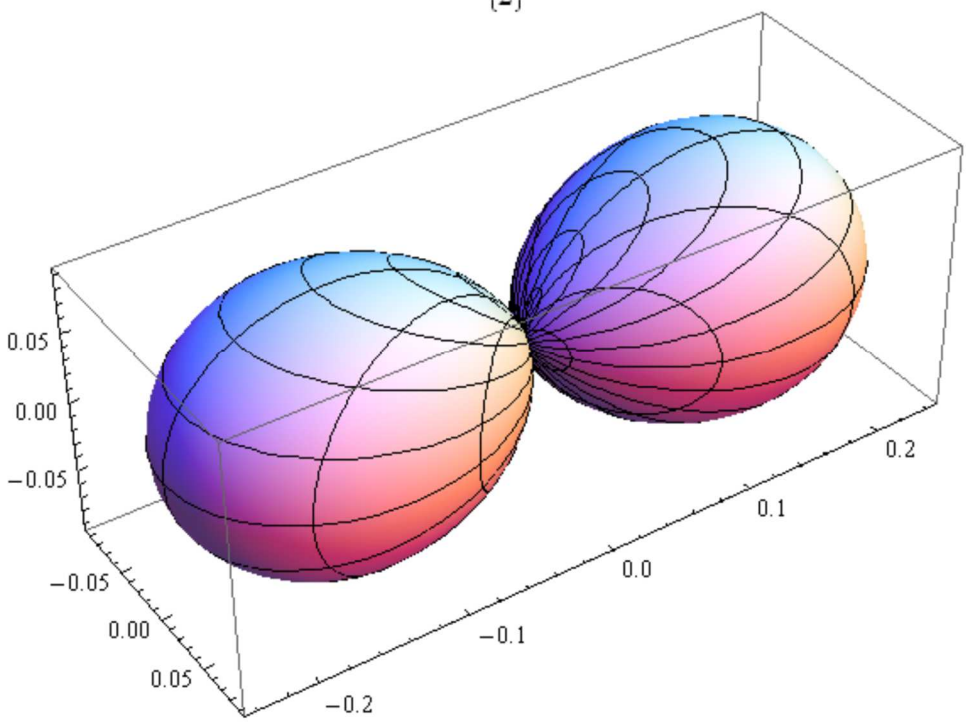
with

$$\langle p_x|p_y\rangle = \langle p_y|p_z\rangle = \langle p_z|p_x\rangle = 0. \tag{2}$$

{1}



{2}



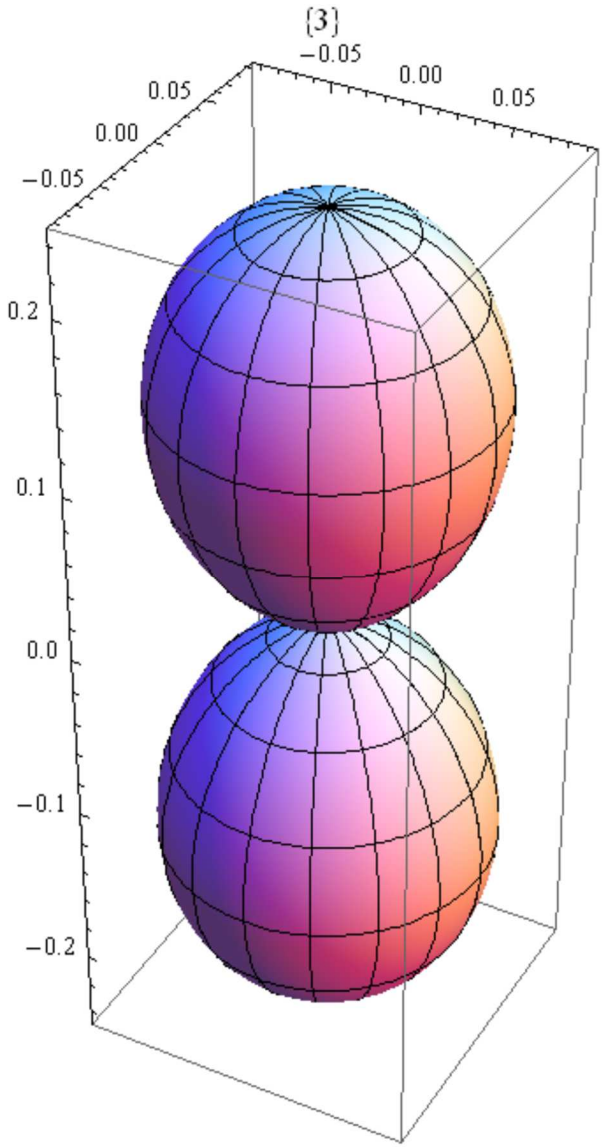


Fig.1 Angular parts of the wavefunctions for (1) $2p_x$, (2) $2p_y$, and (3) $2p_z$

$n = 2$, $l = 1$ ($2p$ electron)

$$R_{21}(r) = \frac{r \exp(-\frac{r}{2a_0})}{2\sqrt{6}a_0^{5/2}}, \tag{3}$$

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

$$Y_1^0(\theta,\phi) = \frac{1}{2}\sqrt{\frac{3}{\pi}}\cos\theta \quad , \tag{4}$$

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

$$\langle \mathbf{r}|p_x\rangle = \frac{1}{\sqrt{2}}[-Y_1^1(\theta,\phi)+Y_1^{-1}(\theta,\phi)]R_{21}(r) = \frac{1}{2}\sqrt{\frac{3}{\pi}}\sin\theta\cos\phi R_{21}(r) = x\frac{1}{2}\sqrt{\frac{3}{\pi}}\frac{R_{21}(r)}{r}$$

$$\langle \mathbf{r}|p_y\rangle = i\frac{1}{\sqrt{2}}[Y_1^1(\theta,\phi)+Y_1^{-1}(\theta,\phi)]R_{21}(r) = \frac{1}{2}\sqrt{\frac{3}{\pi}}\sin\theta\sin\phi R_{21}(r) = y\frac{1}{2}\sqrt{\frac{3}{\pi}}\frac{R_{21}(r)}{r} \quad ,$$

$$\langle \mathbf{r}|p_z\rangle = Y_1^0(\theta,\phi)R_{21}(r) = \frac{1}{2}\sqrt{\frac{3}{\pi}}\cos\theta = z\frac{1}{2}\sqrt{\frac{3}{\pi}}\frac{R_{21}(r)}{r} \tag{5}$$

with the radial wave function given by

$$f(r) = \frac{1}{2}\sqrt{\frac{3}{\pi}}\frac{R_{21}(r)}{r} = \frac{1}{4\sqrt{2\pi}}\frac{\exp(-\frac{r}{2a_0})}{a_0^{5/2}} \, . \tag{6}$$

((**Mathematica**))

```
Clear["Global`*"];
Table[{SphericalHarmonicY[1, m, θ, ϕ]},
  {m, -1, 1, 1}] // TableForm[#,
   TableHeadings → {{"m=-1", "m=0", "m=1"}}] &
```

m=-1	$\frac{1}{2}\, e^{-i\phi}\sqrt{\frac{3}{2\pi}}\,$ Sin[θ]
m=0	$\frac{1}{2}\sqrt{\frac{3}{\pi}}\,$ Cos[θ]
m=1	$-\frac{1}{2}\, e^{i\phi}\sqrt{\frac{3}{2\pi}}\,$ Sin[θ]

2. 3*d*-electrons

We now consider the origin of the splitting of the orbital levels by the crystal field. Suppose that an ion with only one 3d electron ($n = 3$ and $l = 2$). It forms wave functions made up of certain combinations of the 3*d* hydrogen wave functions. The linear combinations we choose are

$$\begin{aligned}
\psi_{xy} &= -i\frac{1}{\sqrt{2}}[Y_2^2(\theta,\phi) - Y_2^{-2}(\theta,\phi)] \\
\psi_{yz} &= i\frac{1}{\sqrt{2}}[Y_2^1(\theta,\phi) + Y_2^{-1}(\theta,\phi)] \\
\psi_{zx} &= -\frac{1}{\sqrt{2}}[Y_2^1(\theta,\phi) - Y_2^{-1}(\theta,\phi)] \quad , \qquad (1) \\
\psi_{x^2-y^2} &= \frac{1}{\sqrt{2}}[Y_2^2(\theta,\phi) + Y_2^{-2}(\theta,\phi)] \\
\psi_{3z^2-r^2} &= Y_2^0(\theta,\phi)
\end{aligned}$$

or

$$\begin{aligned}
|\psi_1\rangle = |\psi_{xy}\rangle &= -i\frac{1}{\sqrt{2}}[|l=2,m=2\rangle - |l=2,m=-2\rangle] \\
|\psi_2\rangle = |\psi_{yz}\rangle &= i\frac{1}{\sqrt{2}}[|2,1\rangle + |2,-1\rangle] \\
|\psi_3\rangle = |\psi_{zx}\rangle &= -\frac{1}{\sqrt{2}}[|2,1\rangle - |2,-1\rangle] \quad . \qquad (2) \\
|\psi_4\rangle = |\psi_{x^2-y^2}\rangle &= \frac{1}{\sqrt{2}}[|2,2\rangle + |2,-2\rangle] \\
|\psi_5\rangle = |\psi_{3z^2-r^2}\rangle &= |2,0\rangle
\end{aligned}$$

Note that the notation of the spherical harmonics used here is the same as that used in the Mathematica.

((**Mathematica**)) Spherical harmonics $Y_l^m(\theta,\phi)$

```
Clear["Global`*"];
Table[{SphericalHarmonicY[2, m, θ, ϕ]},
  {m, -2, 2, 1}] // TableForm[#,
   TableHeadings →
    {{"m=-2", "m=-1", "m=0", "m=1", "m = 2"}}] &
```

m=-2	$\frac{1}{4}\, e^{-2 i \phi} \sqrt{\frac{15}{2\pi}}\, \text{Sin}[\theta]^2$
m=-1	$\frac{1}{2}\, e^{-i \phi} \sqrt{\frac{15}{2\pi}}\, \text{Cos}[\theta]\, \text{Sin}[\theta]$
m=0	$\frac{1}{4} \sqrt{\frac{5}{\pi}}\, \left(-1 + 3\, \text{Cos}[\theta]^2\right)$
m=1	$-\frac{1}{2}\, e^{i \phi} \sqrt{\frac{15}{2\pi}}\, \text{Cos}[\theta]\, \text{Sin}[\theta]$
m = 2	$\frac{1}{4}\, e^{2 i \phi} \sqrt{\frac{15}{2\pi}}\, \text{Sin}[\theta]^2$

Table 1 Spherical harmonics $\{l, m, Y_l^m(\theta,\phi)\}$. $l = 2$. $m = 2, 1, 0, -1, -2$.

The radial part of the wave function ($n = 3$ and $l = 2$) is given by

$$R_{3,2}(r) = 2\sqrt{\frac{2}{15}}\frac{1}{81a_0^{7/2}} r^2 \exp(-\frac{r}{3a_0}) . \qquad (3)$$

There are two types of orbital states: the $d\varepsilon$ orbits d_{xy}, d_{yz}, d_{zx}, the $d\gamma$ orbits: $d_{x2\text{-}y2}$ and $d_{3z^2-r^2}$. The complete wavefunctions are given as follows.

$d\varepsilon(t_{2g})$

$$\left\langle \mathbf{r}\middle| d_{xy}\right\rangle = \frac{1}{81a_0{}^{7/2}}\exp(-\frac{r}{3a_0})\frac{2xy}{\sqrt{2\pi}} = \frac{2}{\sqrt{6\pi}}\frac{1}{81a_0{}^{7/2}}\exp(-\frac{r}{3a_0})\sqrt{3}xy$$

$$\left\langle \mathbf{r}\middle| d_{yz}\right\rangle = \frac{1}{81a_0{}^{7/2}}\exp(-\frac{r}{3a_0})\frac{2yz}{\sqrt{2\pi}} = \frac{2}{\sqrt{6\pi}}\frac{1}{81a_0{}^{7/2}}\exp(-\frac{r}{3a_0})\sqrt{3}yz$$

$$\left\langle \mathbf{r}\middle| d_{zx}\right\rangle = \frac{1}{81a_0{}^{7/2}}\exp(-\frac{r}{3a_0})\frac{2zx}{\sqrt{2\pi}} = \frac{2}{\sqrt{6\pi}}\frac{1}{81a_0{}^{7/2}}\exp(-\frac{r}{3a_0})\sqrt{3}zx \quad ,$$

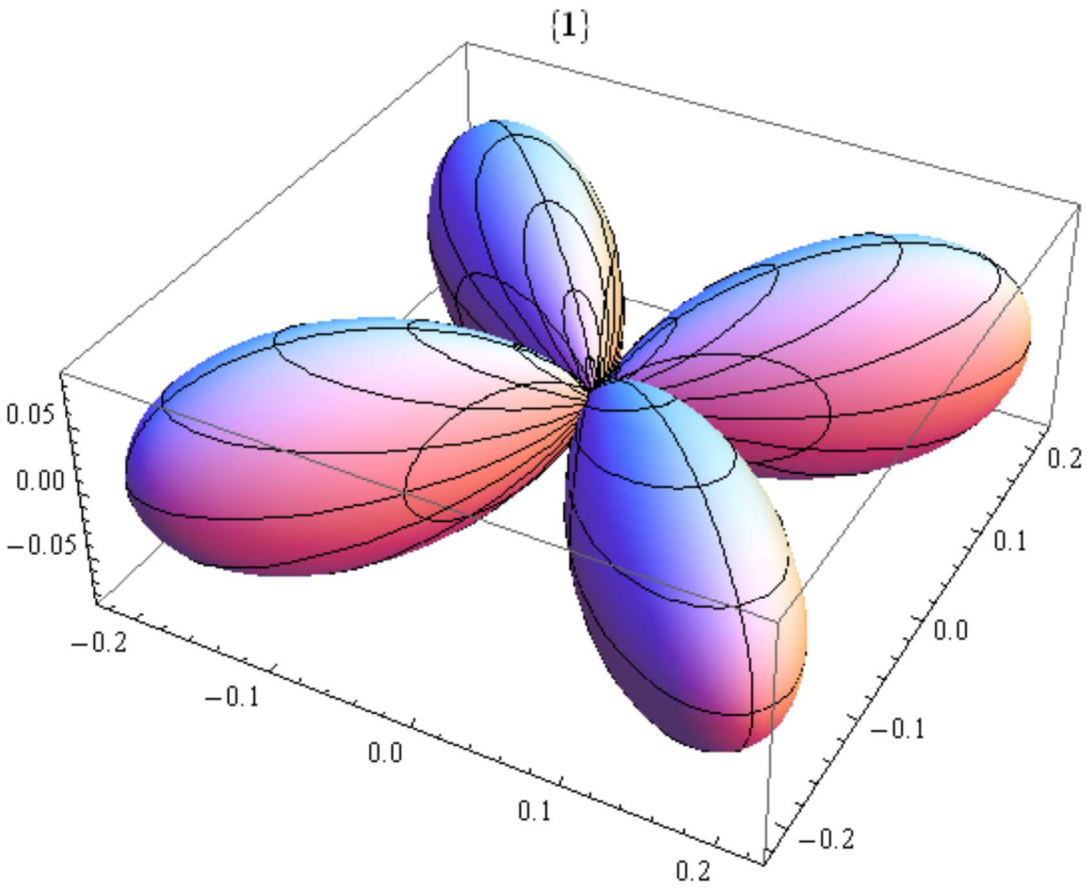
$d\gamma(e_g)$

$$\left\langle \mathbf{r}\middle| d_{x^2-y^2}\right\rangle = \frac{1}{81a_0{}^{7/2}}\exp(-\frac{r}{3a_0})\frac{x^2-y^2}{\sqrt{2\pi}} = \frac{2}{\sqrt{6\pi}}\frac{1}{81a_0{}^{7/2}}\exp(-\frac{r}{3a_0})\frac{\sqrt{3}(x^2-y^2)}{2}$$

$$\left\langle \mathbf{r}\middle| d_{3z^2-r^2}\right\rangle = \frac{1}{81a_0{}^{7/2}}\exp(-\frac{r}{3a_0})\frac{3z^2-r^2}{\sqrt{6\pi}} = \frac{2}{\sqrt{6\pi}}\frac{1}{81a_0{}^{7/2}}\exp(-\frac{r}{3a_0})\frac{3z^2-r^2}{2}$$

