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Understanding Atomic (Hydrogenic) Hybrid Orbitals

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I. SYNOPSIS

The hybrid orbitals which are stressed in Freshman Chemistry, and elucidated somewhat in Organic Chemistry, need to be understood not because of their usefulness in standard Quantum Chemistry, but because all the non-practitioners know about them, and need expert guidance in using them appropriately. In this discussion, we address the elementary (carbon based) hybrid orbital types, with the hopes that their understanding will be enhanced (and therefore not misused).

II. INTRODUCTION

The hybrid orbitals, an invention, to the best of my knowledge, of Linus Pauling, stand almost orthogonal to the natural quantum chemical language employed by specialists. These people, dealing with computer programs mainly, use complicated basis orbitals in their computations, since pictures of what is happening are not needed, or are supplied by computer.

For the naïve user, however, the hybrid orbitals are useful as a beginning explicator of directionality in bonding. We here address them starting with sp orbitals, and continuing on the sp^2 and sp^3, whereupon we stop.

III. sp ORBITALS

We start with un-normalized orbitals ($vide\ infra$), two in number, an s and a p orbital. We arbitrarily choose the p_z orbital, and form

$$\psi_{sp_+} = \psi_{2s} + \psi_{2p_z}$$

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

$$\psi_{2p_z} = r\cos\vartheta e^{r/2}$$

as usual. Therefore, we can form two linear combinations of these two, a "+" combination and a "-" combination. We choose the "+" combination for our work here.

Thus we form the sp orbital

$$\psi_{sp^+} = (2-r)e^{r/2} + r\cos\vartheta e^{r/2}$$

or, in Cartesian coördinates

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

How are we to understand this orbital, as given?

IV. 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

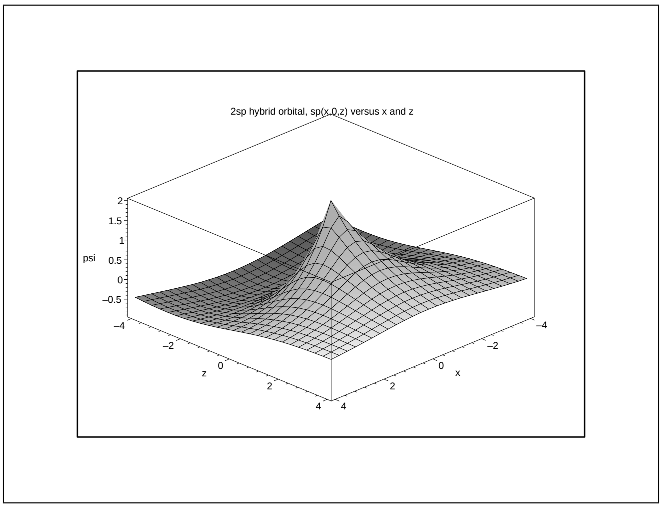

FIG. 1: The pseudo 3D surface of $\psi(x,0,z)$ versus x and z

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.

V. A CONTOUR PLOT

We next create a contour plot of $\psi_{sp^+}(x,0,z)$ versus x and z in two dimensions. This mimics Figure 1 in the sense that there is a sharp set of smaller contours in the region of about $x \approx 1$ and a diffuse set of contours centered about $x \approx 3$, which is the negative set of contours. This is Figure 2, a plot showing loci of constant ψ.

