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Understanding Atomic (Hydrogenic) Orbitals, Part 2, d-Orbitals

Carl W. David
University of Connecticut, Carl.David@uconn.edu

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C. W. David
Department of Chemistry
University of Connecticut
Storrs, Connecticut 06269-3060
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I. SYNOPSIS

This material is an extension of earlier material concerning atomic orbitals and their drawings.

II. INTRODUCTION

The d-orbitals are even less well known than the s and p-orbitals which preceded them. Since they are intimately involved in transition metal chemistry, chemists must understand them reasonably well. We deal with them here, starting with the d_{z^2} orbital, and then considering the d_{xy} orbital and the $d_{x^2-y^2}$ orbital.

III. d_{z^2} ORBITALS

When we get to d-orbitals (and higher) the visualization process becomes harder (and harder). Again, we start with reduced dimensionality plots, leading up, hopefully, to a *Gestalt* of what these orbitals "look like".

What is a typical d-orbital? The easiest one to deal with is the d_{z^2} orbital,

$$(3z^2 - r^2)e^{-r/3}$$

We start by noting that when x=y=0 we have

$$(2z^2)e^{-|z|/3}$$

which we can plot in Figure 1. Notice that the wave function vanishes at the origin, and is positive definite on the z-axis. Notice further that it has two maxima, one on the positive, and one on the negative z-axis.

Next, we attempt to see how this function changes as we go from the z-axis into the space of x and y not equal to zero.

$$(3z^2 - x^2 - y^2 - z^2)e^{-r/3} = (2z^2 - x^2 - y^2)e^{-r/3}$$

If we hold $z = 0$ and plot $\psi_{d_{z^2}}$ versus x and y, we obtain in inkling of what this function is doing, but only an inkling! We see this specialized plot in Figure 2. Notice that the wave function appears negative everywhere in the plot!

This is not a traditional view of this orbital, and we need to progress to the more traditional view. To do this, we plot a contour plot of this same orbital (see Figure 3) as a function of x and z, i.e., $f(x, 0, z)$. It is hard to see
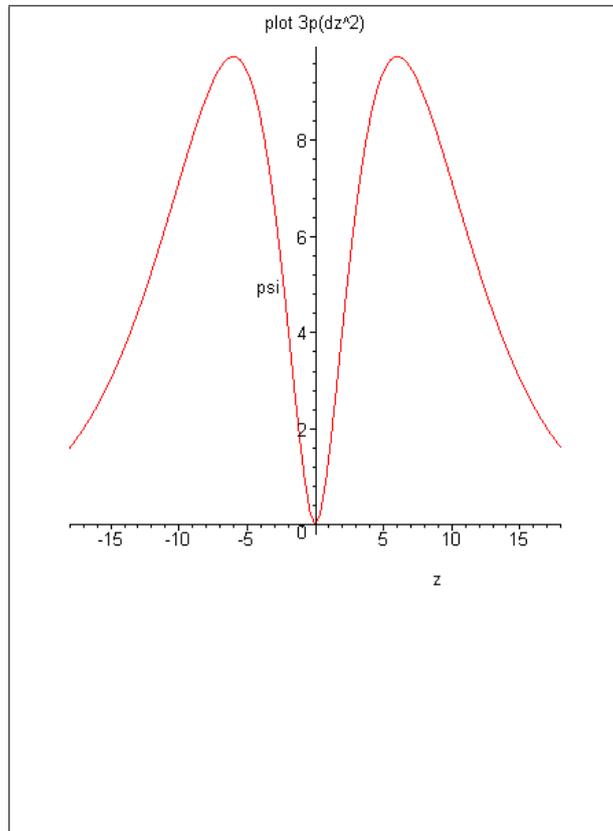
FIG. 1: The d_{z^2} orbital as a function of z with $y = 0$ and $x = 0$.

that the orbital is actually negative at $z = 0$ and $x \neq 0$, but it is, and the lobes along the x axis are actually negative lobes, relative to the positive lobes on the z-axis. Contrary to the p-orbitals, the orbital is positive on the $+z$ and the $-z$ axis!

