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MO visualization of Pi Orbitals

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I. SYNOPSIS

In the spirit of trying to convert people to understanding atomic orbitals centered elsewhere than the origin, we continue the discussion of visualizing molecular orbitals, so called LCAO-MO, using various plotting tricks in Maple.

II. INTRODUCTION

p orbitals come in three varieties, with two representations each. We eschew the magnetic representation here, based on ℓ and m_ℓ, and instead focus, as usual in visualization problems, on the real representations. In Cartesian coördinates, we have

$$\psi_{p_x} = xe^{-r/2}$$

and

$$\psi_{p_y} = ye^{-r/2}$$

while, or course, we have

$$\psi_{p_z} = ze^{-r/2}$$

(remember that $r = \sqrt{x^2 + y^2 + z^2}$.)

The orbitals (above) are textbook examples. They are centered on the origin, since r is measured from the point $(0,0,0)$. But in molecules, the nuclei are dispersed in space (in some pattern determined by minimum energy considerations, but that's another tale). Thus each nucleus in the molecule has a specific $(x_{nuc}, y_{nuc}, z_{nuc})$ which therefore requires us to write orbitals associated with said nuclei <u>centered</u> on each one of them. That's how the quantum mechanical formulation allows the geometry of a molecule to be included in the electronic wave function.

For a diatomic, the tradition is to located the two nuclei at $(0, 0, R/2)$ (called nucleus A) and $(0, 0, -R/2)$ (called nucleus B), so that the distance between them is R, the internuclear separation. Figure 1 shows how the nuclei are arranged.

Thus, an s orbital centered on nucleus A might be

$$e^{-\sqrt{x^2+y^2+\left(z-\frac{R}{2}\right)^2}/2}$$

while one centered on nucleus B might be
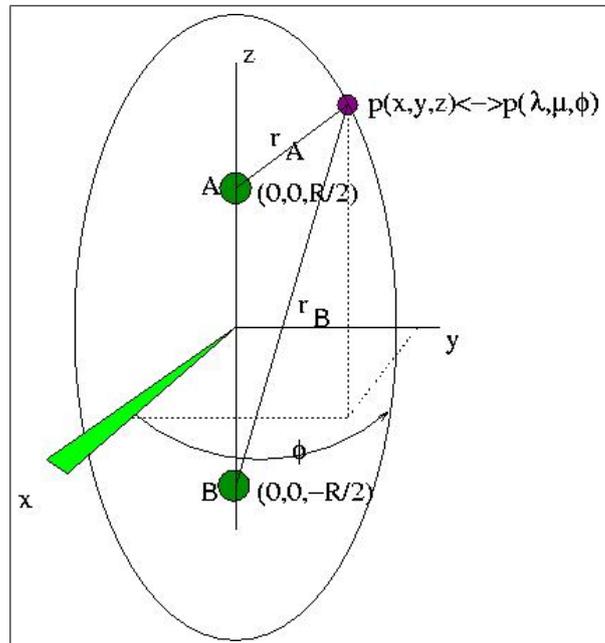
$$e^{-\sqrt{x^2+y^2+\left(z+\frac{R}{2}\right)^2}/2}$$

FIG. 1: The standard coördinate scheme for diatomics.

since the r vectors in each case, i.e., r_A and r_B have different lengths when pointing to the same point in space (x, y, z).

To create π orbitals, we know that we need to "add" two p-orbitals, one located on each contributing nucleus. These contributing atomic orbitals (AO's) are supposed to be perpendicular to the bond line which in our case is the z axis. Therefore, we have a choice of using either the x set or the y set of p orbitals. For no reason, we choose the p_x orbitals as contributors to the emerging π_x and π_x^* MO's.