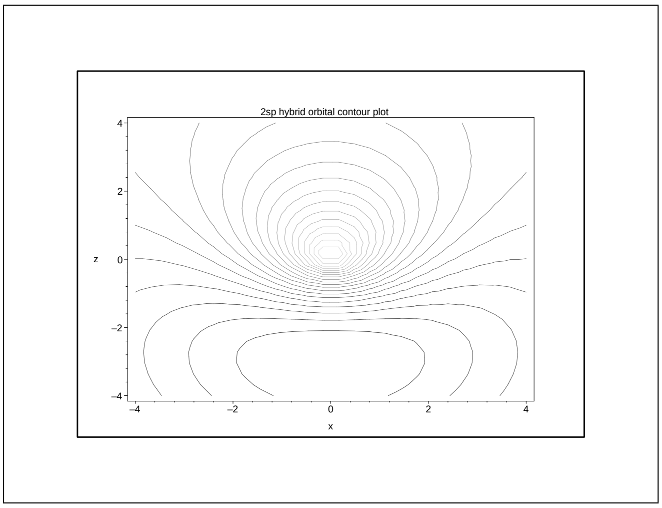

FIG. 2: A contour map of $\psi(x, 0, z)$ with x and z

VI. SOME NON-TRADITIONAL PLOTS

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

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

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

$$\psi_{sp^+}(r = 1, \vartheta) = (2 - 1) + 1\cos\vartheta$$

which allows us to make a polar plot of this function $(1 + \cos\vartheta)$ in the traditional manner. We obtain Figure 3, which certainly is odd! To see what's going on, we plot

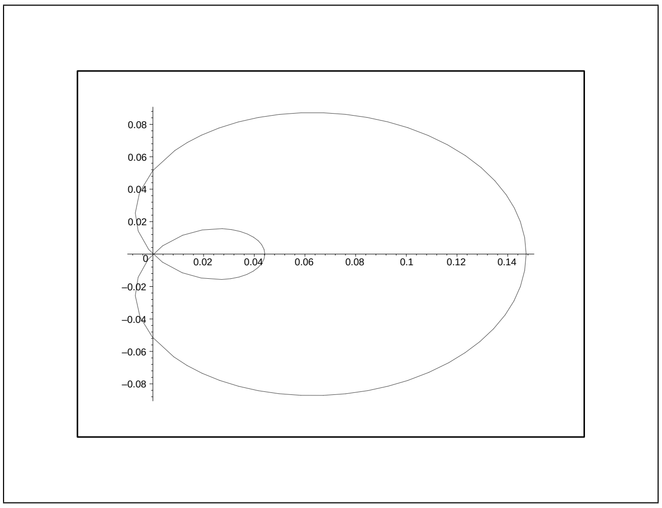

FIG. 3: A very strange contour plot of the sp hybrid orbital's angular dependence.

a related Figure 4 which shows that the wave function is sometimes negative. The polar plot (Figure 3) assigns the value of the function to the radius, and since Maple doesn't know better, it makes negative values plot in the "negative r direction", i.e., backwards. Hence the wierd loop!

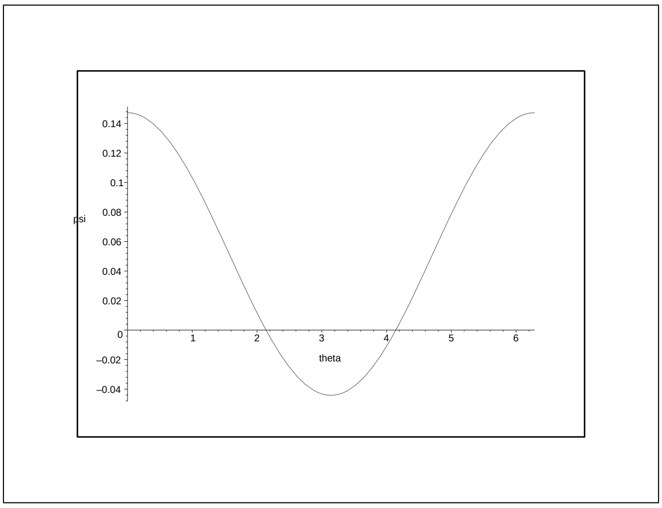

FIG. 4: An explanation of Figure 3.

VII. THE TRADITIONAL PLOT

When we finally turn to the implicitplot3D form which roughly corresponds to textbook images, we have a positive lobe and a negative lobe, done in different colors here. This is Figure 5.