(4)

For convenience, we use the notations: $\left\langle \mathbf{r}\middle| d_{xy}\right\rangle = \psi_1$, $\left\langle \mathbf{r}\middle| d_{yz}\right\rangle = \psi_2$, $\left\langle \mathbf{r}\middle| d_{zx}\right\rangle = \psi_3$, $\left\langle \mathbf{r}\middle| d_{x^2-y^2}\right\rangle = \psi_4$, $\left\langle \mathbf{r}\middle| d_{3z^2-r^2}\right\rangle = \psi_5$. The complete wavefunctions are given by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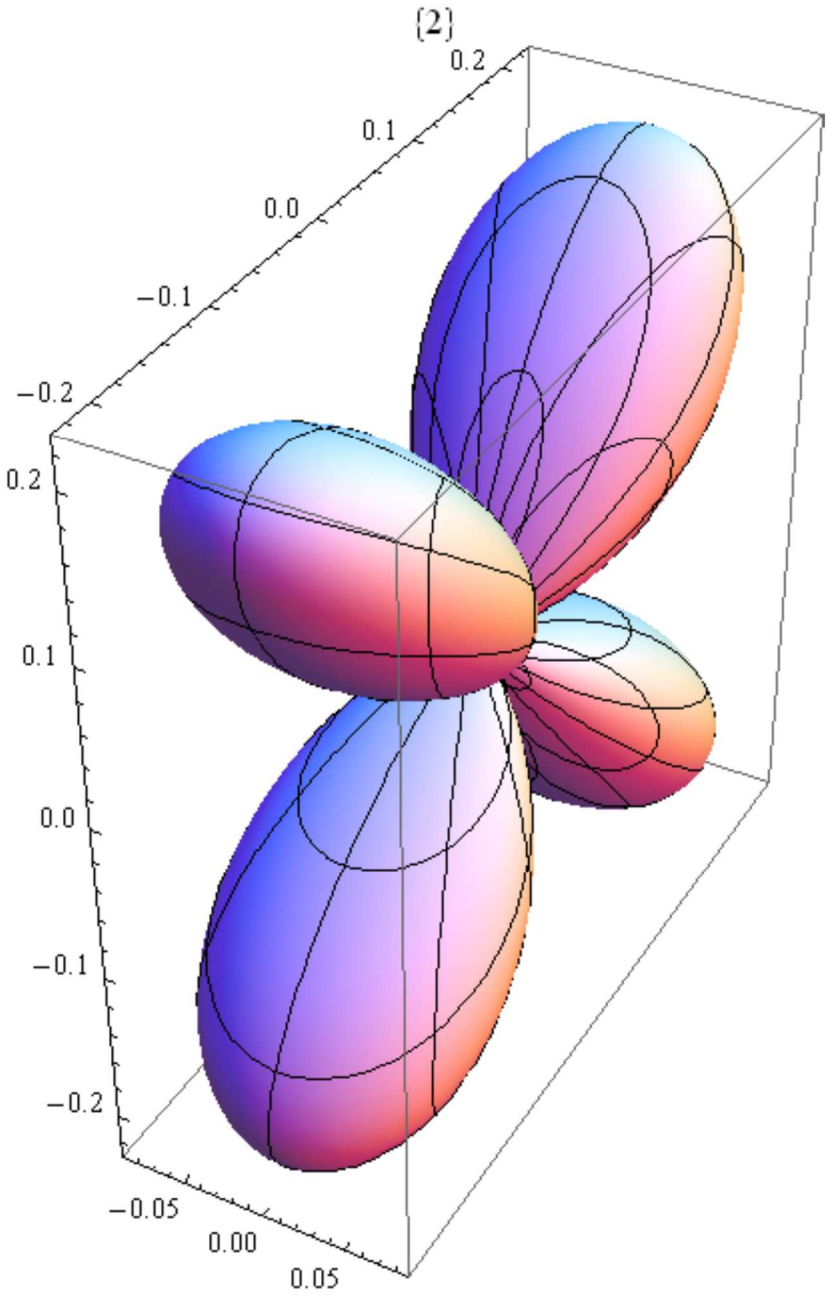
−0.2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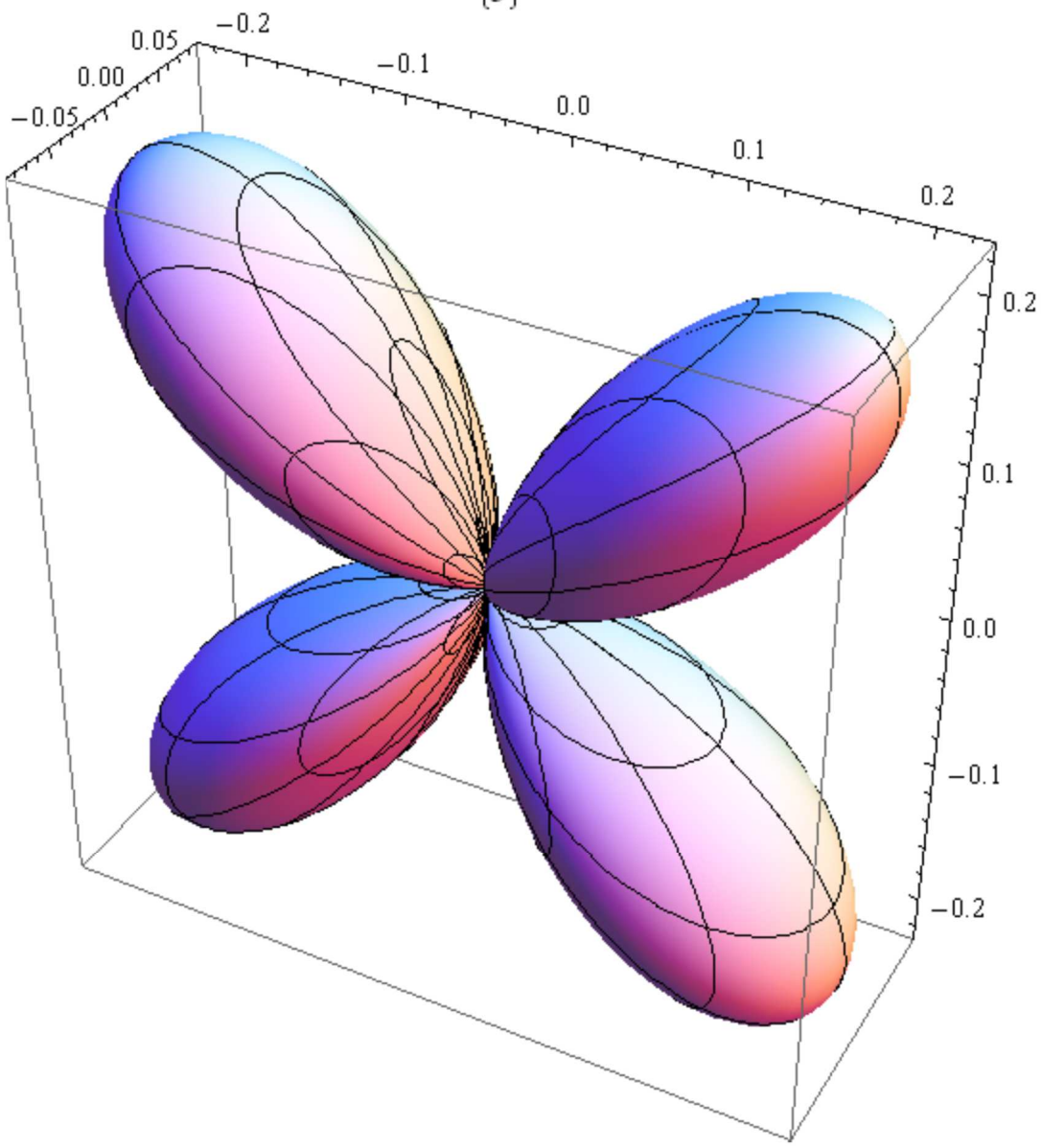
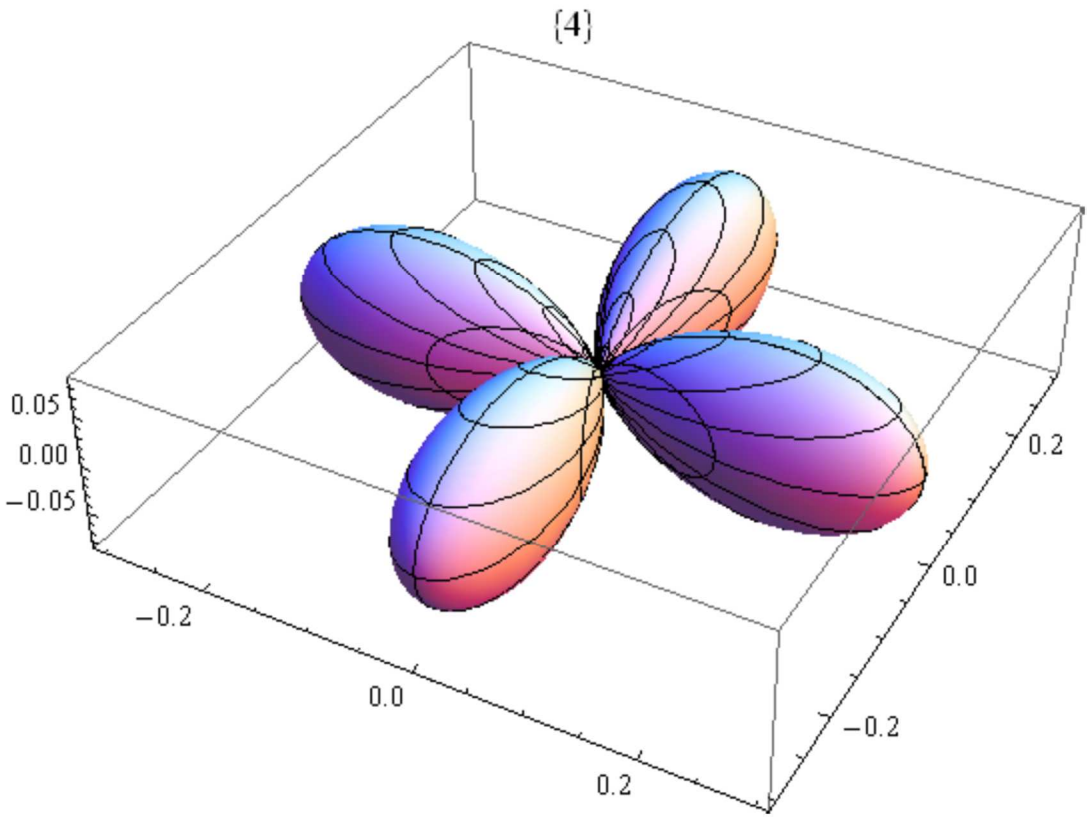
{3}

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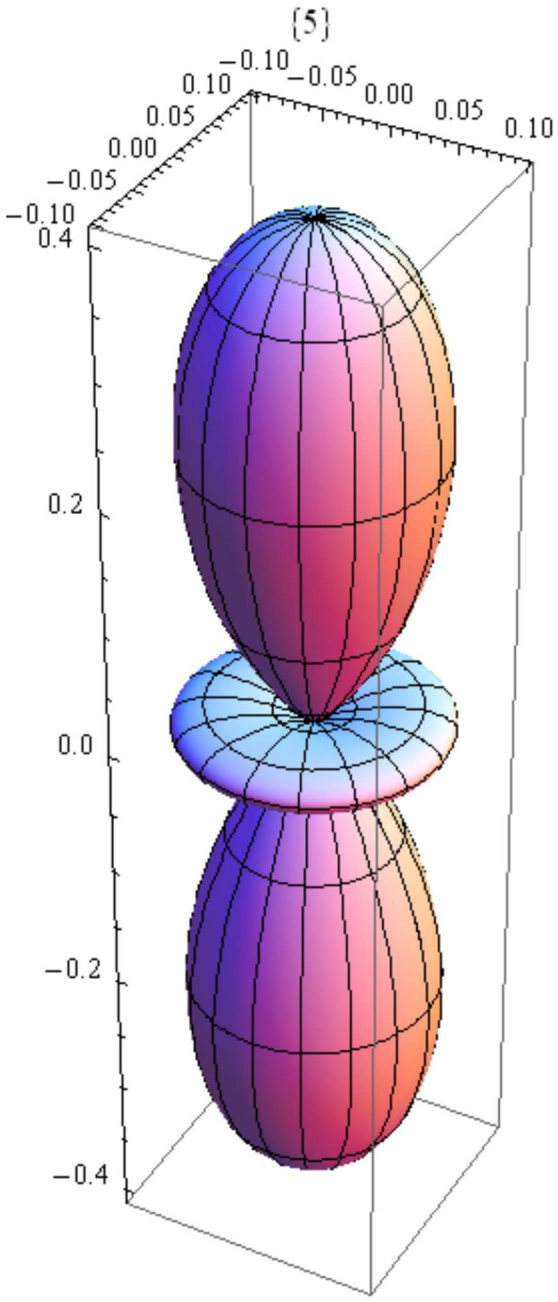


Fig.2 Angular parts of the wavefunctions for (1) d_{xy}, (2) d_{yz}, (3) d_{zx}, (4) $d_{x^2-y^2}$, and (5) $d_{3z^2-r^2}$.

SUPPLEMENT: ContourPlot3D of *s*-orbit, *d*-orbit, and *f*-orbit

S-1 p-orbitals

$$|p_x\rangle = \hat{U}_{2p}|1,1\rangle,$$

$$|p_y\rangle = \hat{U}_{2p}|1,0\rangle,$$

$$|p_z\rangle = \hat{U}_{2p}|1,-1\rangle$$

under the basis of

$$|1,1\rangle = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}, \qquad |1,0\rangle = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}, \qquad |1,-1\rangle = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$$

and

$$\hat{U} = \frac{1}{\sqrt{2}} \begin{pmatrix} -1 & 0 & i \\ 0 & \sqrt{2} & 0 \\ 1 & 0 & i \end{pmatrix} \qquad \text{(unitary operator)}$$

with

$$\hat{U}^{+}\hat{U} = \hat{1}$$

The probability density for the electron in the 2*p* orbit is defined by

$$\left|R_{2p}(r)\right|^2 \left|\langle \theta, \phi | \hat{U}_{2p} | l = 2, m \rangle\right|^2,$$

where m = 2, 1, 0, -1, -2. We make a ContourPlot3D of the probability density using the Mathematica program in the 3D (x, y, z) space. We also make a ContourPlot of

$$\left|R_{2p}(r)\right|^2 \left|\langle \theta, \phi | \hat{U}_{2p} | l = 2, m \rangle\right|^2 \text{ with } x = 0 \text{ } (y\text{-}z \text{ plane}), \text{ or, } y = 0 \text{ } (x\text{-}y \text{ plane}), \text{ or } z = 0 \text{ } (x\text{-}y \text{ plane}$$

in the 2D plane.

(a) $|p_x\rangle$ **state**

$$p_x : \frac{1}{4\sqrt{2\pi}} e^{-r/2} x$$

The sign of p_x is determined by a factor x.