The simplistic method of writing what has been written in words (above) is:

$$\psi_{p_x^A} = xe^{-r_A/2}$$

$$\psi_{p_x^B} = xe^{-r_B/2}$$

as can be found in a multitude of textbooks (the 2 in the denominator is caused by this being a $\underline{2}p_x$ orbital). This notation is delusional, since it implies understanding, where none exists. Instead, we write these contributing orbitals in complete Cartesian coördinates rather than
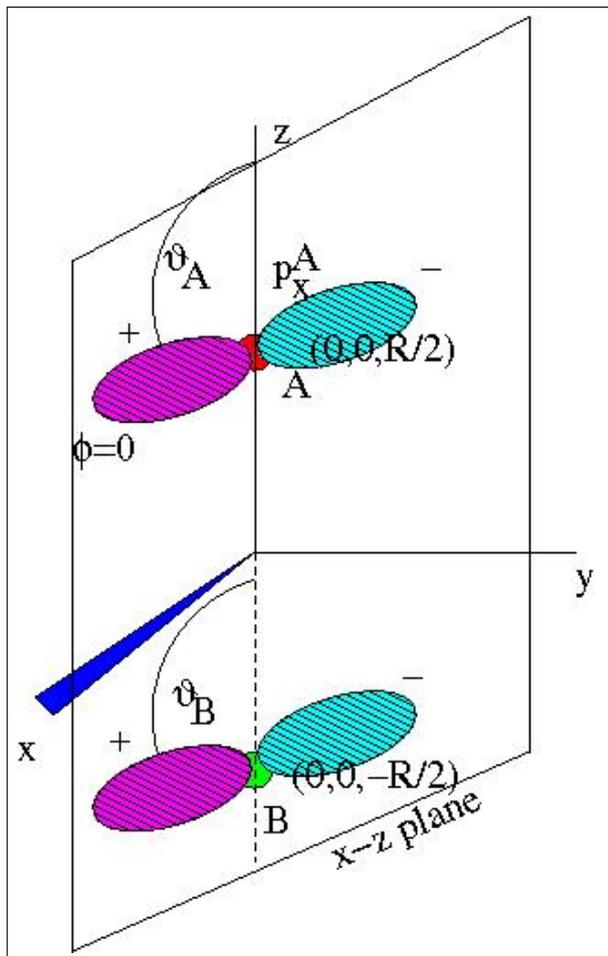
FIG. 2: Two p_x orbitals, one centered at nucleus A and the other centered at nucleus B waiting to be added (or subtracted) to from a π_x MO (or a π_x^* MO) . Notice the classic figure-8 representation of p orbitals, which actually are polar plots! They are incomensurate in the sense that the origins of the two plots differ, one centered on nucleus A, the other on nucleus B. It is the avoidance of this "error" which has motivated all the discussions here!

mixed coördinates, i.e.,

$$\psi_{p_x^A} = xe^{-\sqrt{x^2+y^2+\left(z-\frac{R}{2}\right)^2}/2}$$

$$\psi_{p_x^B} = xe^{-\sqrt{x^2+y^2+(z+\frac{R}{2})^2}/2}$$

We now have the contributing AO's written in a self consistent form which allows us to start plotting the LCAO-MO.

There are two combinations of p-orbitals which lead to two MO's, one uses a plus sign and one uses a minus

sign. If one labors through the Hückel calculation, one finds that the '+' sign corresponds to our usual π_x orbital, and this is what we'll tackle first. We obtain:
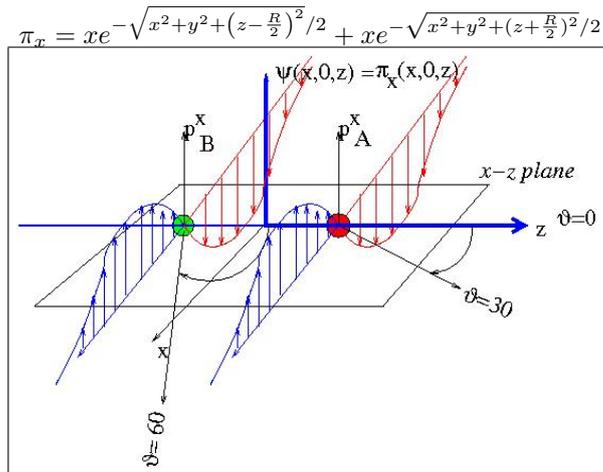