To get closer to standard textbook form, we attempt the polar plot of the angular part of the wave function. We know that the wave function is

$$(3z^2 - r^2)e^{-r/3}$$

which is, in spherical polar coordinates

$$(3(r\cos\theta)^2 - r^2)e^{-r/3}$$
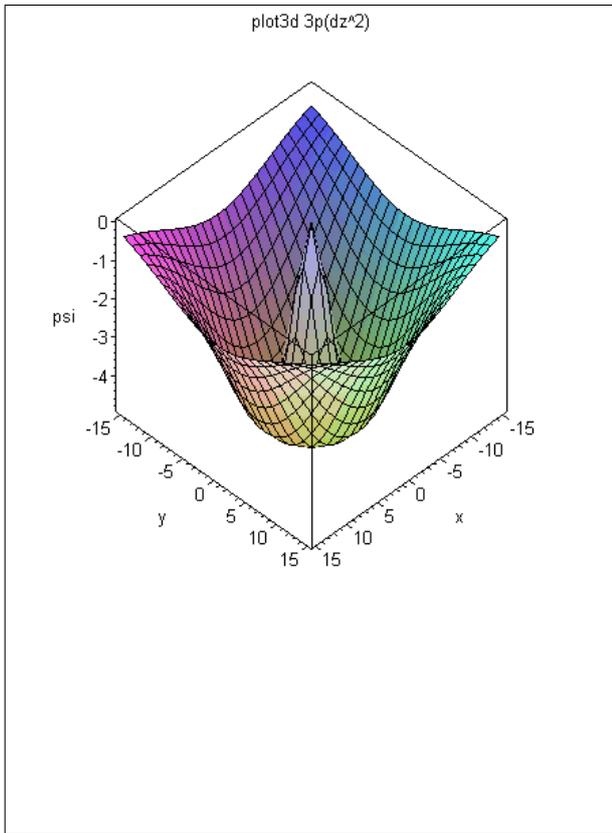
so the polar part is

$$3\cos^2\theta - 1$$

FIG. 2: The d_{z^2} orbital as a function of x and y and $z = 0$.

the negative lobe of which, in polar plot form, can be seen in Figure 3 while the positive lobe can be seen in the same format in Figure 4. Finally, the composite plot, including both lobes, can be seen in Figure 5 Remember, the signs of the three regions are not shown, the donut (or torus) is negative relative to the other two lobes!

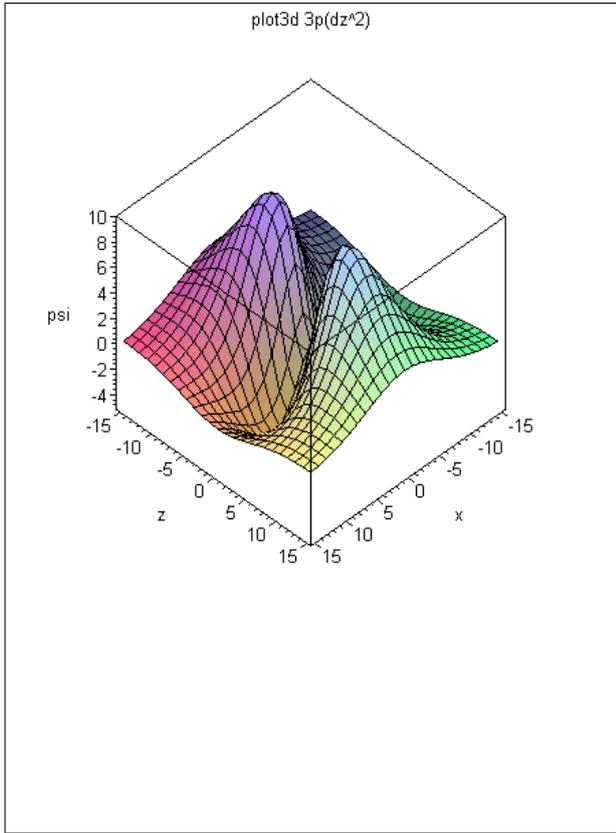The maple code to do these plots follows:

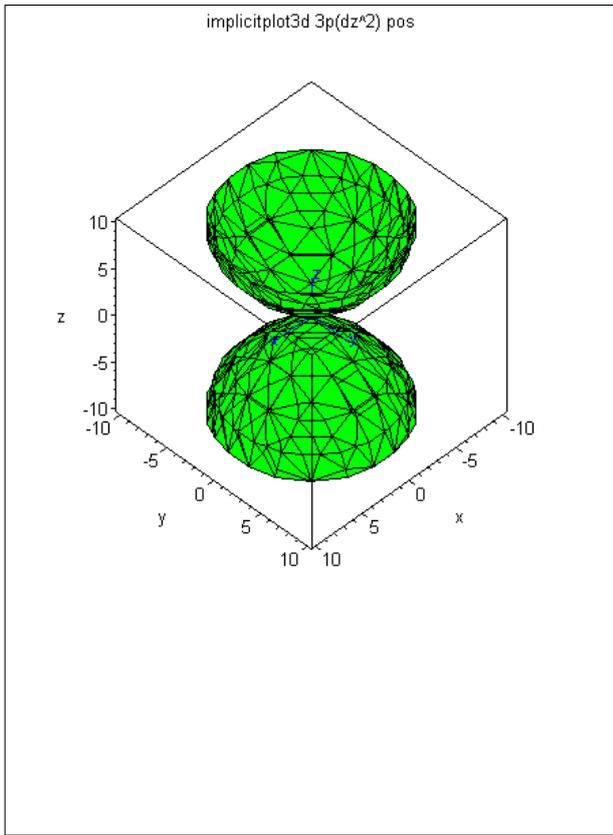FIG. 3: The d_{z^2} orbital as a function of x and z and $y = 0$.