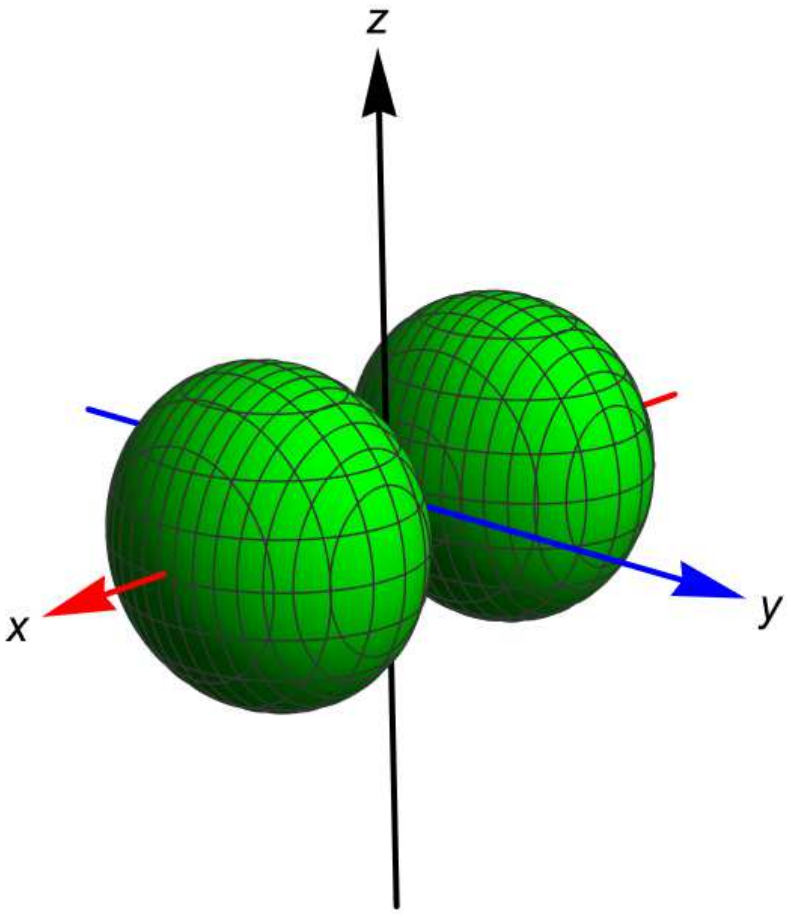


Fig.1(a) ContourPlot3D of $\left|R_{2p}(r)\right|^2 \left|\left\langle \theta,\phi\left|\hat{U}_{2p}\right|l=1,m=1\right\rangle\right|^2$: x .

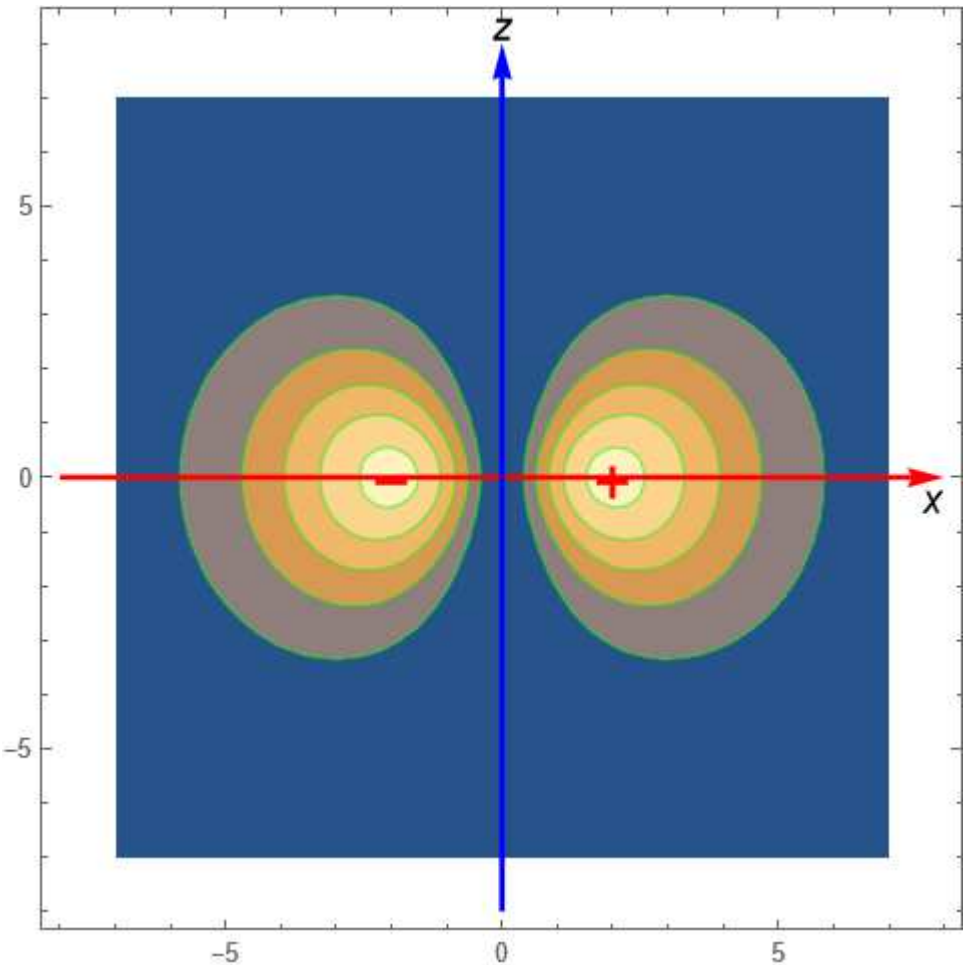


Fig.1(b) ContourPlot of $\left|R_{2p}(r)\right|^2 \left|\langle\theta,\phi|\hat{U}_{2p}|l=1,m=1\rangle\right|^2$ with $y=0$ (z-x plane). The sign indicated on each of them is that of the wave function (which is real).

(b) $|p_y\rangle$ **state**

$$p_y : \frac{1}{4\sqrt{2\pi}} e^{-r/2} y$$

The sign of p_y is determined by a factor y.

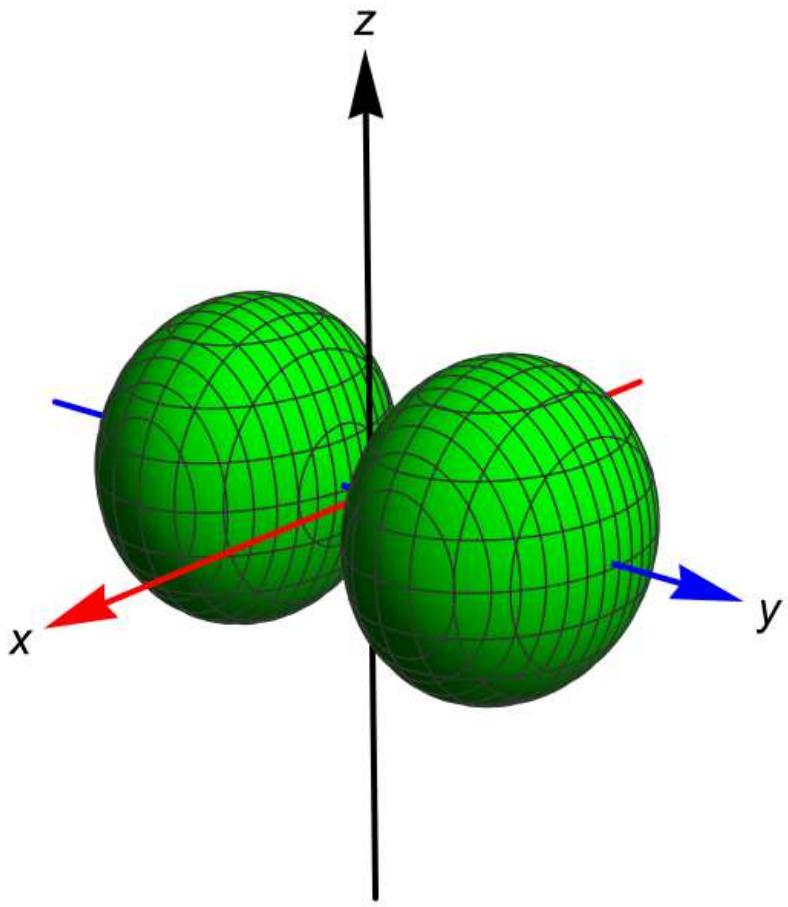


Fig.2(a) ContourPlot3D of $\left|R_{2p}(r)\right|^2 \left|\left\langle \theta,\phi \middle| \hat{U}_{2p} \middle| l=1, m=0 \right\rangle\right|^2 :\ y$

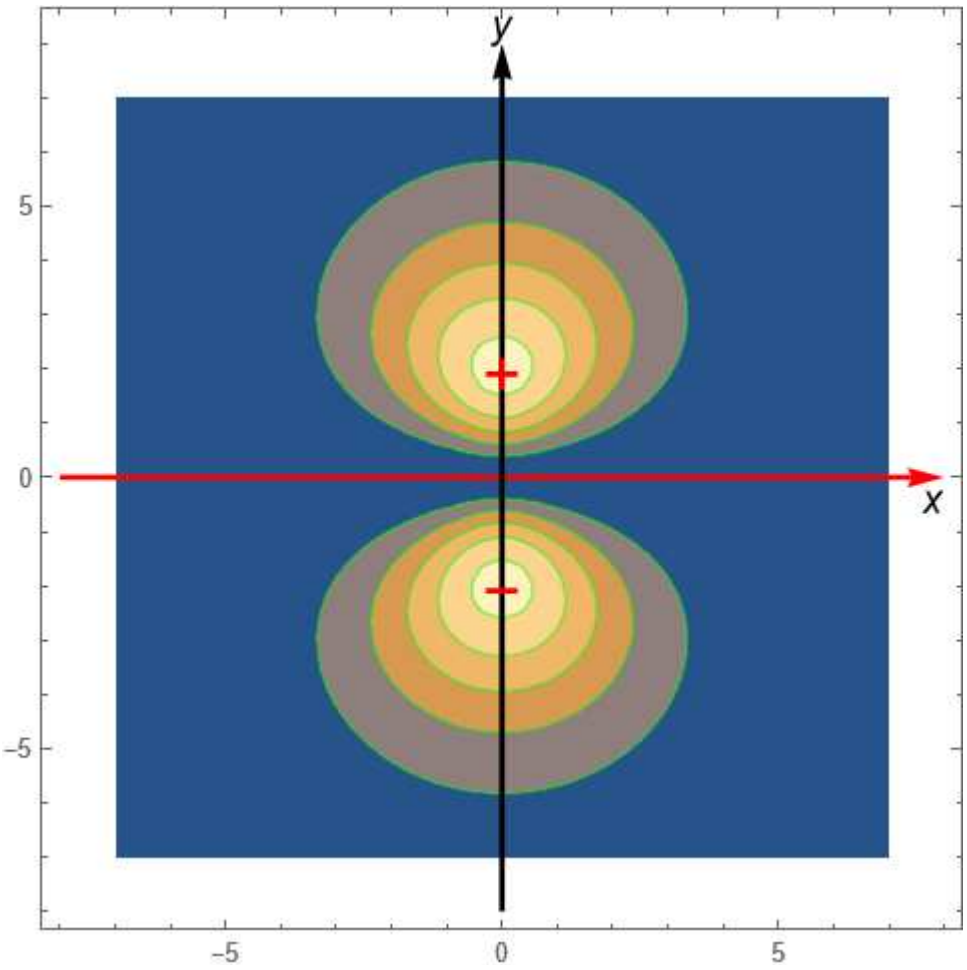


Fig2(b) ContourPlot of $\left|R_{2p}(r)\right|^2 \left|\langle\theta,\phi|\hat{U}_{2p}\,|l=1,m=0\rangle\right|^2$ with $z = 0$ (x-y plane). The sign indicated on each of them is that of the wave function (which is real).

(c) $|p_z\rangle$ **state**

$$p_z : \frac{1}{4\sqrt{2\pi}} e^{-r/2} z$$

The sign of p_z is determined by a factor z.

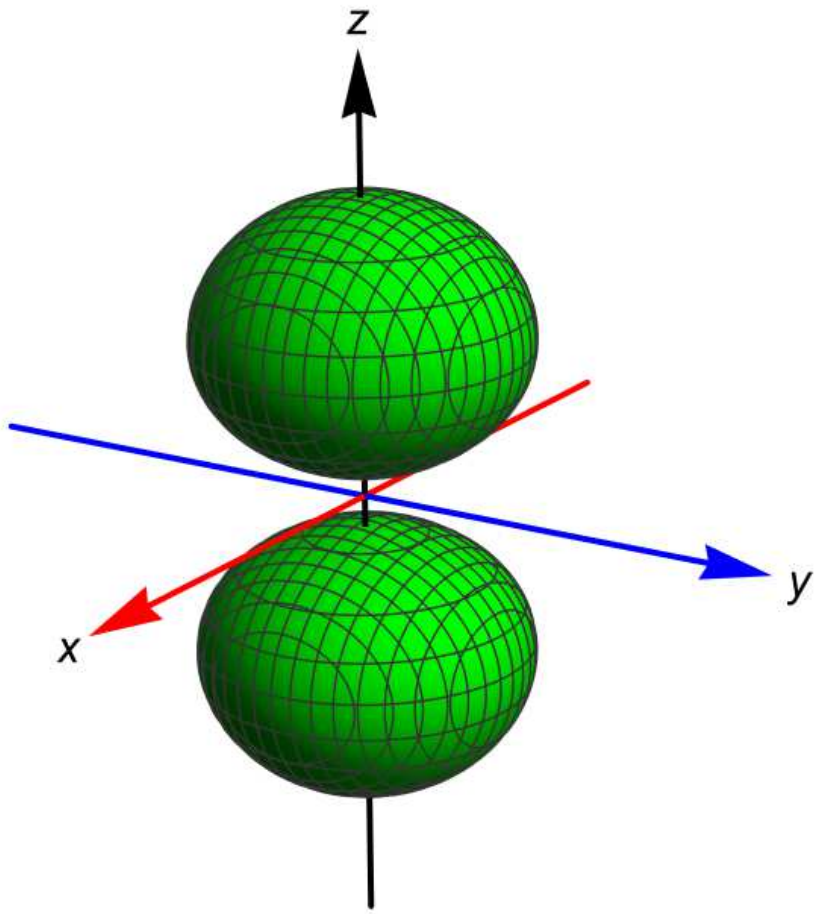


Fig.3(a) ContourPlot3D of $\left|R_{2p}(r)\right|^2 \left|\langle\theta,\phi|\hat{U}_{2p}\,|l=1,m=0\rangle\right|^2$: z

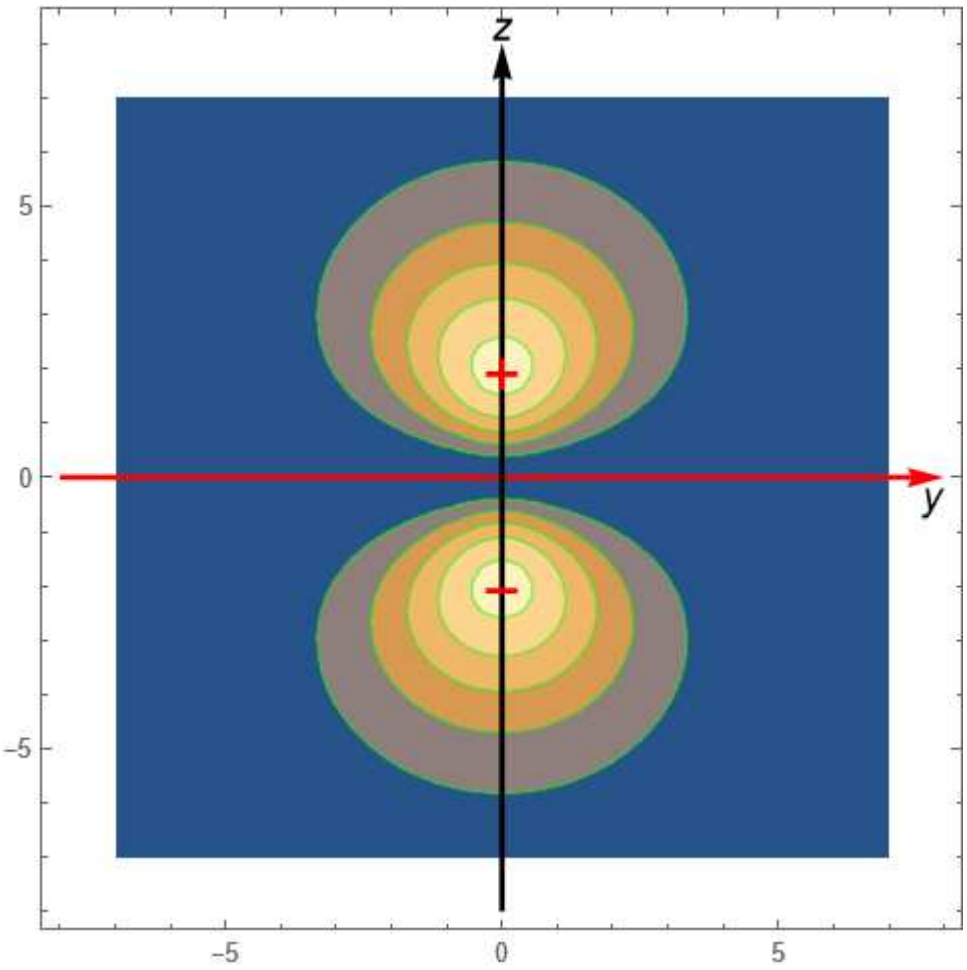


Fig.3(b) ContourPlot of $\left|R_{2p}(r)\right|^2 \left|\langle\theta,\phi|\hat{U}_{2p}|l=1,m=-1\rangle\right|^2$ with $x = 0$ (y-z plane). The sign indicated on each of them is that of the wave function (which is real).

