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Understanding Atomic (Hyrdogenic) Hybrid Orbitals Part 2, sp^2

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I. SYNOPSIS

This is a continuation of the discussion of hybrid orbitals, this time focussing on sp^2 orbitals, the last of the sets which can be plotted easily on a piece of paper.

II. INTRODUCTION

We here address them with sp^2 orbitals. They are combinations of a $2s$ orbital and two $2p$ orbitals, $2p_x$ and $2p_y$. The $2p_z$ orbital is normally reserved for use in π bonding, which is another topic.

III. NORMALIZATION

We show, in the attached Maple code, that the normalization constants for the 2s and 2p orbitals that contribute herein are the same, and therefore ignorable (from our point of view of plotting them).

IV. sp^2 ORBITALS

We start with an s and two p orbitals. The standard choice involves using p_x and p_y orbitals. We arbitrarily choose to keep the p_z orbital by itself (often used to form π bonds, but that's another story) [1].

$$\psi_{sp^2_1} = \frac{1}{\sqrt{3}}\psi_{2s} + \sqrt{\frac{2}{3}}\psi_{2p_x} + 0\psi_{2p_y}$$

and

$$\psi_{sp^2_2} = \frac{1}{\sqrt{3}}\psi_{2s} - \frac{1}{\sqrt{6}}\psi_{2p_x} + \frac{1}{\sqrt{2}}\psi_{2p_y}$$

Note that we do not use a $1s$ orbital!

The $2s$ hydrogenic orbital has the form

$$\psi_{2s} = (2-r)e^{r/2}$$

where we are still assuming an atomic charge of 1 (we could assume a carbon like value, but would learn almost nothing from it, so why bother?). The p_z orbital has the form

$$\psi_{2p_x} = r\sin\vartheta\cos\varphi e^{r/2}$$

$$\psi_{2p_y} = r\sin\vartheta\sin\varphi e^{r/2}$$

as usual.

In Cartesian coördinates we have

$$\psi_{sp^2_1} = \left((2-\sqrt{x^2+y^2+z^2}) + z\right) e^{\sqrt{x^2+y^2+z^2}/2}$$

How are we to understand this orbital, as given?

V. A NON-TRADITIONAL PLOT

Let's do what we did with simple hydrogenic orbitals, i.e., plot $\psi_{sp^+}(x,0,z)$ versus x and z. We see that there is a positive peak somewhere in the region $z > 0$. There is a valley (negative) appearing on the negative z axis. Both of these features tail off as $|x|$ grows.

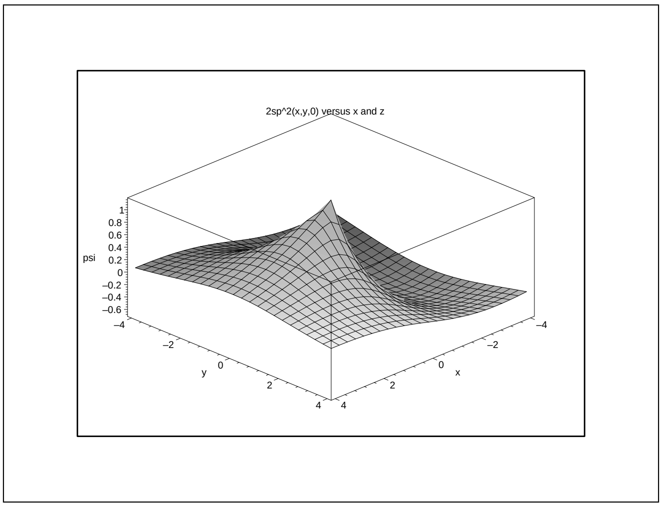

FIG. 1: The pseudo 3D surface of $\psi(x,0,z)$ versus x and y. Notice the captioning error.

VI. A CONTOUR PLOT

We next create a contour plot of $\psi_{sp^2}(x,y,0)$ versus x and y in two dimensions. This is Figure 2, a plot showing loci of constant ψ.