FIG. 3: Two p_x orbitals, one centered at nucleus A and the other centered at nucleus B waiting to be added (or subtracted) to from a π_x MO (or a π_x^* MO) . The definition of positive and negative is arbitrary, so the colors are not intended to match those of earlier figures.

There you have it.

Formally, we have $\pi_x(x, y, z)$ is a function of three variables, x, y, and z. That means, you choose the values for the three coördinates, and the formula will tell you the value of the wave function, i.e., that we need 4 dimensions to map out this function properly. We need to plot $\pi_x(x, y, z)$ as the "dependent" variable, against x, y, and z as independent (you choose their values and $\pi_x(x, y, z)$'s value follows) variables.

Since most of us do not live in that particular world, we need to reduce the dimensionality of our plots so that we can put them on paper. Usually, we take a section when one of the axis is zero (example here y axis), and then plot $\pi_x(x, y, z) \rightarrow \pi_x(x, 0, z)$ versus the other two. Then, we take this three dimensional plot, and put it on a two-dimensional page using perspective as the trick to give the illusion of three dimensionality. Figure 3 shows schematically how we are combining the two contributing orbitals in this pseudo-3D representation. In our case, we've chosen to set $y = 0$ for this original plot (with the intent of plotting at varying values of y to see what happens (which is a shrinkage, nothing more, hence not worth actually doing)). The final Maple plot equivalent to Figure 3 can be seen in Figure 5 below.

```
>   #MO-pi-plot
>   restart;
>   with(plots):
>   fsA := exp(-rA/2);
>   fsB := exp(-rB/2);
>   rA := sqrt(x^2+y^2+(z-R/2)^2);
>   rB := sqrt(x^2+y^2+(z+R/2)^2);
>   p_pi_plus := x*fsA+x*fsB;
>   p_pi_minus := x*fsA-x*fsB;
```

Warning, the name changecoords has been redefined

$$fsA := e^{(-\frac{rA}{2})}$$

$$fsB := e^{(-\frac{rB}{2})}$$

$$rA := \frac{\sqrt{4\,x^2 + 4\,y^2 + 4\,z^2 - 4\,z\,R + R^2}}{2}$$

$$rB := \frac{\sqrt{4\,x^2 + 4\,y^2 + 4\,z^2 + 4\,z\,R + R^2}}{2}$$

$$p\_pi\_plus := x\,e^{(-\frac{\sqrt{4\,x^2+4\,y^2+4\,z^2-4\,z\,R+R^2}}{4})} + x\,e^{(-\frac{\sqrt{4\,x^2+4\,y^2+4\,z^2+4\,z\,R+R^2}}{4})}$$

$$p\_pi\_minus := x\,e^{(-\frac{\sqrt{4\,x^2+4\,y^2+4\,z^2-4\,z\,R+R^2}}{4})} - x\,e^{(-\frac{\sqrt{4\,x^2+4\,y^2+4\,z^2+4\,z\,R+R^2}}{4})}$$

Having defined the orbitals in a consistent coördinate scheme (one origin, one set of x, y, and z axis) we can proceed to plot them

```
>   lim := 16;
plot(subs(R=16,z=0,y=0,p_pi_plus),
x=-lim..lim,labels=['x','pi_x(x,0,0).pdf'],
title='2 pi_x');
```