Shape of p-Orbital

The *p* orbitals are formed like dumbbells.

The *p* orbital node is located at the nucleus's center.

Because of the presence of three orbitals, the p orbital can occupy a maximum of six electrons.

Each *p* orbital is made up of two parts known as lobes that are located on either side of the plane that runs across the nucleus.

Each *p* orbital has parts known as lobes on either side of the plane that runs across the nucleus. At the plane where the two lobes intersect, the likelihood of finding an electron is nil.

The three orbitals are known as degenerate orbitals because they have the same size, shape, and energy.

The sole difference between the orbitals is the orientation of the lobes. Because the lobes are orientated along the x, y, or z-axis, they are given the names 2_{px}, 2_{py}, and 2_{pz}. The formula n –2 is used to calculate the number of nodes.
Similarly to s orbitals, the size and energy of p orbitals rise as the primary quantum number increases (4p > 3p > 2p).

S-2 d-orbitals

dε: t_{2g}

$$|d(xy)\rangle = \hat{U}_{3d}|2,2\rangle = -\frac{i}{\sqrt{2}}[|2,2\rangle - |2,-2\rangle],$$
$$|d(yz)\rangle = \hat{U}_{3d}|2,1\rangle = \frac{i}{\sqrt{2}}[|2,1\rangle + |2,-1\rangle],$$
$$|d(zx)\rangle = \hat{U}_{3d}|2,-1\rangle = -\frac{1}{\sqrt{2}}[|2,1\rangle - |2,-1\rangle],$$

dγ e_g

$$|d(x^2-y^2)\rangle = \hat{U}_{3d}|2,-2\rangle = \frac{1}{\sqrt{2}}[|2,2\rangle + |2,-2\rangle],$$
$$|d(3z^2-r^2)\rangle = \hat{U}_{3d}|2,0\rangle = |2,0\rangle$$

$$\hat{U}_{3d} = \frac{1}{\sqrt{2}}\begin{pmatrix} -i & 0 & 0 & 0 & 1 \\ 0 & i & 0 & -1 & 0 \\ 0 & 0 & \sqrt{2} & 0 & 0 \\ 0 & i & 0 & 1 & 0 \\ i & 0 & 0 & 0 & 1 \end{pmatrix} \qquad \text{(unitary operator)}$$

$$\hat{U}_{3d}{}^{+} = \frac{1}{\sqrt{2}}\begin{pmatrix} i & 0 & 0 & 0 & -i \\ 0 & -i & 0 & -i & 0 \\ 0 & 0 & \sqrt{2} & 0 & 0 \\ 0 & -1 & 0 & 1 & 0 \\ 1 & 0 & 0 & 0 & 1 \end{pmatrix}$$

with $\hat{U}^{+}\hat{U} = \hat{1}$, under the basis of

$$|l=2,m=2\rangle=\begin{pmatrix}1\\0\\0\\0\\0\end{pmatrix},\qquad |2,1\rangle=\begin{pmatrix}0\\1\\0\\0\\0\end{pmatrix},\qquad |2,0\rangle=\begin{pmatrix}0\\0\\1\\0\\0\end{pmatrix}$$

$$|2,-1\rangle=\begin{pmatrix}0\\0\\0\\1\\0\end{pmatrix},\qquad |2,-2\rangle=\begin{pmatrix}0\\0\\0\\0\\1\end{pmatrix},$$

Note

$$3z^2-r^2=2z^2-x^2-y^2=(z^2-x^2)-(y^2-z^2)$$

Since

$$(x^2-y^2)+(y^2-z^2)+(z^2-x^2)=0$$

we pick up two independent states; $d(x^2-y^2)$ and $d(3z^2-r^2)$.

The probability density for the electron in the 3d orbit is defined by

$$\left|R_{4f}(r)\right|^2\left|\langle\theta,\phi|\hat{U}_{3d}|l=2,m\rangle\right|^2,$$

where *m* = 2, 1, 0, -1, -2. We make a ContourPlot3D of the probability density using the Mathematica program.

(a) $|d(xy)\rangle=\hat{U}_{3d}|2,2\rangle=-\frac{i}{\sqrt{2}}[|2,2\rangle-|2,-2\rangle]$

$$\langle\mathbf{r}|d(xy)\rangle=\frac{1}{81}\sqrt{\frac{2}{\pi}}\exp(-\frac{1}{3}r)(xy)$$

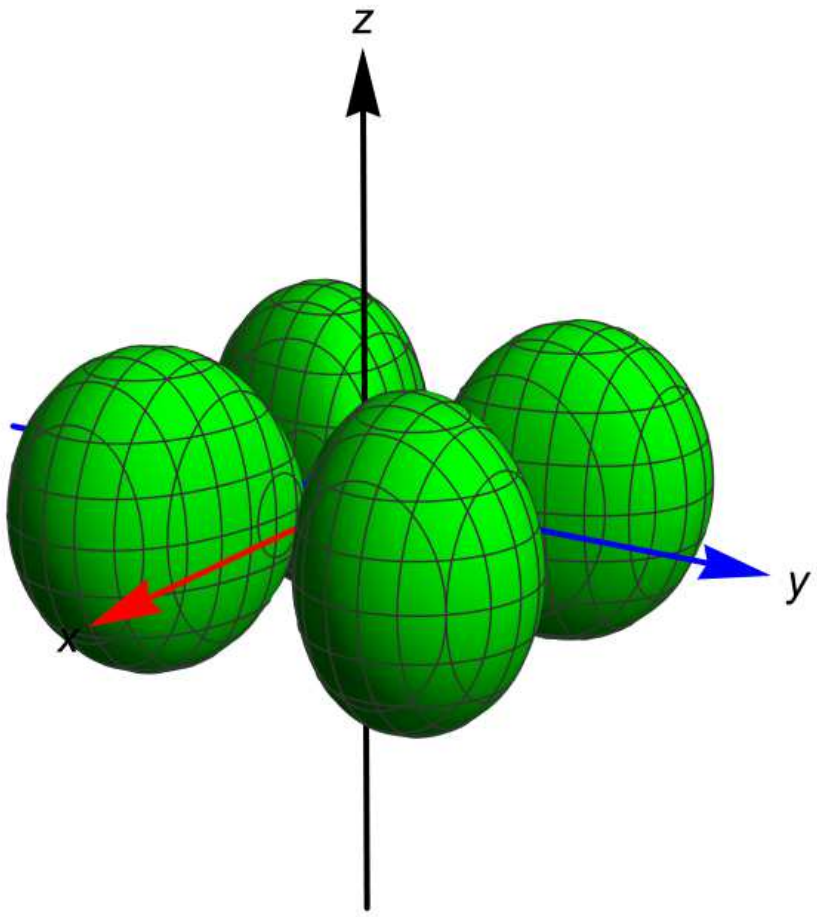


Fig.4a ContourPlot3D of $\left|R_{3d}(r)\right|^2 \left|\left\langle \theta,\phi \right| \hat{U}_{3d} \left| l=2, m=2 \right\rangle\right|^2$: xy

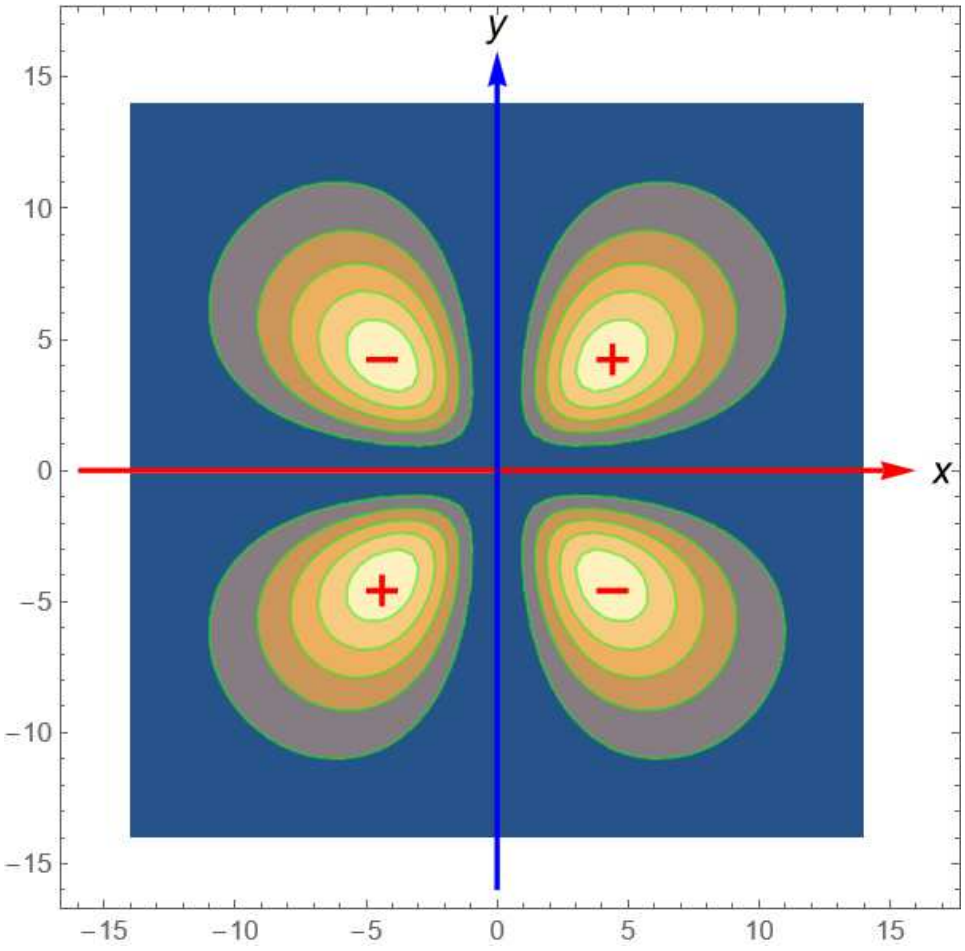


Fig.4b ContourPlot of $\left|R_{3d}(r)\right|^2 \left|\left\langle \theta,\phi \middle| \hat{U}_{3d} \middle| l=2, m=2 \right\rangle\right|^2$ with $z = 0$ (x-y plane).

(b) $\left|d(yz)\right\rangle = \hat{U}_{3d}\left|2,1\right\rangle = \frac{i}{\sqrt{2}}[\left|2,1\right\rangle + \left|2,-1\right\rangle]$

$$\left\langle \mathbf{r} \middle| d(yz) \right\rangle = \frac{1}{81}\sqrt{\frac{2}{\pi}} \exp(-\frac{1}{3}r)(yz)$$

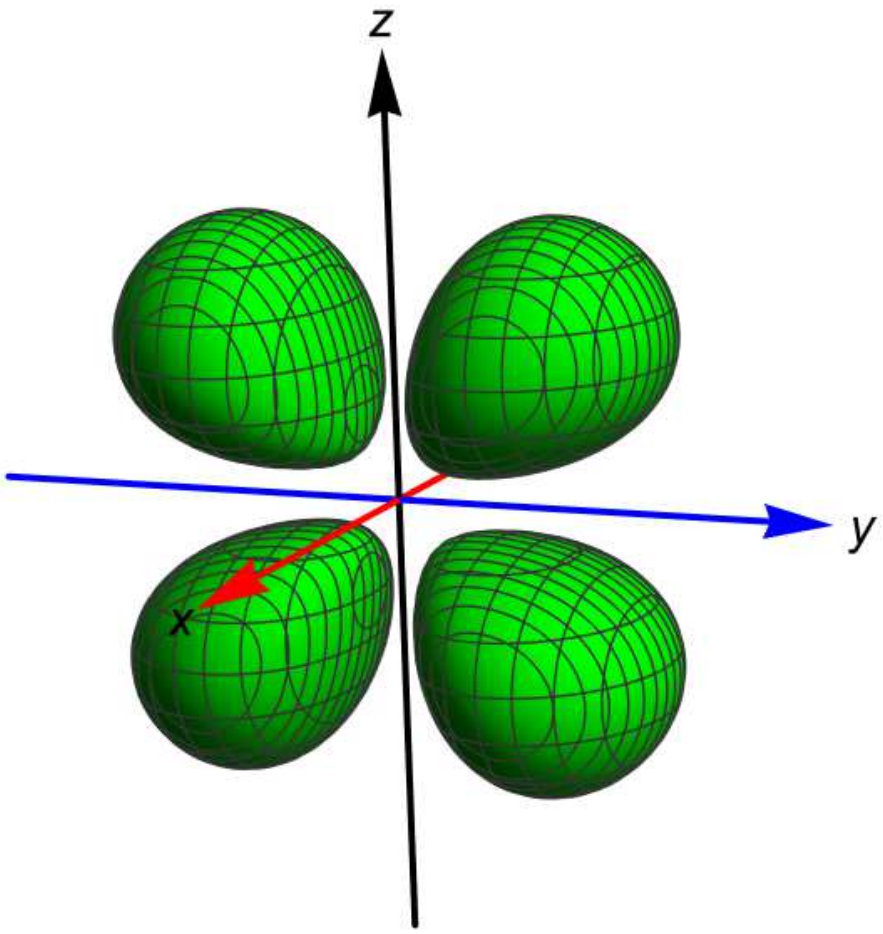


Fig.5a ContourPlot3D of $\left|R_{3d}(r)\right|^2 \left|\left\langle \theta,\phi \right| \hat{U}_{3d} \left| l=2, m=1 \right\rangle\right|^2$: yz

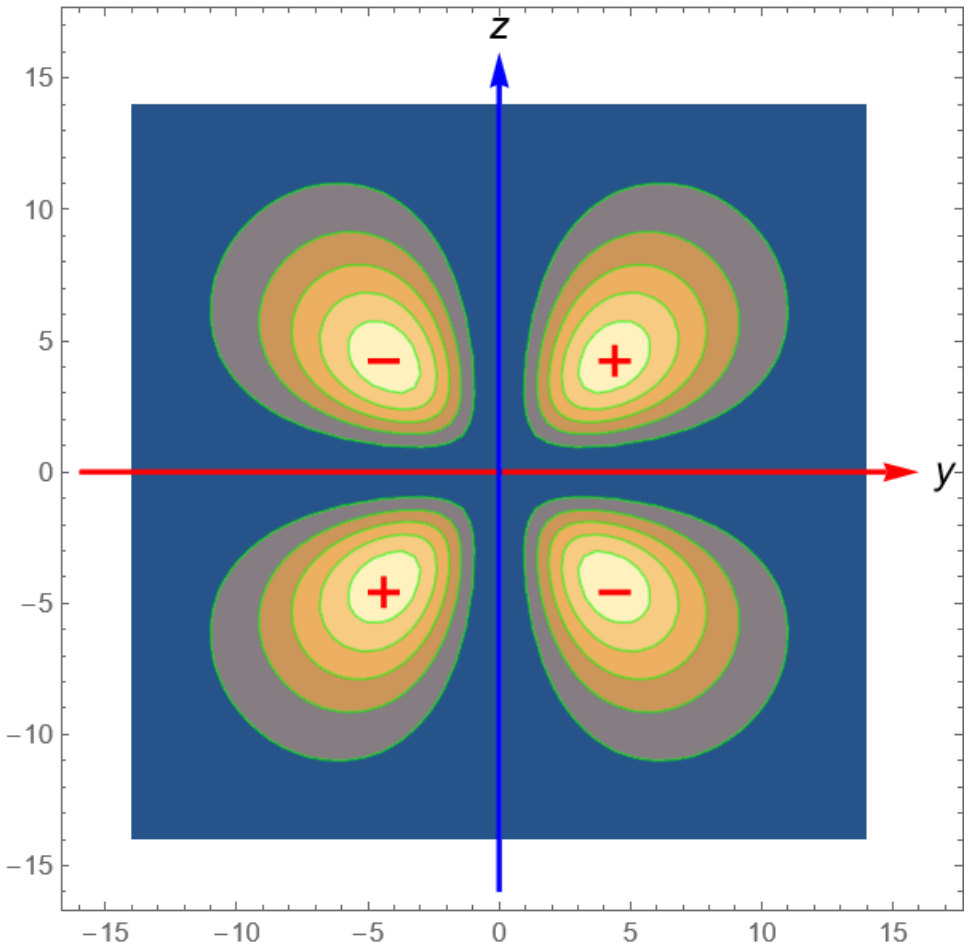


Fig.5b ContourPlot of $\left|R_{3d}(r)\right|^2 \left|\langle\theta,\phi|\hat{U}_{3d}\,|l=2,m=1\rangle\right|^2$ with $x=0$ (y-$z$plane).