Typeset by REVTEX

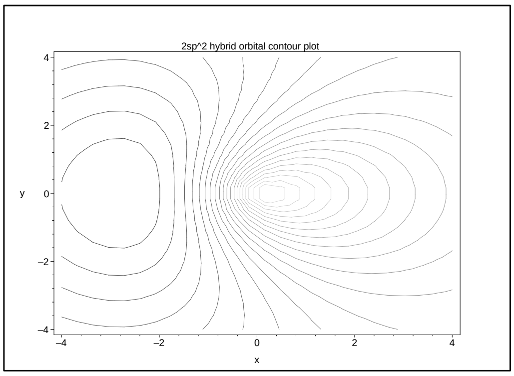

FIG. 2: A contour map of $\psi(x, y, 0)$ with x and y

VII. NON-TRADITIONAL PLOTS

Now, we want to look a little more at this function. First, we re-write it as

$$\psi_{sp_1^2} = ((2-r) + r\sin\vartheta\cos\varphi)\, e^{r/2}$$

and fix the value of r at some (arbitrary) value, say “1”. Then, ignoring the exponential, we have

$$\psi_{sp_1^2} = ((2-1) + 1\sin\vartheta\cos\varphi)\, e^{r/2}$$

and we now set $\vartheta = \frac{\pi}{2}$ so that we are “in the x-y plane. this allows us to make a polar plot of this function $(1 + \cos\varphi)$ in the traditional manner. We eschew this here, since we've done it before for the sp case.

Instead, we construct the 3-dimensional contour plot in x, y, and z space in Figure 3. Notice that this is really two plots, one for the positive lobe, the other for the negative one, superimposed.

VIII. ANOTHER sp^2 ORBITAL

We will see here that the next sp^2 orbital is canted relative to the first one we drew. Actually, as shown in some texts, they are 120^o apart, as is the last one. Thus the trigonal structure of sp^2 central atom bonding is established.

Figure 4 shows the $\psi_{sp^2}(x, y, 0)$ versus x and y, while Figures 5 and 6 show the contour map and contour surface, respectively of this canted orbital.

IX. MAPLE

To help in this learning, perhaps the following code will be found useful.

```
>  #sp2-hybrid-plot
>  restart;
>  with(plots);
>  fs := exp(-r/2);
>  psi_2s := (2-r)*fs;
>  cart_psi_2p_x := x*fs;
>  cart_psi_2p_y := y*fs;
>  cart_psi_2p_z := z*fs;
>  psi_2p_x := r*sin(theta)*cos(phi)*fs;
>  psi_2p_y := r*sin(theta)*sin(phi)*fs;
>  psi_2p_z := r*cos(theta)*fs;
>  t11 := int(r^2*sin(theta)*psi_2p_x^2,phi=0..2*Pi):
>  t21 := int(t11,theta=0..Pi):
>  t31 := int(t21,r=0..infinity):
>  N_2px := sqrt(t31);
>  t12 := int(r^2*sin(theta)*psi_2s^2,phi=0..2*Pi):
>  t22 := int(t12,theta=0..Pi):
>  t32 := int(t22,r=0..infinity):
>  N_2s := sqrt(t32);
>  print (‘the normalization constants are the
same, so we can ignore
>  them‘);

Warning, the name changecoords has been redefined
```

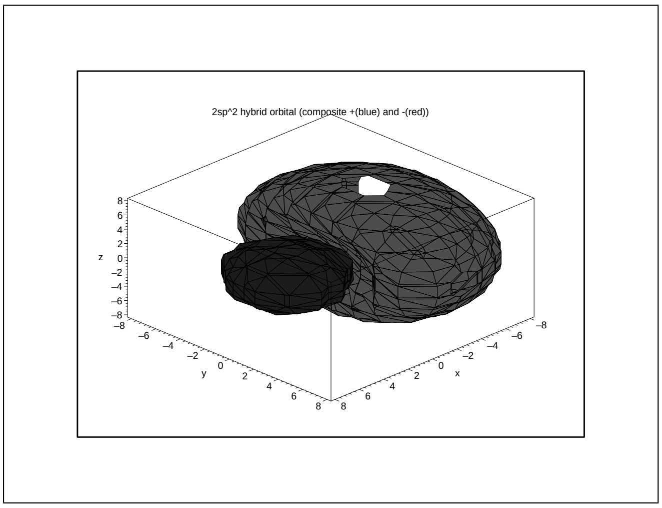

FIG. 3: $\psi = constant$ contour 3D plot. This is a composite, with the positive and negative lobes colored differently.

