Exploring Orbitals

In Quantum Mechanics or Electronic Structure we are concerned with the location and energy of the electrons in the atom. The Schrödinger equation ($H\Psi = E\Psi$) is a mathematical expression that gives these values. An orbital is a specific solution to the Schrödinger equation and using the Greek letter psi (Ψ). Psi-squared ($\Psi^*\Psi$) gives the electron density of the orbital. The mathematics involves differential equations and is beyond the scope of this course. We will talk only briefly about the math; visualization of orbital shapes and relative energies are the emphasis. Orbital pictures like those found in Figure 1 show the $\Psi^*\Psi$ with a boundary where 90% of the electron density lies inside the boundary. We will explore orbital shapes and some mathematical aspects of orbitals using the visualization tools at https://chemapps.colostate.edu/chem120/orbitals. The orbitals on these pages are for the single electron hydrogen atom.

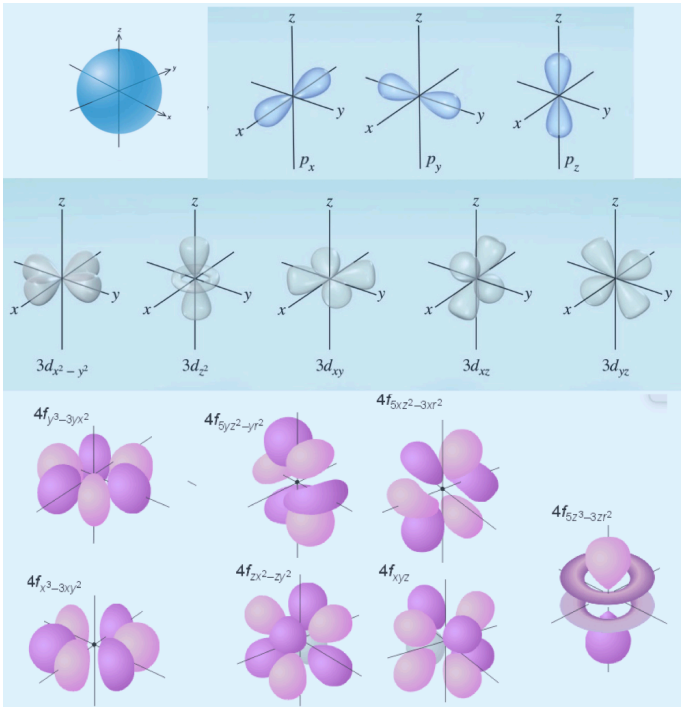

Figure 1. Atomic Orbitals

The 1*s* Orbital

Click on the link in the Table of Contents for the 1*s* orbital. We will only focus on the 2D graphs at the top (Ψ and $\Psi^*\Psi$) as a function of the distance from the radius, r, and the 3D graphs to the right. Notice the 3D graph to the bottom right. This shows Ψ by default. The pulldown menu lets you switch to $\Psi^*\Psi$ (which looks the same for a 1*s* orbital). The slider controls the boundary as described earlier. The red dot in the middle represents the nucleus. The 1*s* is spherical in shape. You can click on the orbital and drag with your mouse or trackpad to rotate and drag (without clicking) to resize. The blue sphere represents the boundary for the orbital and the orbital electron density. The 3D graph at the upper right gives more detail. There you can see that the function has a high value at zero (the nucleus) and then exponentially decays as you move away from the nucleus. If we graphing more than just the boundary in the spherical plot, we would see more electron density close to the nucleus on the inside of the sphere and becoming less as you move further away. This can be visualized as in Figure 2 with a cut-away view showing the interior of the sphere. You can get the idea of this by using the boundary slider with the visualization tool. As you move the slider to the right the sphere gets small meaning that the boundary is at a higher density. The 2D graphs give you the same idea for Ψ and $\Psi^*\Psi$, respectively. Here we see the value of Ψ as we move away from the nucleus as r increases (or as r decreases in the negative direction. The 1*s* orbital is the lowest energy orbital (most negative) for a given atom. Notice the energies that are reported.