(c) $|d(zx)\rangle = \hat{U}_{3d}\,|2,-1\rangle = -\frac{1}{\sqrt{2}}[|2,1\rangle - |2,-1\rangle]$,

$$\langle \mathbf{r}\,|d(yz)\rangle = \frac{1}{81}\sqrt{\frac{2}{\pi}}\exp(-\frac{1}{3}r)(zx)$$

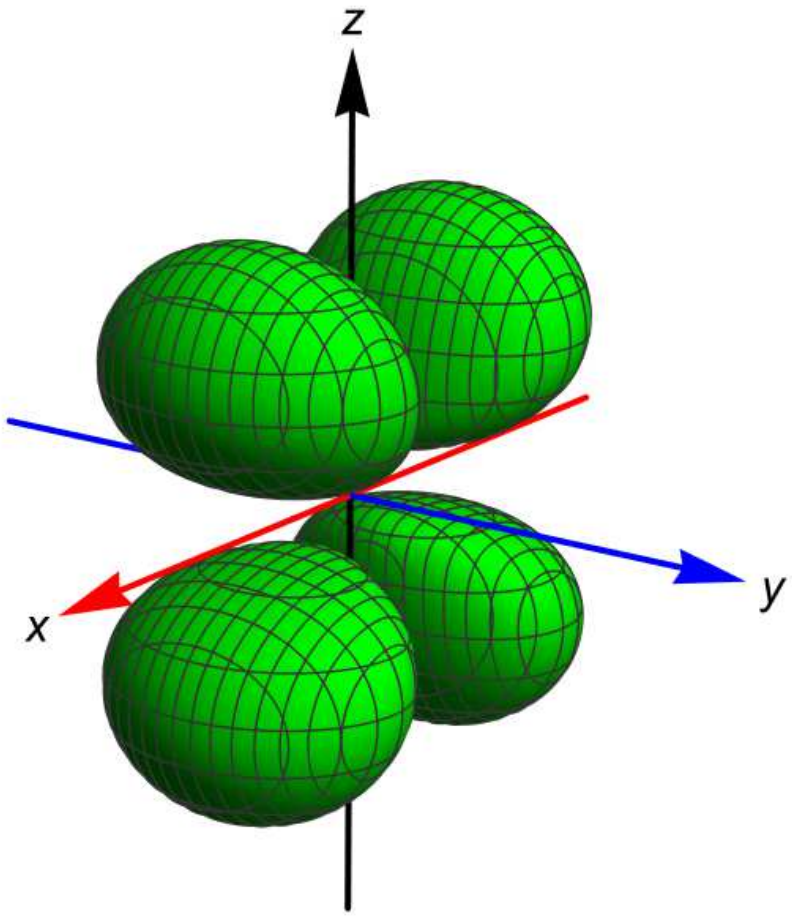


Fig.6a ContourPlot3D of $\left|R_{3d}(r)\right|^2 \left|\left\langle \theta,\phi \right| \hat{U}_{3d} \left| l=2, m=-1 \right\rangle\right|^2$: zx

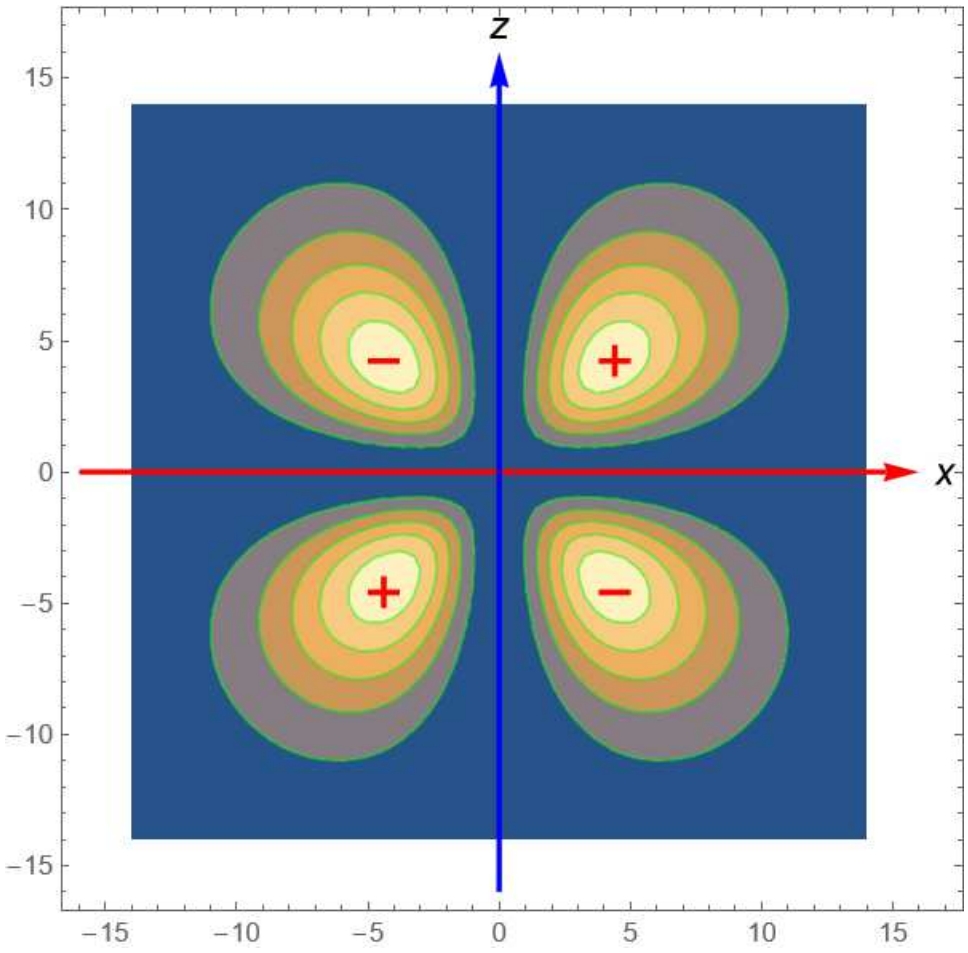


Fig.6b ContourPlot of $\left|R_{3d}(r)\right|^2 \left|\left\langle \theta,\phi\right|\hat{U}_{3d}\left|l=2,m=-1\right\rangle\right|^2$ with $y=0$ (z-x plane).

(d) $\left|d(x^2-y^2)\right\rangle = \hat{U}_{3d}\left|2,-2\right\rangle = \frac{1}{\sqrt{2}}[\left|2,2\right\rangle + \left|2,-2\right\rangle]$,

$$\left\langle \mathbf{r}\right|\left.d(x^2-y^2)\right\rangle = \frac{1}{81\sqrt{2\pi}}\exp(-\frac{1}{3}r)(x^2-y^2)$$

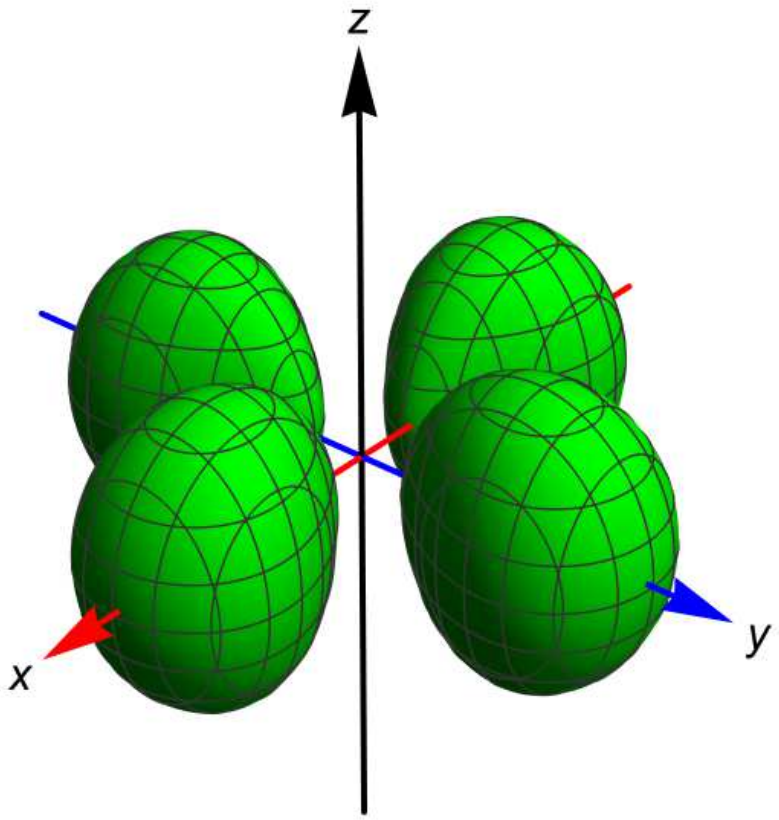


Fig.7a ContourPlot3D of $\left|R_{3d}(r)\right|^2 \left|\left\langle \theta,\phi \right| \hat{U}_{3d} \left| l=2, m=-2 \right\rangle\right|^2 :\ x^2 - y^2$

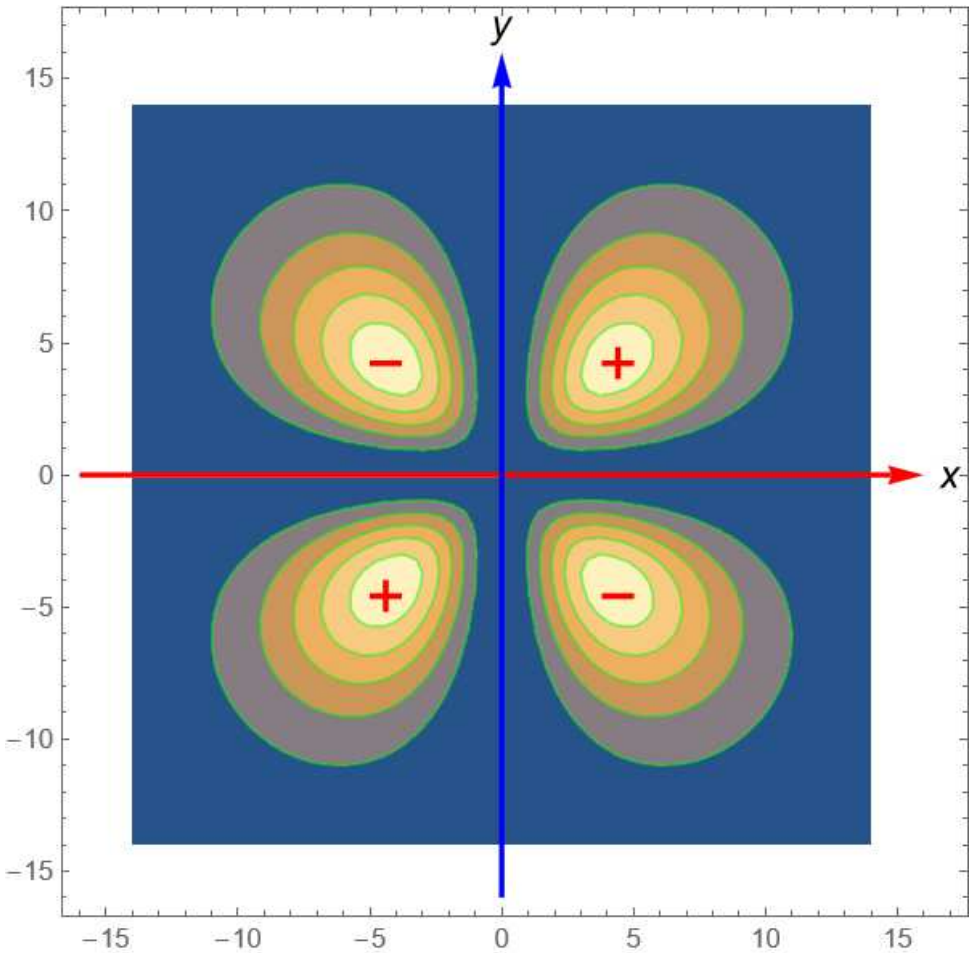


Fig.7b ContourPlot of $\left|R_{3d}(r)\right|^2 \left|\left\langle \theta,\phi\right|\hat{U}_{3d}\left|l=2,m=-2\right\rangle\right|^2$ with $y = 0$ (z-x plane).