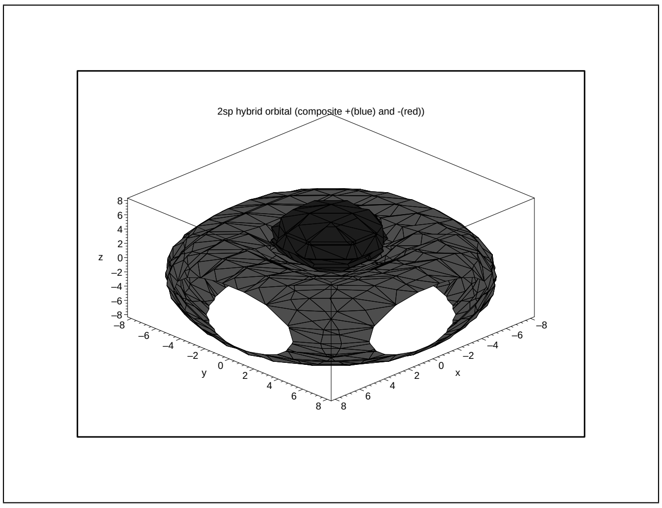

FIG. 5: The pseudo 3D implicitplot3D surface of $\psi(x, y, z)$ versus x, y, and z. This is a composite of the two lobes, one postitive, one negative.

VIII. MAPLE

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

```
> #sp-hybrid-plot
> restart;
> with(plots);
> t_spher := ((2-r)+r*cos(theta))*exp(-r/2);
> t_sp_1 := int(t_spher,theta = 0..Pi);
> r := sqrt(x^2+y^2+z^2);
> #note, un-normalized orbitals in use!
> fs := exp(-r/2);
> psi_2s := (2-r)*fs;
> psi_2p_z := z*fs;
> t := (psi_2s+psi_2p_z);
> lim := 4;
> plot3d(subs(y=0,t),x=-lim..lim,z=-lim..lim,axes=BOXED,labels=[‘x‘,‘z‘,
> ‘psi‘],title=‘2sp hybrid orbital, sp(x,0,z)
versus x and z‘);
> contourplot(subs(y=0,t),x=-lim..lim,z=-lim..lim,axes=BOXED,labels=[‘x‘
> ,‘z‘],title=‘2sp hybrid orbital contour
plot ‘,contours = 20);
> lim := 8;
> f1 :=
> implicitplot3d(t=0.08,x=-lim..lim,y=-lim..lim,z=-lim..lim,axes=BOXED,l
> abels=[‘x‘,‘y‘,‘z‘],color=blue):
> f2 :=
> implicitplot3d(t=-0.08,x=-lim..lim,y=-lim..lim,z=-lim..lim,axes=BOXED,
> labels=[‘x‘,‘y‘,‘z‘],title=‘2sp hybrid
orbital (composite +(blue) and
> -(red))‘,color=red):
> display(f1,f2);
```

```
Warning, the name changecoords has been redefined
```

[*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*]

$$t\_spher := (2 - r + r\cos(\theta))\, e^{(-\frac{r}{2})}$$

$$t\_sp\_1 := 2\, e^{(-\frac{r}{2})}\, \pi - e^{(-\frac{r}{2})}\, r\, \pi$$

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

$$fs := e^{(-\frac{\sqrt{x^2+y^2+z^2}}{2})}$$

$$psi\_2s := (2 - \sqrt{x^2 + y^2 + z^2})\, e^{(-\frac{\sqrt{x^2+y^2+z^2}}{2})}$$

$$psi\_2p\_z := z\, e^{(-\frac{\sqrt{x^2+y^2+z^2}}{2})}$$

$$t := (2 - \sqrt{x^2 + y^2 + z^2})\, e^{(-\frac{\sqrt{x^2+y^2+z^2}}{2})} + z\, e^{(-\frac{\sqrt{x^2+y^2+z^2}}{2})}$$

$$lim := 4$$

$$lim := 8$$