FIG. 4: The d_{z^2} orbital in "implicitplot3D" form. Shown is the negative lobe.
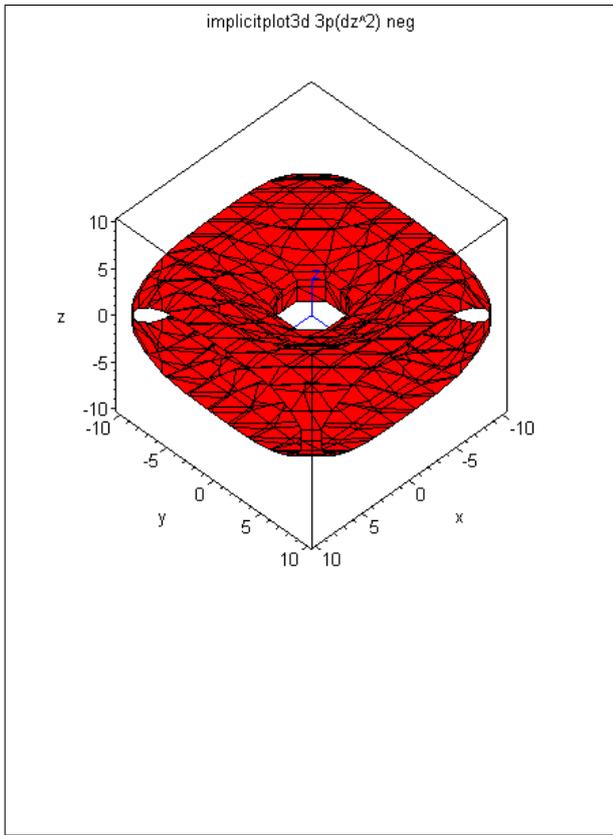
FIG. 5: The d_{z^2} orbital as a function of z with $y = 0$ and $x = 0$. Shown is the composite of the two lobes
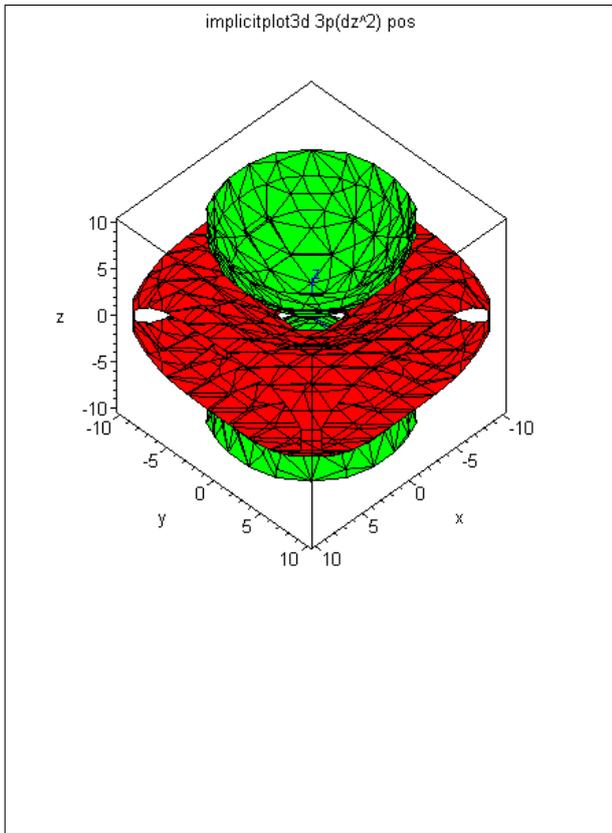
FIG. 6: The d_{z^2} orbital as a function of x, y, and z in a pseudo-polar implicitplot3D (Maple) form. Shown are the two lobes which have one sign, and the toroidal portion which has the opposite sign.

```
>  #hybrid1a-p6
>  restart;#this will be the d-zsq orbitals
>  with(plots):
>  with (plottools);
>  #G:=textplot([1,1,'function'],[0.75,0.45,'derivative']):
>  #  display(F,G);
>  psi_3d := proc(x,y,z)
>  return(3*z^2-(x^2+y^2+z^2))*exp(-sqrt(x^2+y^2+z^2)/3);
>  end proc;
>  #a1:=arrow([2,0.5], [2,0], .2, .4,
.1,harpoon, color=blue):
>  #a2:=textplot ([2, 0.5, "Node"],
align={ABOVE,RIGHT}, colour=blue):
>  F:=plot(psi_3d(0,0,z),z=-18..18,labels=['z','psi'],title='plot
>  3p(dz^2)'):
>  display(F);
>  #G:=textplot([1,1,'function'],[0.75,0.45,'derivative']):
>  #  display(F,G);
>  plot3d(psi_3d(x,y,0),x=-15..15,y=-15..15,axes=BOXED,labels=['x','y','p
>  si'],title='plot3d 3p(dz^2)');
>  plot3d(psi_3d(x,0,z),x=-15..15,z=-15..15,axes=BOXED,labels=['x','z','p
>  si'],title='plot3d 3p(dz^2)');
>  #contourplot3d(psi_3d(x,y,0),x=-15..15,y=-15..15,axes=BOXED,labels=['x
>  ','y','psi'],
>  #contours=40,title='contourplot3d
3p(dz^2)',orientation=[25,74]);
>  a1:=arrow([0,0,0], [4,0,0], .2, .4,
.1,harpoon, color=blue):
>  a2:=arrow([0,0,0], [0,4,0], .2, .4,
.1,harpoon, color=blue):
>  a3:=arrow([0,0,0], [0,0,4], .2, .4,
.1,harpoon, color=blue):
>  a2t:=textplot3d ([0,4, 0, "y"],
align={ABOVE,RIGHT}, colour=blue):
>  a3t:=textplot3d ([4.5,0, 0, "x"],
align={ABOVE,RIGHT}, colour=blue):
>  a4t:=textplot3d ([0,0, 4, "z"],
align={ABOVE,RIGHT}, colour=blue):
>  lim := 10;
>  Contour := 2;#value for which we're getting
a plot
>  F1 :=
>  implicitplot3d(psi_3d(x,y,z)=Contour,x=-lim..lim,y=-lim..lim,z=-lim..l
>  im,axes=BOXED,labels=['x','y','z'],title='implicitplot3d
3p(dz^2)
>  pos',color=green):
>  display(F1,a1,a2,a3,a2t,a3t,a4t);
>  F2 :=
>  implicitplot3d(psi_3d(x,y,z)=-Contour,x=-lim..lim,y=-lim..lim,z=-lim..
>  lim,axes=BOXED,labels=['x','y','z'],title='implicitplot3d
3p(dz^2)
>  neg',color=red):
>  display(F2,a1,a2,a3,a2t,a3t,a4t);
>  display(F1,F2,a2,a3,a2t,a3t,a4t);
```