(e) $\left|d(3z^2-r^2\right\rangle = \hat{U}_{3d}\left|2,0\right\rangle = \left|2,0\right\rangle$

$$\left\langle \mathbf{r}\left|d(3z^2-r^2)\right\rangle = -\frac{1}{81\sqrt{6\pi}}\exp(-\frac{1}{3}r)(2z^2-x^2-y^2)\right.$$

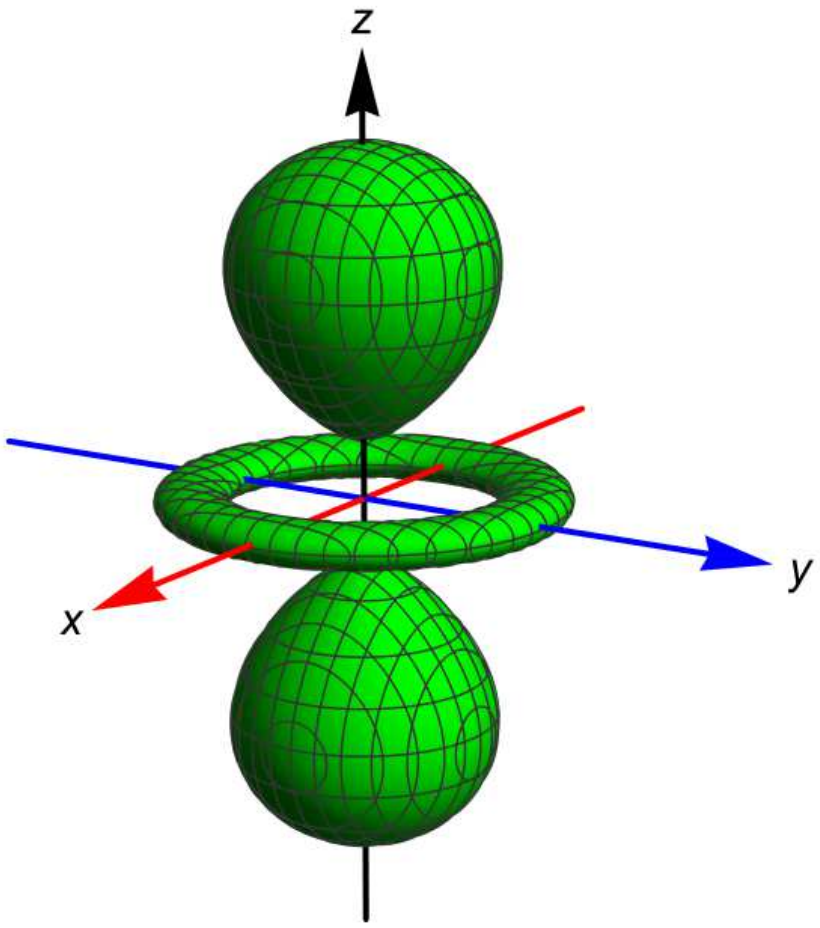


Fig.8a ContourPlot3D of $\left|R_{3d}(r)\right|^2 \left|\left\langle \theta,\phi \right| \hat{U}_{3d} \left| l=2, m=0 \right\rangle\right|^2 :\ 3z^2 - r^2$

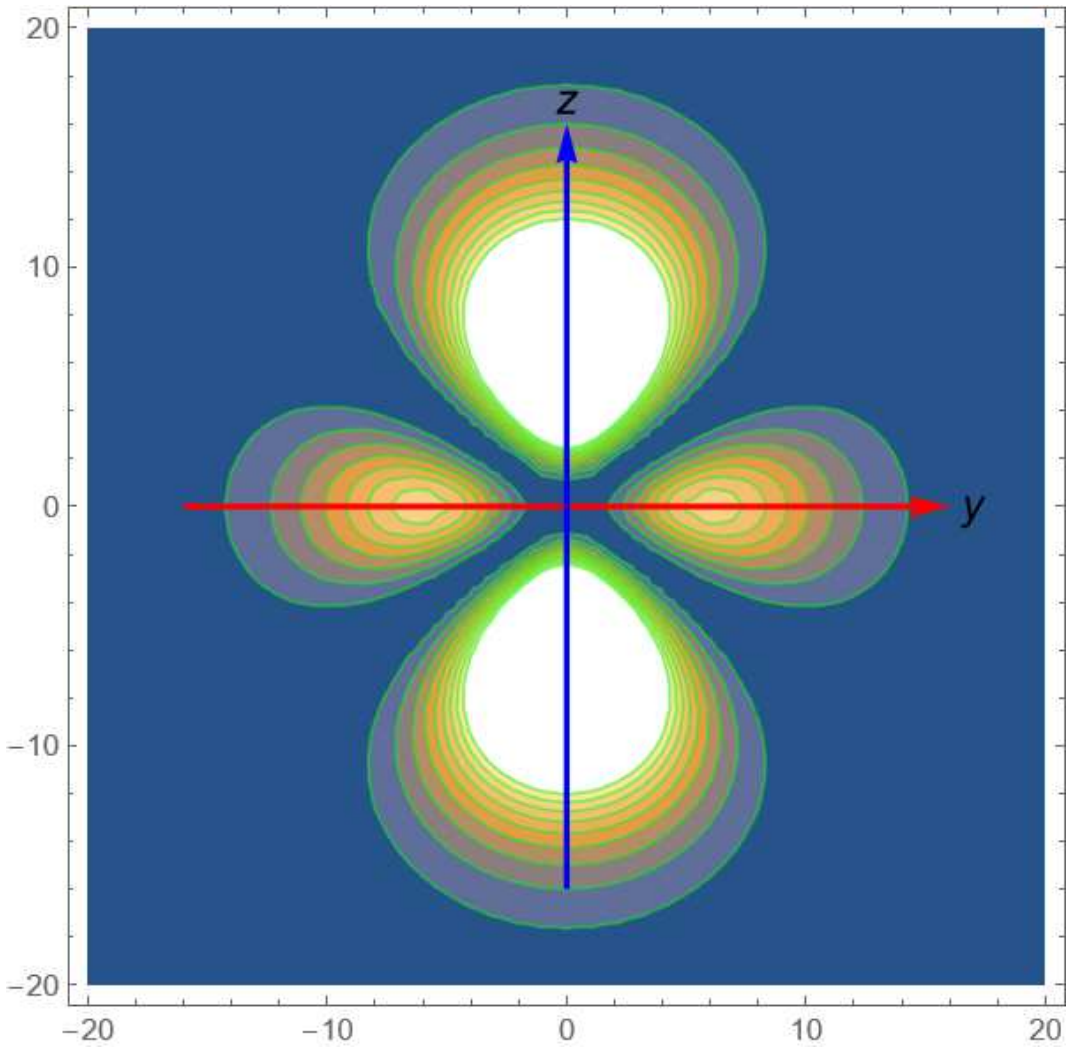


Fig.8b ContourPlot of $\left|R_{3d}(r)\right|^2 \left|\left\langle \theta,\phi\left|\hat{U}_{3d}\right|l=2,m=0\right\rangle\right|^2$ with $x = 0$ (y-z plane).

Shape of d-Orbital

For *d* orbitals, the magnetic orbital quantum number is given as (2, 1, 0, -1, -2). As a result, we can claim there are five *d*-orbitals. These orbitals are denoted by the symbols d_{xy}, d_{yz}, d_{xz}, $d_{x^2-y^2}$, and d_{z^2}.The forms of the first four d orbitals are similar to each other, which differs from the d_{z^2} orbital, but the energy of all five d orbitals is the same.

***f*-orbit**

The unitary operator

$$\hat{U}_{4f} = \frac{1}{4}\begin{pmatrix} -\sqrt{5} & \sqrt{3} & 0 & 0 & 0 & -i\sqrt{3} & -i\sqrt{5} \\ 0 & 0 & 2\sqrt{2} & 0 & -i2\sqrt{2} & 0 & 0 \\ \sqrt{3} & \sqrt{5} & 0 & 0 & 0 & i\sqrt{5} & -i\sqrt{3} \\ 0 & 0 & 0 & 4 & 0 & 0 & 0 \\ -\sqrt{3} & -\sqrt{5} & 0 & 0 & 0 & i\sqrt{5} & -i\sqrt{3} \\ 0 & 0 & 2\sqrt{2} & 0 & i2\sqrt{2} & 0 & 0 \\ \sqrt{5} & -\sqrt{3} & 0 & 0 & 0 & -i\sqrt{3} & -i\sqrt{5} \end{pmatrix}$$

$$\hat{U}_{4f}{}^{+} = \frac{1}{4}\begin{pmatrix} -\sqrt{5} & 0 & \sqrt{3} & 0 & -\sqrt{3} & 0 & \sqrt{5} \\ \sqrt{3} & 0 & \sqrt{5} & 0 & -\sqrt{5} & 0 & -\sqrt{3} \\ 0 & 2\sqrt{2} & 0 & 0 & 0 & 2\sqrt{2} & 0 \\ 0 & 0 & 0 & 4 & 0 & 0 & 0 \\ 0 & i2\sqrt{2} & 0 & 0 & 0 & -i2\sqrt{2} & 0 \\ i\sqrt{3} & 0 & -i\sqrt{5} & 0 & -i\sqrt{5} & 0 & i\sqrt{3} \\ i\sqrt{5} & 0 & i\sqrt{3} & 0 & i\sqrt{3} & 0 & i\sqrt{5} \end{pmatrix} --$$

$$\hat{U}_{4f}{}^{+}\hat{U}_{4f} = \hat{1}$$

((**K. Yosida**))
K. Yosida, Theory of Magnetism (Springer-Verlag, 1996)

$$\hat{U}_{4f}|3,3\rangle = \frac{1}{4}(-\sqrt{5}|3,3\rangle + \sqrt{3}|3,1\rangle - \sqrt{3}|3,-1\rangle + \sqrt{5}|3,-3\rangle) \qquad x(5x^2-3r^2)$$

$$\hat{U}_{4f}|3,2\rangle = \frac{1}{4}(\sqrt{3}|3,3\rangle + \sqrt{5}|3,1\rangle - \sqrt{5}|3,-1\rangle - \sqrt{3}|3,-3\rangle) \qquad x(y^2-z^2)$$

$$\hat{U}_{4f}|3,1\rangle = \frac{1}{\sqrt{2}}(|3,2\rangle + |3,-2\rangle) \qquad z(x^2-y^2)$$

$$\hat{U}_{4f}|3,0\rangle = |3,0\rangle \qquad z(5z^2-3r^2)$$

$$\hat{U}_{4f}|3,-1\rangle = \frac{i}{\sqrt{2}}(-|3,2\rangle + |3,-2\rangle) \qquad xyz$$

$$\hat{U}_{4f}|3,-2\rangle = \frac{i}{4}(-\sqrt{3}|3,3\rangle + \sqrt{5}|3,1\rangle + \sqrt{5}|3,-1\rangle - \sqrt{3}|3,-3\rangle) \qquad y(z^2-x^2)$$

$$\hat{U}_{4f}|3,-3\rangle = -\frac{i}{4}(\sqrt{5}|3,3\rangle + \sqrt{3}|3,1\rangle + \sqrt{3}|3,-1\rangle + \sqrt{5}|3,-3\rangle) \qquad y(5y^2-3r^2)$$

The probability density for the electron in the 4f orbit is defined by

$$\left|R_{4f}(r)\right|^2 \left|\langle\theta,\phi|\hat{U}_{4f}\,|l=3,m\rangle\right|^2$$

where m = 3, 2, 1, 0, -1, -2, -3. We make a ContourPlot3D of the probability density using the Mathematica program.

$\hat{U}_{4f}\,|3,3\rangle$: $x(5x^2-3r^2)$

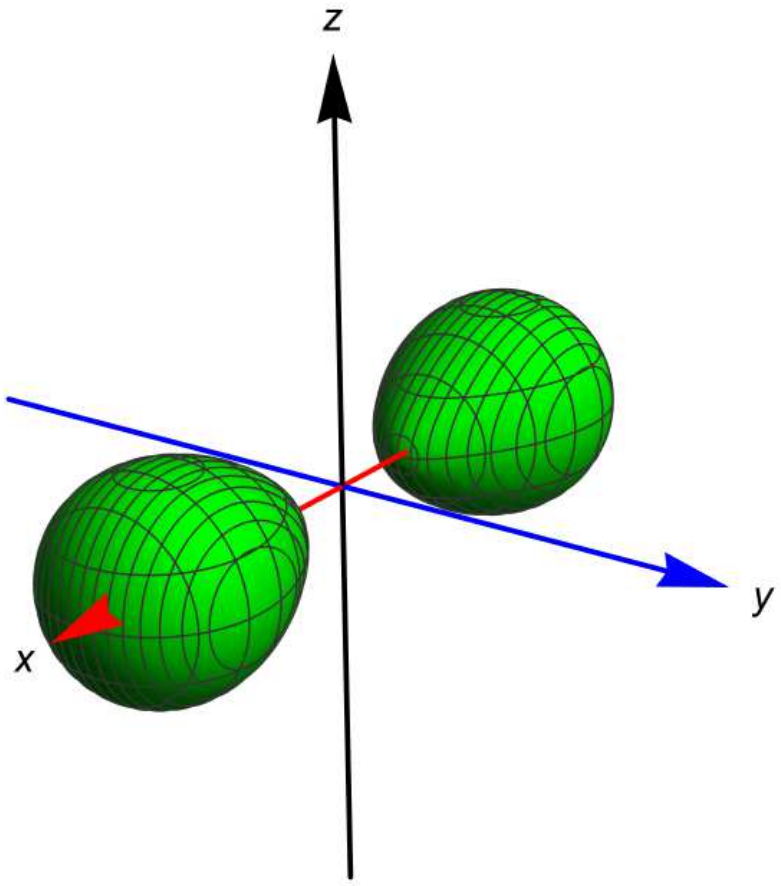


Fig.9 ContourPlot3D of $\left|R_{4f}(r)\right|^2 \left|\langle\theta,\phi|\hat{U}_{4f}\,|l=3,m=3\rangle\right|^2$: $x(5x^2-3r^2)$

$\hat{U}_{4f}\,|3,2\rangle$ $x(y^2-z^2)$

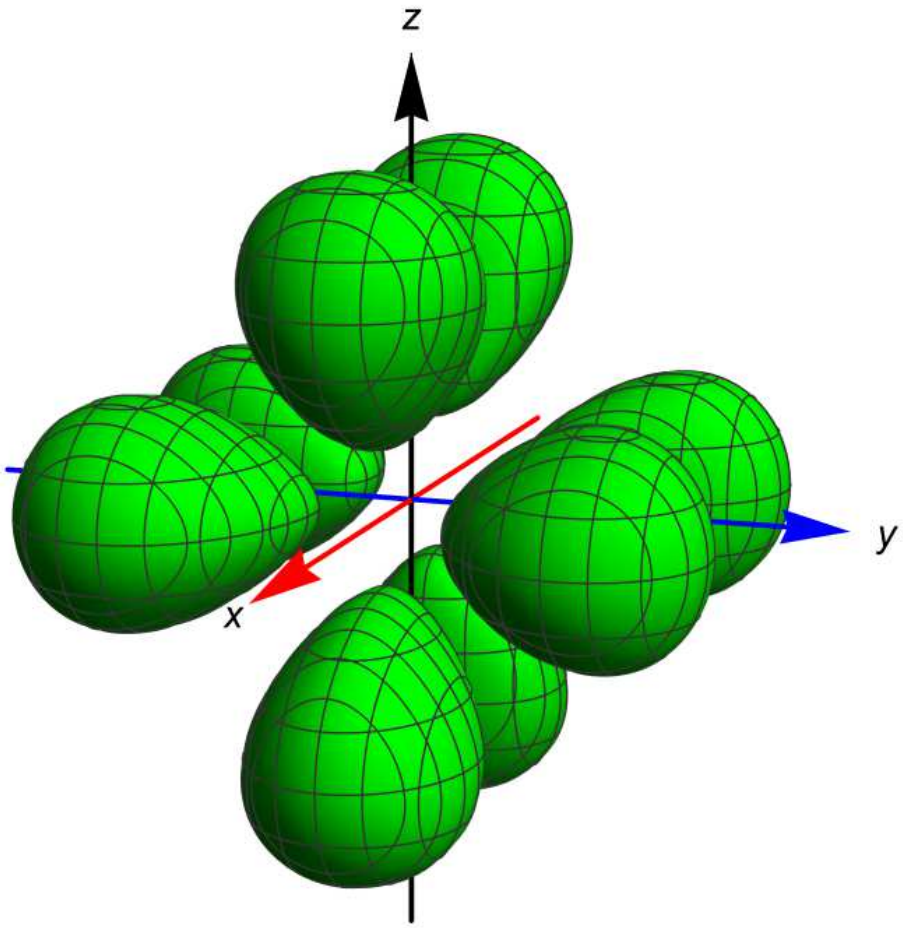


Fig.10 ContourPlot3D of $\left|R_{4f}(r)\right|^2 \left|\langle\theta,\phi|\hat{U}_{4f}\,|l=3,m=2\rangle\right|^2 : x(y^2-z^2)$