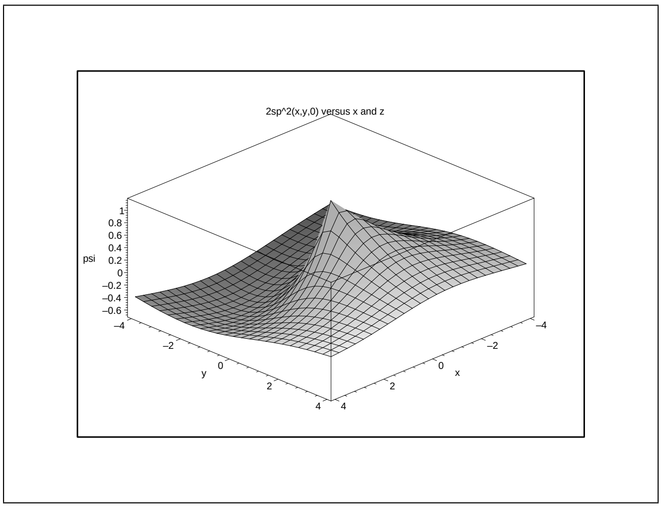

FIG. 4: Similar to the first sp^2 orbital, but pointing elsewhere. Again, notice the captioning error.

$$[animate, animate3d, animatecurve, arrow, changecoords, complexplot, complexplot3d, conformal, conformal3d, contourplot, contourplot3d, coordplot, coordplot3d, cylinderplot, densityplot, display, display3d, fieldplot, fieldplot3d, gradplot, gradplot3d, graphplot3d, implicitplot, implicitplot3d, inequal, interactive, listcontplot, listcontplot3d, listdensityplot, listplot, listplot3d, loglogplot, logplot, matrixplot, odeplot, pareto, plotcompare, pointplot, pointplot3d, polarplot, polygonplot, polygonplot3d, polyhedra\_supported, polyhedraplot, replot, rootlocus, semilogplot, setoptions, setoptions3d, spacecurve, sparsematrixplot, sphereplot, surfdata, textplot, textplot3d, tubeplot]$$

$$fs := e^{(-\frac{r}{2})}$$

$$psi\_2s := (2 - r)\, e^{(-\frac{r}{2})}$$

$$cart\_psi\_2p\_x := x\, e^{(-\frac{r}{2})}$$

$$cart\_psi\_2p\_y := y\, e^{(-\frac{r}{2})}$$

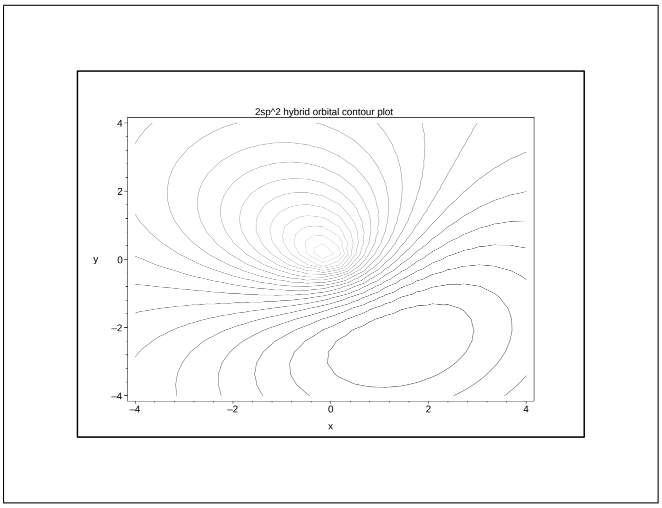

FIG. 5: The contour map of the second sp^2 orbtial.

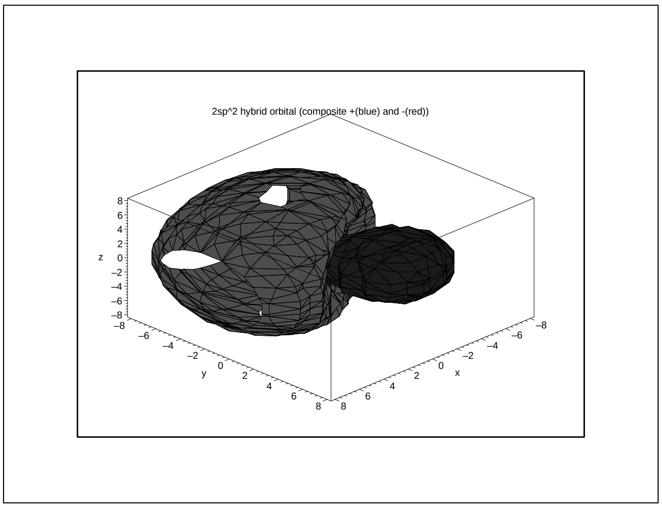

FIG. 6: The pseudo 3D implicitplot03D surface of $\psi(x,y,z)$ versus x, y, and z. This is a composite of the two lobes, one postitive, one negative.