Warning, the name changecoords has been redefined

Warning, the name arrow has been redefined

$$[arc,\ arrow,\ circle,\ cone,\ cuboid,\ curve,\ cutin,\ cutout,\ cylinder,\ disk,\ dodecahedron,$$
$$ellipse,\ ellipticArc,\ hemisphere,\ hexahedron,\ homothety,\ hyperbola,\ icosahedron,$$
$$line,\ octahedron,\ pieslice,\ point,\ polygon,\ project,\ rectangle,\ reflect,\ rotate,\ scale,$$
$$semitorus,\ sphere,\ stellate,\ tetrahedron,\ torus,\ transform,\ translate,\ vrml]$$

$$psi\_3d := \mathbf{proc}(x,\ y,\ z)$$
$$\mathbf{return}\ (2*z^2 - x^2 - y^2)*\exp(-1/3*\mathrm{sqrt}(x^2+y^2+z^2))$$
$$\mathbf{end\ proc}$$

$$lim := 10$$
$$Contour := 2$$

IV. OTHER D-ORBITALS

The other d-orbitals are *a posteriori* more difficult to understand.

$$xye^{-r/3} \equiv \psi_{d_{xy}}$$

is a typical d-orbital (of the complicated type). This is in a mixed coordinate system, since x and y are in Cartesian coördinates, while the r is in spherical polar. We see that this can be rewritten as

$$r^2 \sin^2\theta \sin\phi\cos\phi e^{-r/3}$$

when written in spherical polar coördinates. Alternatively, we could write

$$xye^{-\sqrt{x^2+y^2+z^2}/3}$$

which would be in Cartesian coordinates.