$\hat{U}_{4f}\,\|3,1\rangle$	$z(x^2-y^2)$

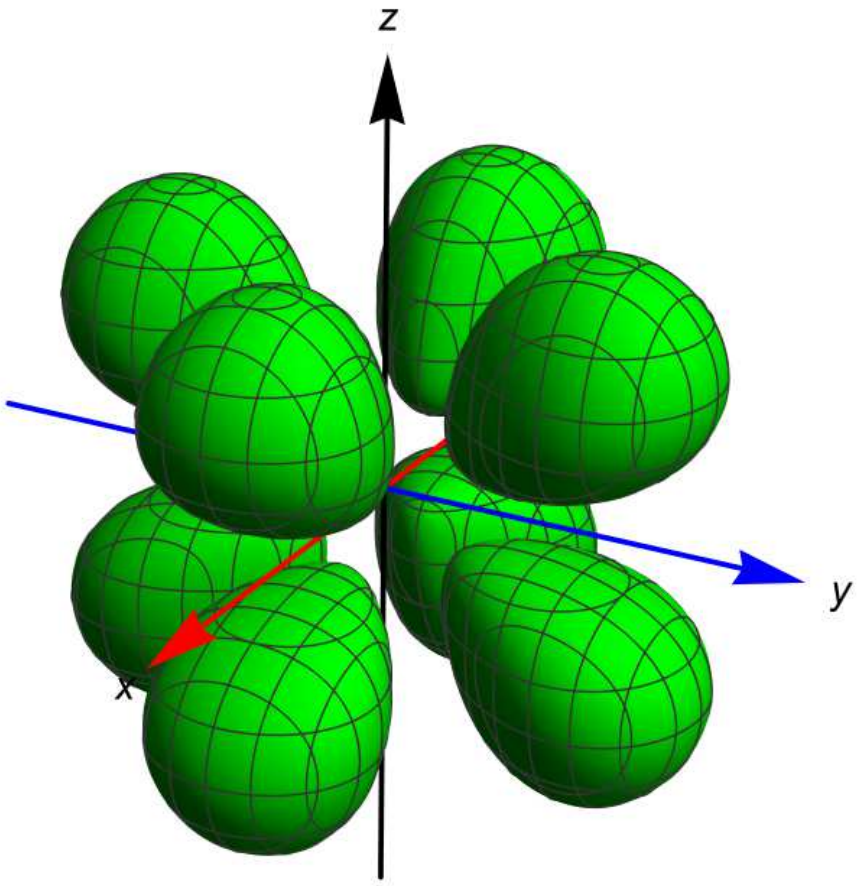


Fig.11 ContourPlot3D of $\left|R_{4f}(r)\right|^2 \left|\langle\theta,\phi|\hat{U}_{4f}|l=3,m=1\rangle\right|^2 :\ z(x^2-y^2)$

$\hat{U}_{4f}|3,0\rangle$ $z(5z^2-3r^2)$

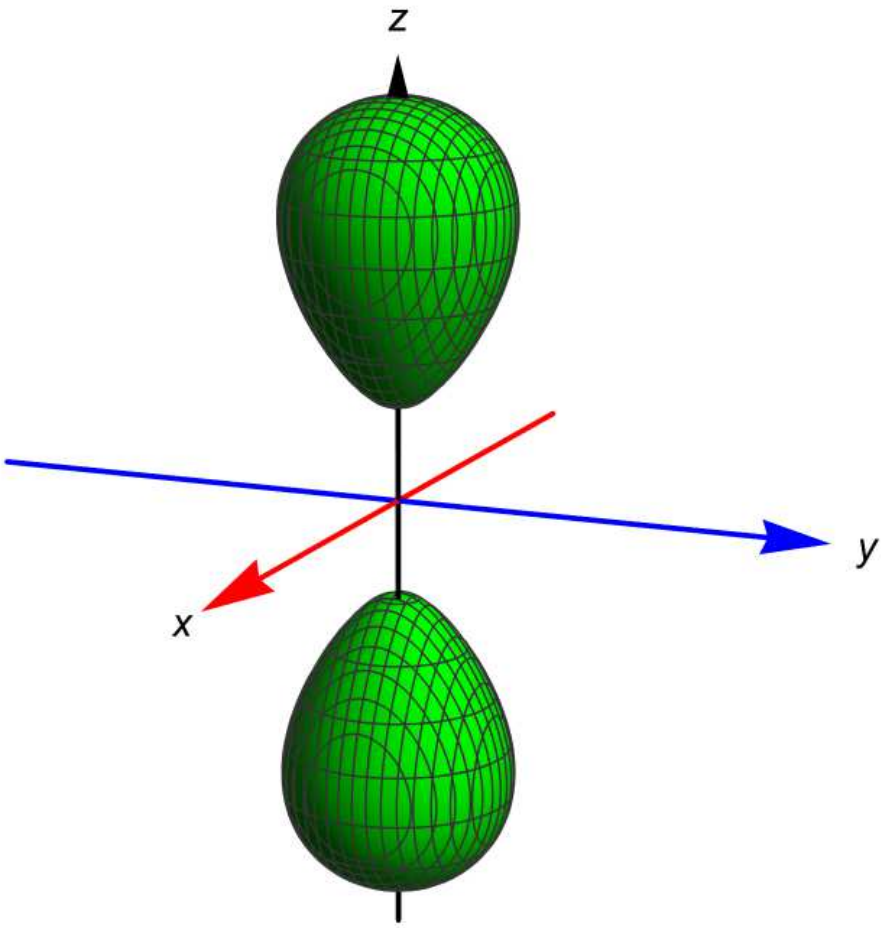


Fig.12 ContourPlot3D of $\left|R_{4f}(r)\right|^2 \left|\langle\theta,\phi|\hat{U}_{4f}\,|l=3,m=0\rangle\right|^2 :\ z(5z^2-3r^2)$

---

xyz

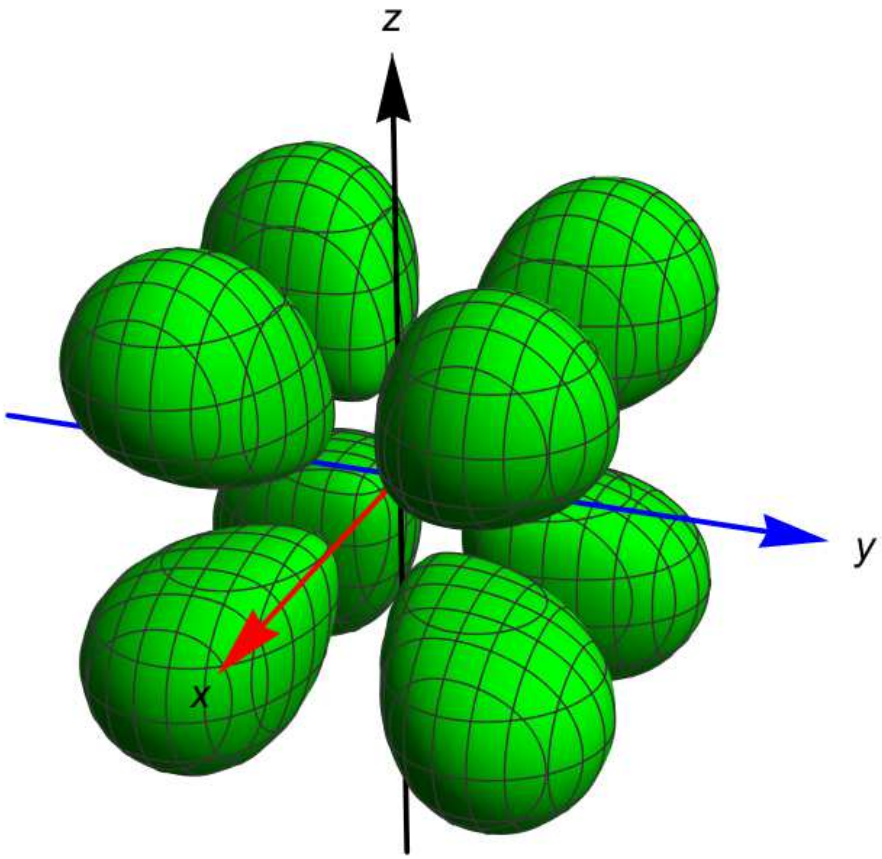


Fig.13 ContourPlot3D of $\left|R_{4f}(r)\right|^2 \left|\langle\theta,\phi|\hat{U}_{4f}\,|l=3,m=-1\rangle\right|^2$: xyz

---

$\hat{U}_{4f}\,|3,-2\rangle$ $y(z^2-x^2)$

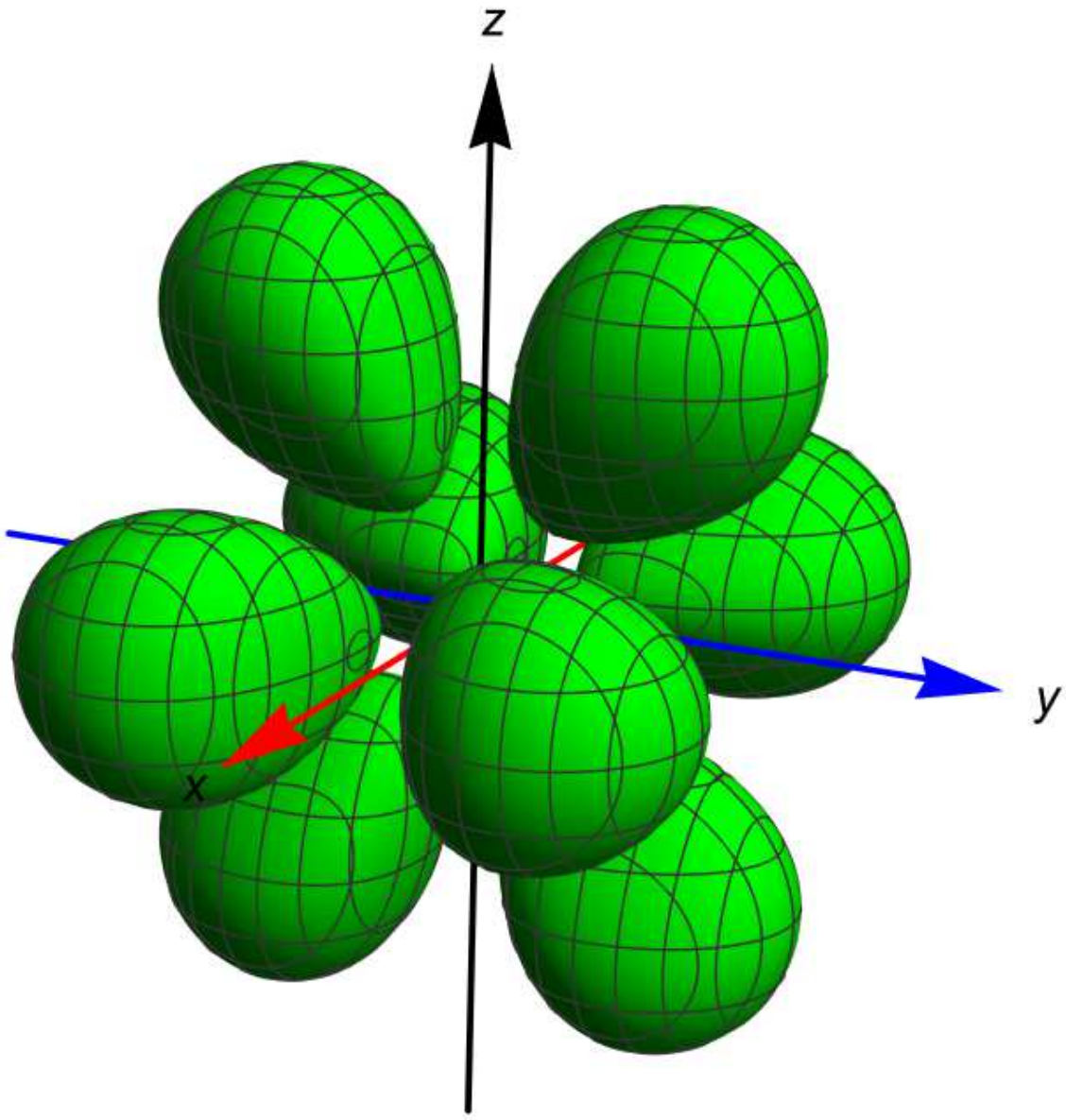


Fig.14 ContourPlot3D of $\left|R_{4f}(r)\right|^2\left|\langle\theta,\phi|\hat{U}_{4f}\,|l=3,m=-2\rangle\right|^2$: $y(z^2-x^2)$.