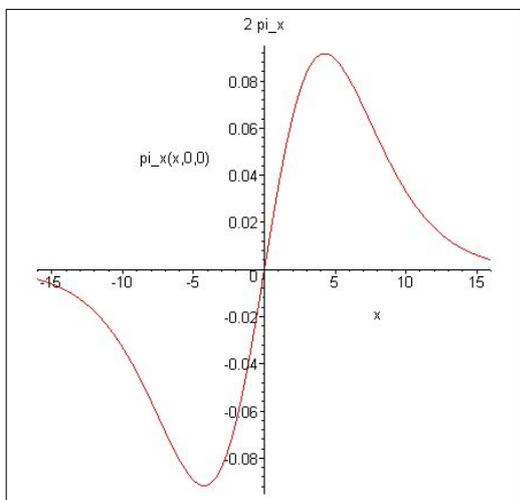Figure 4 shows the $\psi(x,0,0)$ versus x section.

FIG. 4: $\psi_{\pi_x}(x,0,0)$ versus x. This plot demonstrates that the wave function of the π orbital changes sign as one goes from the $+x$ axis to the $-x$ axis.

```
plot3d(subs(R=8,y=0,p_pi_plus),
x=-lim..lim,z=-lim..lim,axes=BOXED,
labels=['x','z','p_pi'],
title='(pi_x) MO(x,0,z) versus x and z');
```

To get a better understanding of this π orbital, we plot next the value of the wave function when x and z are allowed to vary, all with $y = 0$, i.e., y fixed at zero. We obtain Figure 5 using the Maple code:

```
plot3d(subs(R=8,y=0,p_pi_minus),
x=-lim..lim,z=-lim..lim,.pdf
axes=BOXED,
labels=['x','z','p_pi'],
title='(pi_x^*) MO(x,0,z) versus x and z');
```
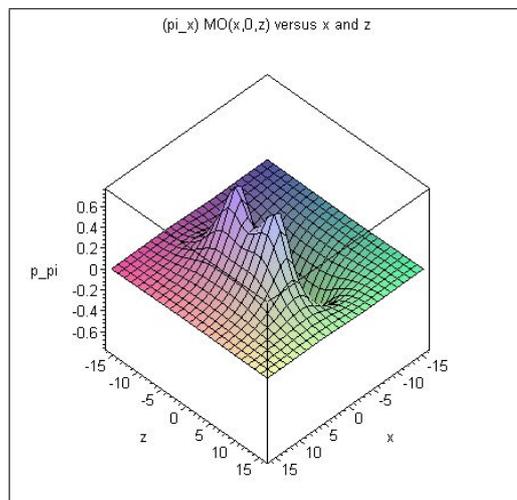

FIG. 5: $\psi(_{\pi_x}x,0,z)$ versus x and z. This plot also demonstrates that the wave function of the π orbital changes sign as one goes from the $+x$ axis to the $-x$ axis. For negative values of x, the wave function lies below the $\psi = 0$ plane.

Finally, we plot $\psi_{\pi_x^*}$, the anti-bonding (π^*) orbital. Here, the wave function has a node between the nuclei, making bonding impossible.
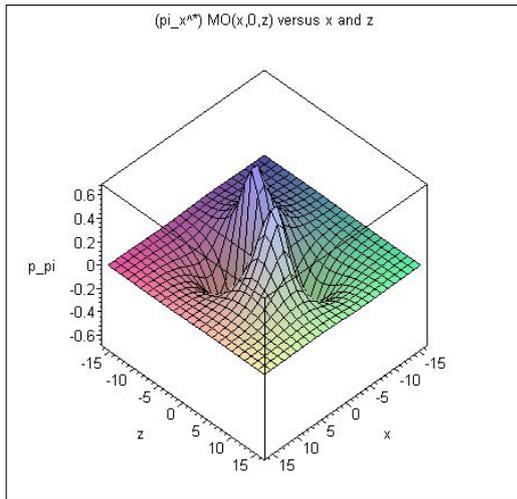
Next, we plot a 3 dimensional contour map (Fig-