One sees immediately that there are two different ways of plotting the function, based on Cartesian or spherical polar coordinates. The Cartesian form would require us to declare one of the cartesian coordinates to be zero, so we could plot the wave function against the other two. Clearly, we should choose $z = 0$, since choosing either x or y to be zero would result in a null wavefunction plot (Figure 7). What we see is a set of minima and maxima
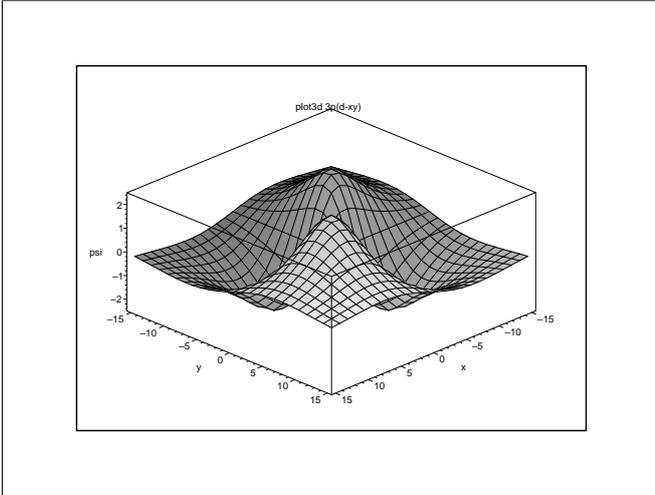

FIG. 7: The d_{xy} orbital as a function of x and y and $z = 0$.

which are "between" the x and y axis. The contour map $\psi(x, y, 0) = constant$ versus x and y shows explicitly that this is true (Figure 8)

When we turn to more traditional plots, we get some strange behaviour. Consider the positive lobes of the function. Clearly,

$$xye^{-\sqrt{x^2+y^2+z^2}/3}$$

is positive when x and y are positive and when both x and y are negative. Therefore, there will be two positive lobes
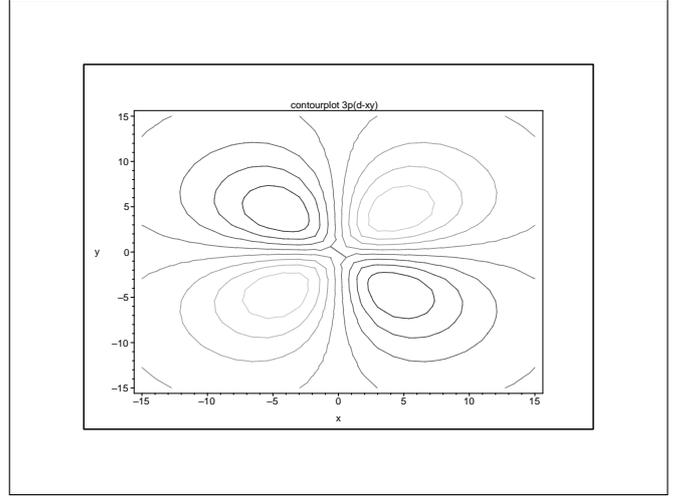

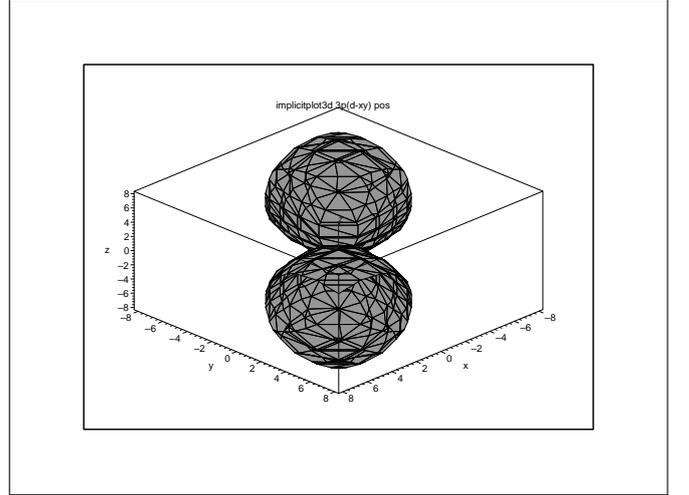FIG. 8: The contour map of d_{xy} orbital as a function of x and y and $z = 0$.

FIG. 9: The d_{xy} orbital as a function of x, y and z.

(Figure 9). The negative lobes are when either (but not both) x or y are negative and the other positive (Figure 10). As a result, the composite plot is complicated, as can be seen in Figure 11). Each of these Figures show that the wave function is largest when $x = y$ or when $x = -y$ (in absolute magnitude). Our plots do not show the signs of the wave function, but it is clear that the sign of the wave function follows the sign of x and y, so when one is positive and the other negative, the wave function is negative. When they are both positive, or both negative, then the wave function is positive.