$$cart\_psi\_2p\_z := z\, e^{(-\frac{r}{2})}$$

$$psi\_2p\_x := r \sin(\theta) \cos(\phi)\, e^{(-\frac{r}{2})}$$

$$psi\_2p\_y := r \sin(\theta) \sin(\phi)\, e^{(-\frac{r}{2})}$$

$$psi\_2p\_z := r \cos(\theta)\, e^{(-\frac{r}{2})}$$

$$N\_2px := 4\sqrt{2}\sqrt{\pi}$$

$$N\_2s := 4\sqrt{2}\sqrt{\pi}$$

the normalization constants are the same, so we can ignore them

```
> #note, un-normalized orbitals in use!
> r := sqrt(x^2+y^2+z^2):
> t1 := ((1/sqrt(3))*psi_2s+(sqrt(2/3))*cart_psi_2p_x);#page 372
> Karplus & Porter
> lim := 4;
> plot3d(subs(z=0,t1),x=-lim..lim,y=-lim..lim,axes=BOXED,labels=[`x`,`y`
> ,`psi`],title=`2sp^2(x,y,0) versus x and z`);
> contourplot(subs(z=0,t1),x=-lim..lim,y=-lim..lim,axes=BOXED,labels=[`x
> `,`y`],title=`2sp^2 hybrid orbital contour plot `,contours = 20);
> lim := 8;
> f1 :=
> implicitplot3d(t1=0.08,x=-lim..lim,y=-lim..lim,z=-lim..lim,axes=BOXED,
> labels=[`x`,`y`,`z`],color=blue):
> f2 :=
> implicitplot3d(t1=-0.08,x=-lim..lim,y=-lim..lim,z=-lim..lim,axes=BOXED
> ,labels=[`x`,`y`,`z`],title=`2sp^2 hybrid orbital (composite +(blue)
> and -(red))`,color=red):
> display(f1,f2);
> #============================================
> t2 := ((1/sqrt(3))*psi_2s-(sqrt(1/6))*cart_psi_2p_x
> +(1/sqrt(2))*cart_psi_2p_y);#page 372  Karplus & Porter
> lim := 4;
> plot3d(subs(z=0,t2),x=-lim..lim,y=-lim..lim,axes=BOXED,labels=[`x`,`y`
> ,`psi`],title=`2sp^2(x,y,0) versus x and z`);
> contourplot(subs(z=0,t2),x=-lim..lim,y=-lim..lim,axes=BOXED,labels=[`x
> `,`y`],title=`2sp^2 hybrid orbital contour plot `,contours = 20);
> lim := 8;
> f1 :=
> implicitplot3d(t2=0.08,x=-lim..lim,y=-lim..lim,z=-lim..lim,axes=BOXED,
> labels=[`x`,`y`,`z`],color=blue):
> f2 :=
> implicitplot3d(t2=-0.08,x=-lim..lim,y=-lim..lim,z=-lim..lim,axes=BOXED
> ,labels=[`x`,`y`,`z`],title=`2sp^2 hybrid orbital (composite +(blue)
> and -(red))`,color=red):
> display(f1,f2);
```

$$t1 := \frac{1}{3}\sqrt{3}\,(2-\sqrt{x^2+y^2+z^2})\,e^{(-\frac{\sqrt{x^2+y^2+z^2}}{2})}+\frac{1}{3}\sqrt{6}\,x\,e^{(-\frac{\sqrt{x^2+y^2+z^2}}{2})}$$

$$lim := 4$$

$$lim := 8$$

$$t2 := \frac{1}{3}\sqrt{3}\,(2-\sqrt{\%1})\,e^{(-\frac{\sqrt{\%1}}{2})}-\frac{1}{6}\sqrt{6}\,x\,e^{(-\frac{\sqrt{\%1}}{2})}+\frac{1}{2}\sqrt{2}\,y\,e^{(-\frac{\sqrt{\%1}}{2})}$$
$$\%1 := x^2+y^2+z^2$$

$$lim := 4$$

$$lim := 8$$

[1] M. Karplus and R. N. Porter, “Atoms & Molecules”, W. A. Benjamin, Inc., Phillippines, 1970.