FIG. 6: $\psi_{\pi_x^*}$ versus x for the antibonding π^* orbital. This plot demonstrates that the wave function of the π orbital changes sign as one goes from the $+x$ axis to the $-x$ axis as well as when one goes from the z to the $-z$ axis.

ure 7) of the π_x orbital, showing again that the wave function changes sign in company with the x-axis.
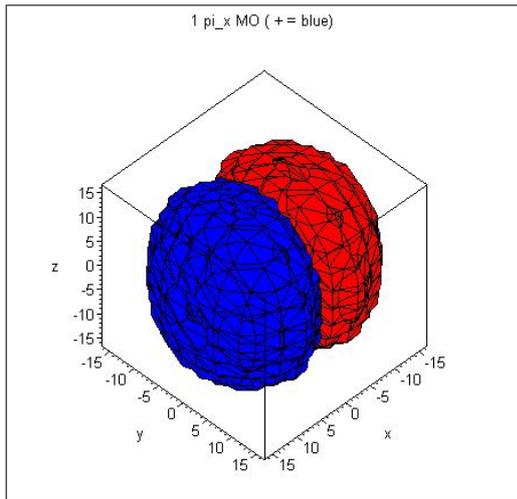

FIG. 7: Contour map in 3-dimensions, showing a contour of positive and negative (red) wave function for a π orbital.

```
>  f1 :=
>  implicitplot3d(subs(R=8,
>  p_pi_minus)=-0.006,
>  x=-lim..lim,y=-lim..lim,z=-lim..lim,
>  axes=BOXED,labels=['x','y','z'],color=red):
>  f2 :=
>  implicitplot3d(subs(R=8,p_pi_minus)=0.006,
>  x=-lim..lim,y=-lim..lim,z=-lim..lim,
>  axes=BOXED,labels=['x','y','z'],color=blue):
>  display(f1,f2,title='1 pi_x^* MO ( +(blue)
and -(red))');
```

IV.   A NON-π ORBITAL

Just to make sure that one understands what is going on, a plot of the orbital obtained by using p_z orbitals is shown in Figure 8:
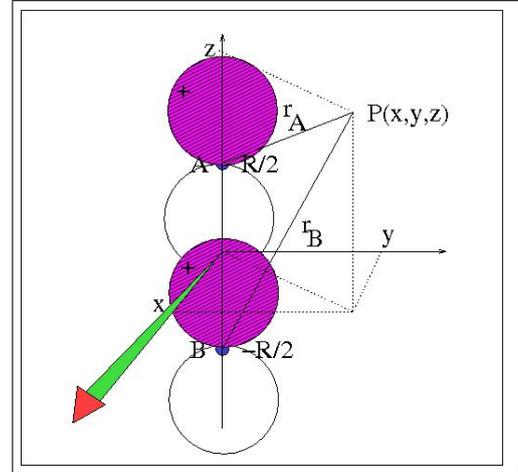

FIG. 8: When contributing p_z orbitals are used, one gets a p_σ orbital (and p_σ^*).

Here, we obtain a cylidrically symmetric (about the z-axis) orbital. The basis orbitals are shown in the plot, sufficient that one can see that the plus sign joining the two contributing p_z orbitals would lead to anti-bonding, while the minus sign would lead to the bonding (p_σ) orbital. Specifically, we plot

$$\psi_{2p_\sigma} = p_z^A - p_z^B$$

(the usual, semi-meaningless notation), i.e.,

$$\psi_{2p_\sigma} = \left(z - \frac{R}{2}\right) e^{-sqrtx^2+y^2+(z-R/2)^2/2} \ - $$
$$\left(z + \frac{R}{2}\right) e^{-sqrtx^2+y^2+(z+R/2)^2/2}$$

ane plot $\psi_{2p_\sigma}(x, 0, z)$ versus z and x (Figure 8). Since the signs are opposite to the usual experience, means that extra thought is needed to put the signs into mental perspective.