When we look at the polar form of the wave function, then it is clear that the maximum (and minimum) of the wave function occurs when $z = 0$ which means when
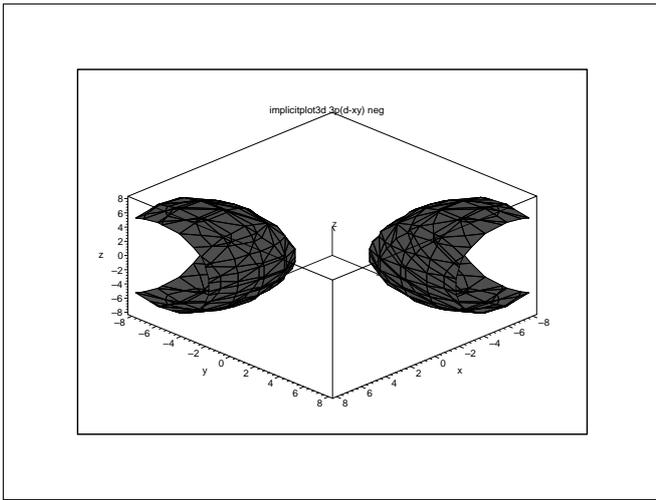
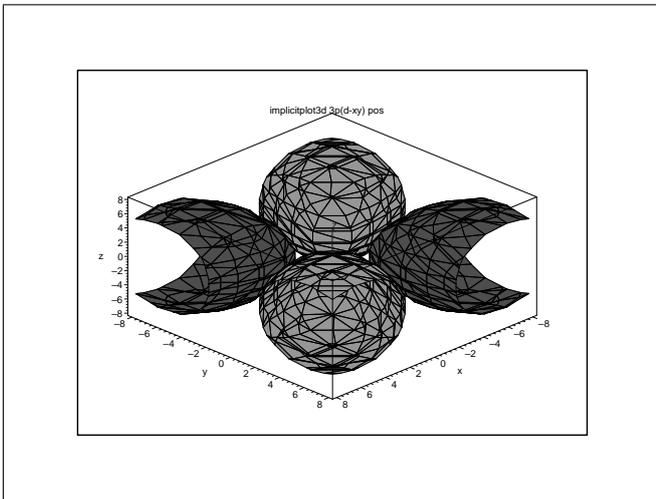FIG. 10: The d_{xy} orbital as a function of x, y and z.

FIG. 11: The d_{xy} orbital as a function of x, y and z.

$\theta = 90^o$. This is the $x - y$ plane, of course.

$$r^2 \sin^2 \theta \sin \phi \cos \phi e^{-r/3} =$$
$$r^2 \sin^2 \frac{\pi}{2} \sin \phi \cos \phi e^{-r/3} =$$
$$r^2 \sin \phi \cos \phi e^{-r/3}$$

We plot our wave function now by picking (and ignoring) a constant value of "r", and make a polar plot of $\sin \phi \cos \phi$ versus ϕ, which is the swing angle from the x-axis, which runs from zero to 2π.

Here is a "contour plot" of the positive lobes of this function: Figure 9 shows the positive lobes, while Figure 10 shows the negative lobes of this orbital. Notice that the lobes' signs reflect the product of the signs of the product "x×y". Figure 11 shows teh composite of Figures 9 and 10.

V. $d_{x^2-y^2}$

It should now be clear where $d_{x^2-y^2}$ orbital must point. It should also be clear where the d_{xz} and d_{yz} orbitals point. The names reflect the pre-expontential multipliers, whose signs and magnitudes tell us where the maxima are.

Figure 12 shows the plot of $\psi_{x^2-y^2}(x, y, 0)$ versus x and y. Figure 13 shows the similar contour map, highlighting
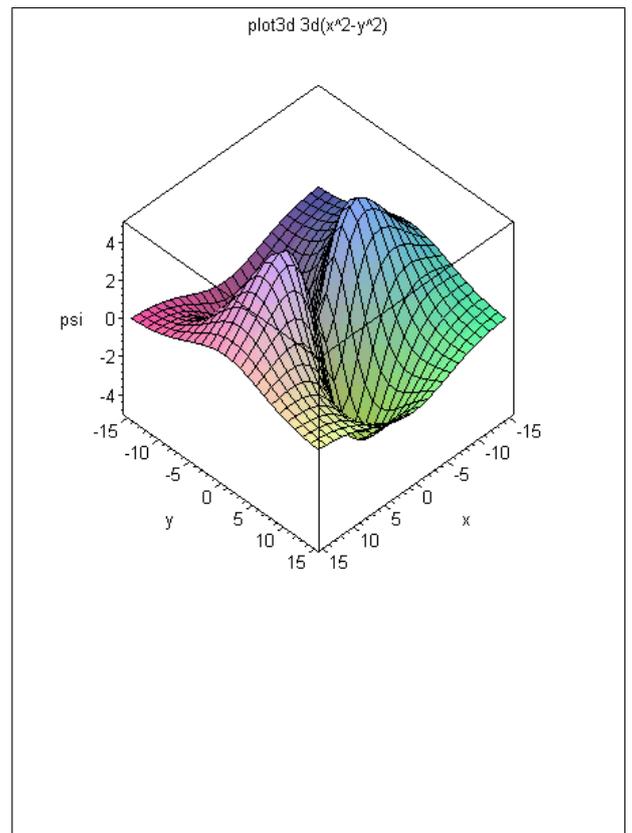

FIG. 12: The $d_{x^2-y^2}$ orbital as a function of x and y with $z = 0$.

level loci of constant ψ. Figure 14 shows the postitive lobes of this wave function while Figure 15 shows the negative lobes. The composite diagram is not shown.