$\hat{U}_{4f}\,\|3,-3\rangle$	$y(5y^2-3r^2)$

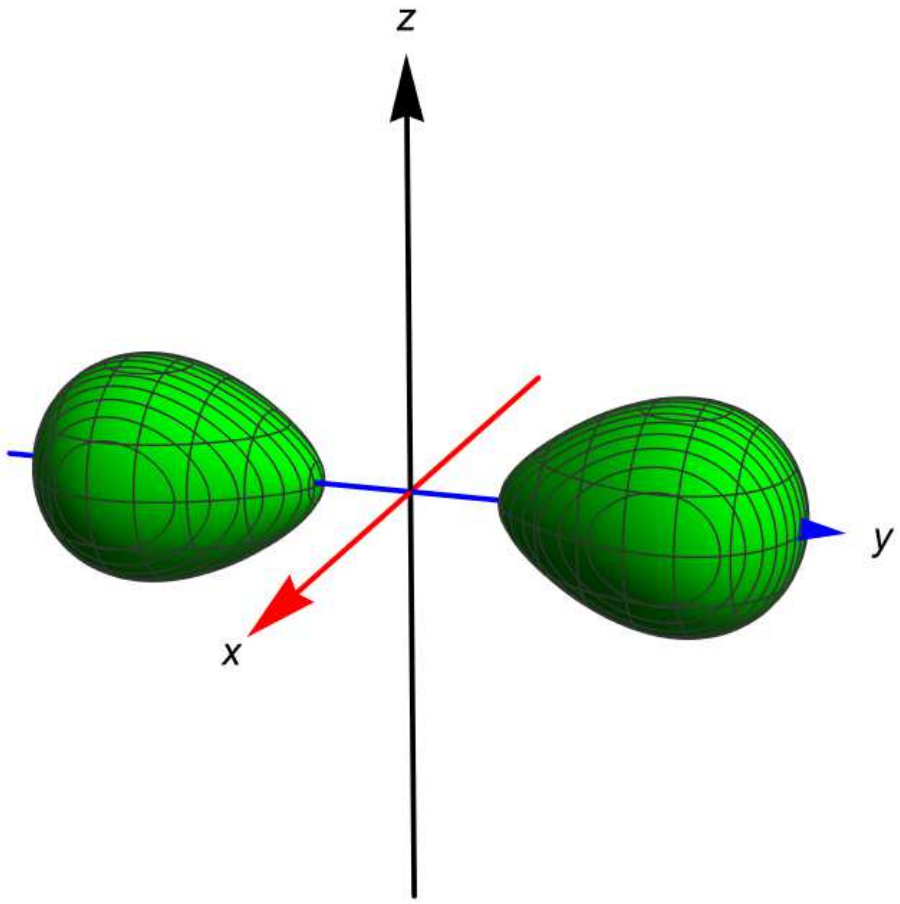
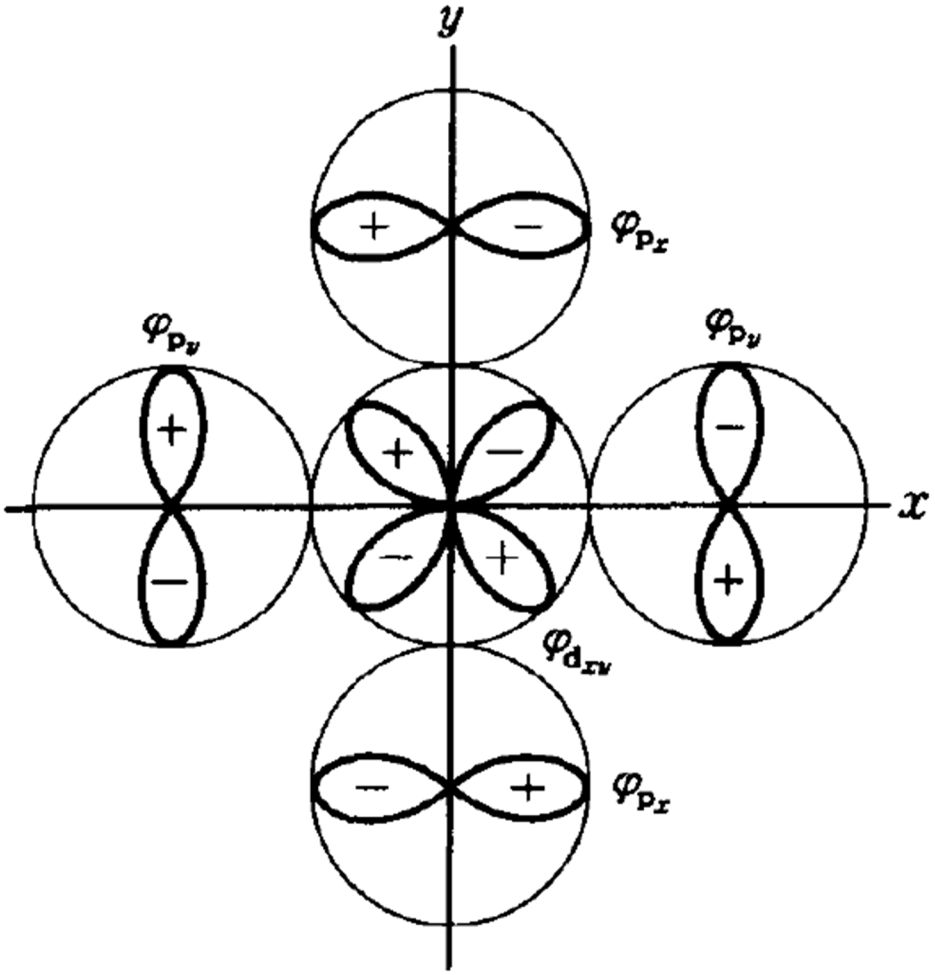
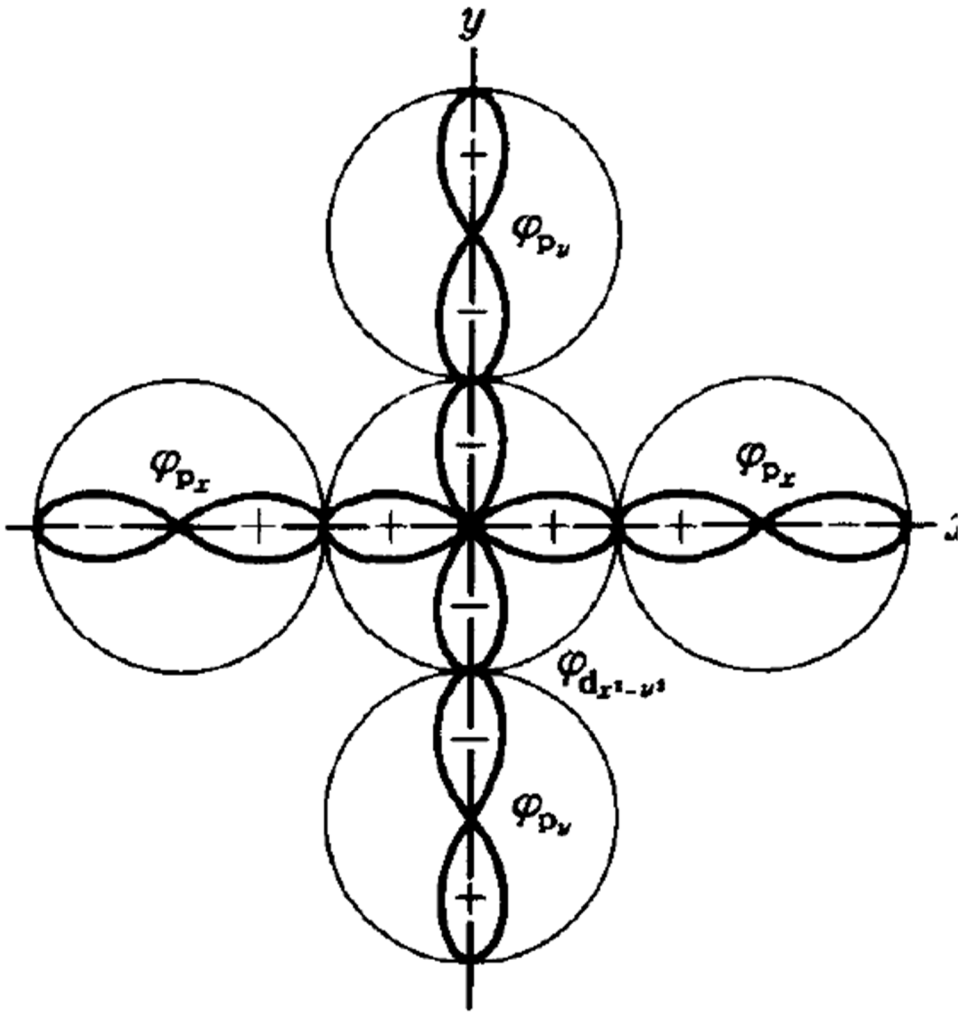


Fig.15 ContourPlot3D of $\left|R_{4f}(r)\right|^2 \left|\left\langle \theta,\phi \left| \hat{U}_{4f} \right| l=3, m=-3 \right\rangle\right|^2 :\ y(5y^2-3r^2)$

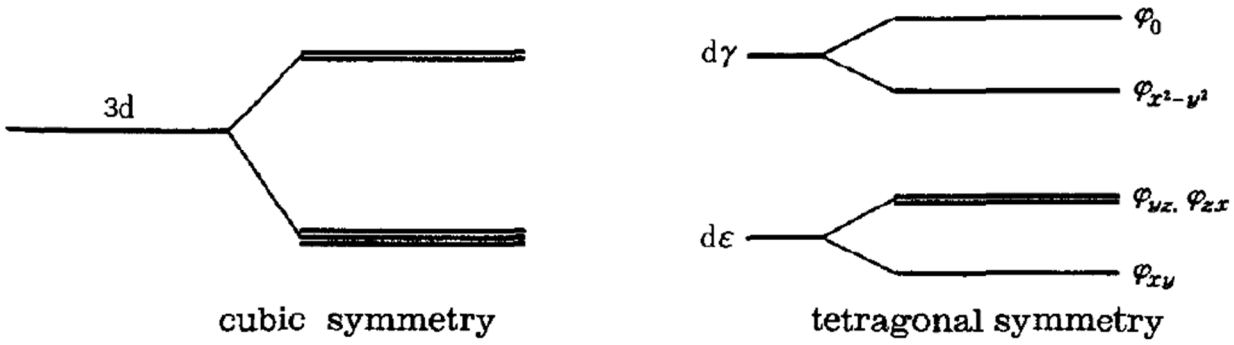
Discussion



(a)



(b)



First, having in mind an ionic crystal with the NaCl-type structure, we assume that the magnetic ion is surrounded octahedrally by O^{2-} anions, For the five independent 3d wave functions, we have

$d\varepsilon$: $d(xy)$, $d(yz)$, $d(zx)$

$d\gamma$: $d(x - y)$ $d(3z^2 - r^2)$

The electron transfer Hamiltonian combines these wave functions with the *p*-orbitals on neighboring O^{2-} ions. As a result, the 3*d* orbitals are mixed with the appropriate combinations of the *p* orbitals of surrounding anions. We define three *p* orbitals of O^{2-} as

$p(x)$, $p(y)$, $p(z)$

from symmetry, they mix with the 3*d* orbitals. As is evident from the figure, the $d\varepsilon$ and $d\gamma$ orbitals mix differently with the *p* orbitals and consequently the $d\varepsilon$ and $d\gamma$ orbitals have different energies.

((**Mathematica**))

ContourPlot3D

dxy, dyz, dzx, dx2y2, d3zr

```
Clear["Global`*"];
r2xRule = {r → Sqrt[x^2 + y^2 + z^2], θ → ArcCos[z/Sqrt[x^2 + y^2 + z^2]],
  ϕ → ArcTan[x, y]};
rwave[n_, ℓ_, r_] :=
 1/Sqrt[(n + ℓ)!] (2^(1+ℓ) a0^(-ℓ-3/2) e^(-r/(a0 n)) n^(-ℓ-2) r^ℓ Sqrt[(n - ℓ - 1)!]
    LaguerreL[-1 + n - ℓ, 1 + 2 ℓ, 2 r/(a0 n)]) /. a0 → 1;
```

Combination of spherical harmonics for d orbitals

```
dxy[θ_, ϕ_] :=
 -i/Sqrt[2] (-SphericalHarmonicY[2, 2, θ, ϕ] +
    SphericalHarmonicY[2, -2, θ, ϕ]) // Simplify;
dyz[θ_, ϕ_] :=
 i/Sqrt[2] (SphericalHarmonicY[2, 1, θ, ϕ] +
    SphericalHarmonicY[2, -1, θ, ϕ]) // Simplify;
```

```
dzx[θ_, ϕ_] :=
  1/√2 (-SphericalHarmonicY[2, 1, θ, ϕ] +
     SphericalHarmonicY[2, -1, θ, ϕ]) // Simplify;
dx2y2[θ_, ϕ_] :=
  1/√2 (SphericalHarmonicY[2, 2, θ, ϕ] +
     SphericalHarmonicY[2, -2, θ, ϕ]) // Simplify;
d3zr[θ_, ϕ_] := SphericalHarmonicY[2, 0, θ, ϕ] // Simplify;

a1 = 14;
```

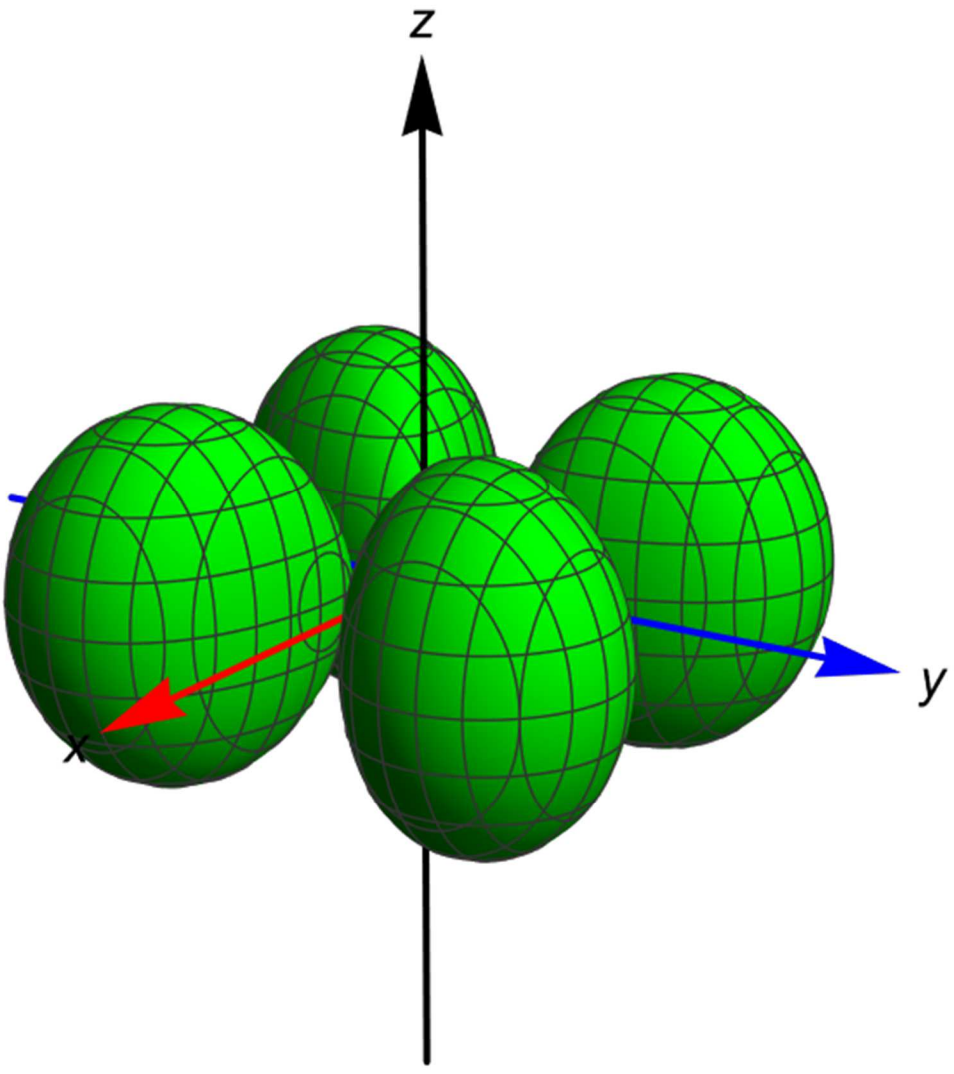
CountourPlot 3D of probability density

```
Ψxy[r_, θ_, ϕ_] := rwave[3, 2, r]^2 Abs[dxy[θ, ϕ]]^2;
 Ψyz[r_, θ_, ϕ_] := rwave[3, 2, r]^2 Abs[dyz[θ, ϕ]]^2;
 Ψzx[r_, θ_, ϕ_] := rwave[3, 2, r]^2 Abs[dzx[θ, ϕ]]^2;
 Ψx2y2[r_, θ_, ϕ_] := rwave[3, 2, r]^2 Abs[dx2y2[θ, ϕ]]^2;
 Ψ3zr[r_, θ_, ϕ_] := rwave[3, 2, r]^2 Abs[d3zr[θ, ϕ]]^2;
 Kxy = ContourPlot3D[Evaluate[Ψxy[r, θ, ϕ] //. r2xRule],
    {x, -a1, a1}, {y, -a1, a1}, {z, -a1, a1}, PlotPoints → 20,
    ContourStyle → {Green}, Boxed → False, Axes → False];
```

```
Kyz = ContourPlot3D[Evaluate[Ψyz[r, θ, ϕ] //. r2xRule],
  {x, -a1, a1}, {y, -a1, a1}, {z, -a1, a1}, PlotPoints → 20,
  ContourStyle → {Green}, Boxed → False, Axes → False];
Kzx = ContourPlot3D[Evaluate[Ψzx[r, θ, ϕ] //. r2xRule],
  {x, -a1, a1}, {y, -a1, a1}, {z, -a1, a1}, PlotPoints → 20,
  ContourStyle → {Green}, Boxed → False, Axes → False];
Kx2y2 = ContourPlot3D[Evaluate[Ψx2y2[r, θ, ϕ] //. r2xRule],
  {x, -a1, a1}, {y, -a1, a1}, {z, -a1, a1}, PlotPoints → 20,
  ContourStyle → {Green}, Boxed → False, Axes → False];
K3zr = ContourPlot3D[Evaluate[Ψ3zr[r, θ, ϕ] //. r2xRule],
  {x, -a1, a1}, {y, -a1, a1}, {z, -a1, a1}, PlotPoints → 20,
  ContourStyle → {Green}, Boxed → False, Axes → False];
```

```
Z1 = {0, 0, 16};
f1 = Graphics3D[{Red, Thick, Arrowheads[0.04], Arrow[{{-X1, )
    Blue, Arrow[{{-Y1, Y1}}], Black, Arrow[{{-Z1, Z1}}],
    Text[Style["x", Black, Italic, 15], {17, 0, 0}],
    Text[Style["y", Black, Italic, 15], {0, 17, 0}],
    Text[Style["z", Black, Italic, 15], {0, 0, 17}]}];

Show[Kxy, f1, PlotRange → All]
```



```
Show[Kyz, f1, PlotRange → All]
```