Figure 2. Cut-away View of a 1*s* Orbital

The 2*p* Orbital

Switch now to the 2*p* orbital page by going back to the Table of Contents page or using the menu at the top left to select the Two p option. Let's start again with the 3D visualization at the lower right using the 2p*2p option in the pulldown menu. Notice the dumbbell shape, the two

blue lobes of orbital electron density, and the red dot in the middle, where for p orbitals there is no electron density. We call that a node (think of a 1D wave where the wave crosses the x-axis as it goes from peak to trough). Notice also that the teardrop shaped p orbital drawings are an exaggeration of the actual orbital shape. Here rotating the orbital is more interesting. Rotate the image around to get a good feel for what it looks like in three dimensions. Now switch back to the 2p Function view in the pulldown menu. Now you see a red lobe and a blue lobe. This the the Ψ function. As a mathematical function (vs. the physical reality of electron density), it can have a negative value, the red lobe is negative. Think again about the relationship between Ψ and $\Psi^*\Psi$. If you multiply a negative number by itself you get a positive value. Orbital electron density must always be a positive number. You can see the plot of 2p and 2p*2p with the contour map in the upper right. In the 2p, the Ψ value, there is a positive peak and a negative trough, whereas in the 2p*2p, the orbital electron density, there are two positive peaks. You see the same thing with the 2D plots of the 2p function and the 2p*2p function. Notice that the scales on the two 2D plots are not the same. Three p orbitals exist at each energy level starting with n=2, one in the x-direction, one in the y-direction, one in the z-direction, perpendicular to each other. You can orient the orbital displayed in the bottom right frame in these three views to see how they would look relative to each other.

The 3*d* Orbital

Switch now to the 3*d* orbital page using the Table of Contents page or the menu. As with the 2p orbital, look first at the bottom right frame with the 3d*3d pulldown. The default view shows only the nucleus. Move the slider to the left so you can see the four lobes of orbital electron density that looks like a “four leaf clover”. Rotate this around so you can get a good sense of how it looks in three dimensions. Notice that there are two nodes in the 3*d* orbital. The orbital electron density goes to zero along two perpendicular planes. There are 5 different *d* orbitals. 4 of the 5 have this shape and are just oriented in different planes perpendicular to each other (d_{xy}, d_{xz}, d_{yz}) or rotated in the plane relative to each other ($d_{x^2-y^2}$). The 5th *d* orbital has the appearance of dumbbell with a donut ring around the center. We don’t yet have a visualization developed for the d_{z^2} orbital. As with the p orbital, switch back to the 3d Function image and notice that some of the lobes are negative. As before, now we are viewing Ψ and not the orbital electron density ($\Psi^*\Psi$). You can see the four lobes on the contour plot for both the 3d Function and 3d*3d. Because *d* orbitals are increasingly three-dimensional, it becomes harder to represent them completely with 2D graphs. d orbitals do not have radial symmetry, even along one axis (as in p orbitals). The Ψ and $\Psi^*\Psi$ shown in the 2D graphs are along the diagonal shown in the contour plot. Both (only two of the four can be shown at a time on a 2D plot) are positive.

The 4f Orbital

Switch now to the 4*f* orbital page using the Table of Contents page or the menu. Again, start with the lower right image using the 4f*4f pulldown. Here you may have to click in the box then (without clicking) drag to get a smaller image that fits completely in the box. Notice there are now 8 lobes and 3 nodes. Think of it as a 3D “eight leaf clover”. Rotate this around to get the full 3D effect. There are seven different types of *f* orbitals. Two of the seven look like the one you are seeing now. Four of the seven have a more planar arrangement. The 7th one has a dumbbell with two donut rings. Notice the same sort of things relating the 3D plot to the contour plot and the 2D plots as was noted for the 3*d* orbital. Here, because of the fully 3D character of the orbital, even the contour plot can’t capture all aspects of the orbital, but only the orbital relative to one of the planes.