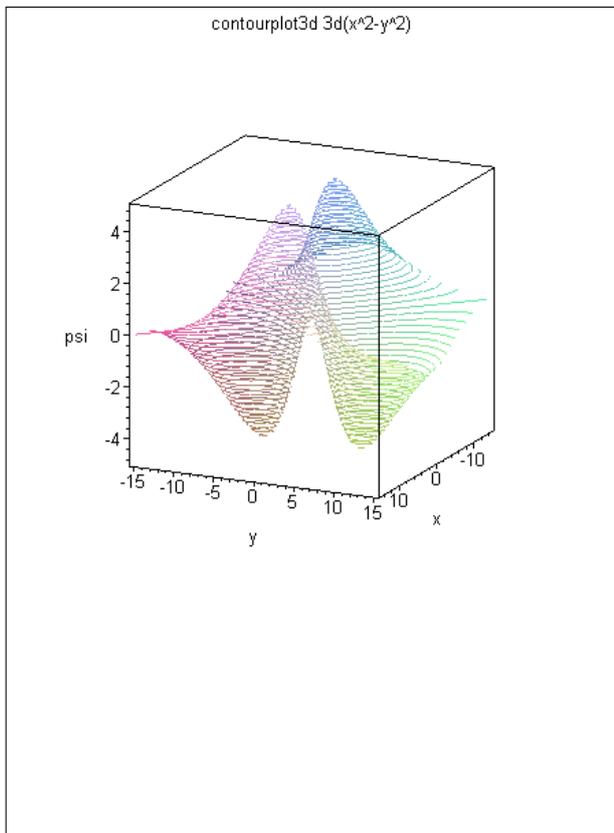Here is the Maple code which generated the figures to follow:

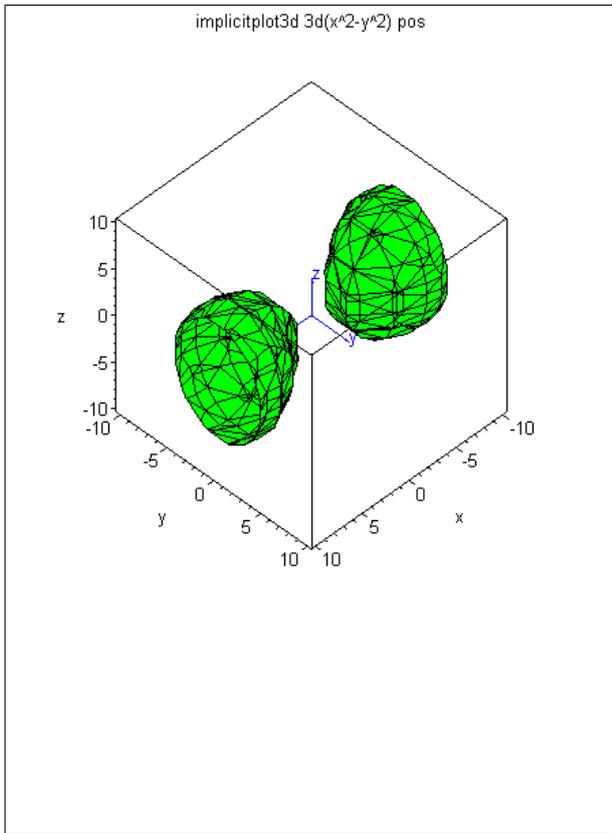FIG. 13: The "contour" plot of the $d_{x^2-y^2}$ orbital as a function of x and y with $z = 0$.

FIG. 14: The traditional plot of the $d_{x^2-y^2}$ orbital as a function of x and y with $z = 0$, showing only the positive lobes.
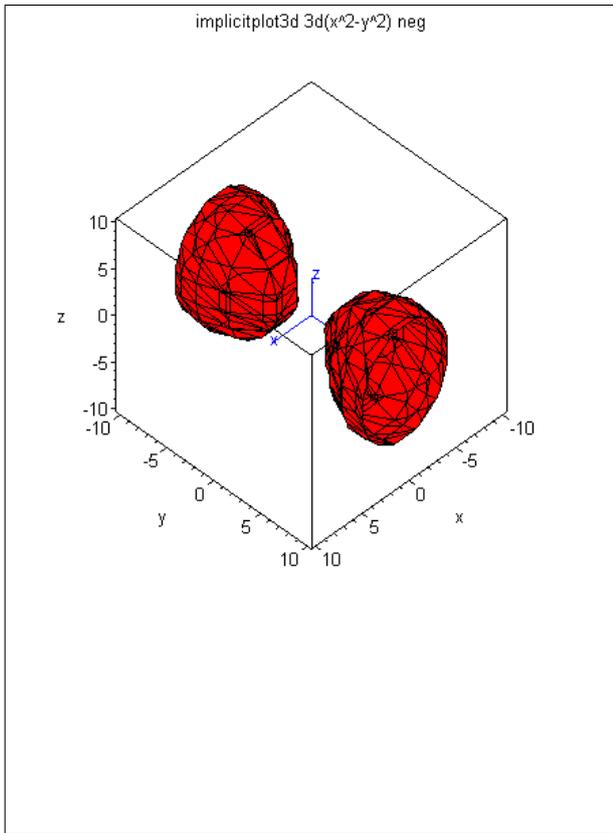
FIG. 15: The traditional plot of the $d_{x^2-y^2}$ orbital as a function of x and y with $z = 0$, showing only the negative lobes.

```
>   #hybrid1a-p5
>   restart;#this will be the d-xsq-ysq
orbitals
>   with(plots):
>   with (plottools);
>   #G:=textplot([1,1,'function'],[0.75,0.45,'derivative']):
>   #  display(F,G);
>   psi_3d := proc(x,y,z)
>   return((x^2-y^2)*exp(-sqrt((x^2+y^2+z^2))/3));
>   end proc;
>   plot3d(psi_3d(x,y,0),x=-15..15,y=-15..15,axes=BOXED,labels=['x','y','p
>   si'],title='plot3d 3d(x^2-y^2)');
>   contourplot3d(psi_3d(x,y,0),x=-15..15,y=-15..15,axes=BOXED,labels=['x'
>   ,'y','psi'],contours=40,title='contourplot3d
>   3d(x^2-y^2)',orientation=[25,74]);
>   a1:=arrow([0,0,0], [4,0,0], .2, .4,
.1,harpoon, color=blue):
>   a2:=arrow([0,0,0], [0,4,0], .2, .4,
.1,harpoon, color=blue):
>   a3:=arrow([0,0,0], [0,0,4], .2, .4,
.1,harpoon, color=blue):
>   a2t:=textplot3d ([0,4, 0, "y"],
align={ABOVE,RIGHT}, colour=blue):
>   a3t:=textplot3d ([4.5,0, 0, "x"],
align={ABOVE,RIGHT}, colour=blue):
>   a4t:=textplot3d ([0,0, 4, "z"],
align={ABOVE,RIGHT}, colour=blue):
>   lim := 10;
>   Contour := 2;#value for which we're getting
a plot
>   F1 :=
>   implicitplot3d(psi_3d(x,y,z)=Contour,x=-lim..lim,y=-lim..lim,z=-lim..l
>   im,axes=BOXED,labels=['x','y','z'],title='implicitplot3d
3d(x^2-y^2)
>   pos',color=green):
>   display(F1,a1,a2,a3,a2t,a3t,a4t);
>   F2 :=
>   implicitplot3d(psi_3d(x,y,z)=-Contour,x=-lim..lim,y=-lim..lim,z=-lim..
>   lim,axes=BOXED,labels=['x','y','z'],title='implicitplot3d
3d(x^2-y^2)
>   neg',color=red):
>   display(F2,a1,a2,a3,a2t,a3t,a4t);
```

Warning, the name changecoords has been redefined

Warning, the name arrow has been redefined

$$[arc,\ arrow,\ circle,\ cone,\ cuboid,\ curve,\ cutin,\ cutout,\ cylinder,\ disk,\ dodecahedron,$$
$$ellipse,\ ellipticArc,\ hemisphere,\ hexahedron,\ homothety,\ hyperbola,\ icosahedron,$$
$$line,\ octahedron,\ pieslice,\ point,\ polygon,\ project,\ rectangle,\ reflect,\ rotate,\ scale,$$
$$semitorus,\ sphere,\ stellate,\ tetrahedron,\ torus,\ transform,\ translate,\ vrml]$$

$$psi\_3d := \mathbf{proc}(x,\ y,\ z)\,\mathbf{return}\ (x^2 - y^2) * \exp(-1/3 * \mathrm{sqrt}(x^2 + y^2 + z^2))\,\mathbf{end\ proc}$$

$$lim := 10$$
$$Contour := 2$$