Chapter 14

Atomic Orbitals

In this chapter, we will be talking primarily about the Hydrogen atom. However, a lot of what we are saying will be an approximation to other atoms. In the Hydrogen atom, there are just two particles interacting, an electron and a proton. The proton is more than a thousand times more massive than the electron. That means that as a result of their interaction, the electron moves far more than the proton does. As such, we can view it as an electron moving about in the potential of the proton. Except for the fact that it provides this potential, to first order we can ignore the proton, and just consider the electron as the quantum mechanical particle.

For other atoms, there are additional electrons. The energy levels that we have calculated for Hydrogen can very easily be adapted to take into account a nucleus with more protons— all you have to do is multiply all of the energy levels by Z^2, the square of the number of protons in the nucleus (which is also the positive charge of the nucleus). We can then *approximate* other atoms by putting electrons into all of these energy levels. Because electrons are fermions, we can only put two into any given orbital. (Two because there are two possible spin states for an electron.) However, this implicitly assumes that the electrons are interacting only with the nucleus, and not with each other. That approximation will allow us to get a lot of insight into the structure of (for example) the Periodic Table of the elements, but is too much of an approximation to be able to figure out precise energy levels.

14.1 The Schrödinger Equation

The one-dimensional Coulomb potential was presented in section 13.6. Of course, the real Hydrogen atom is three-dimensional. The Schrödinger equation that results is almost identical:

$$\hat{K}\,\psi(\vec{r}) \;+\; V(r)\,\psi(\vec{r}) \;=\; E\,\psi(\vec{r})$$

First, remember that when we say $\psi(\vec{r})$, that's a shorthand for $\psi(x, y, z)$. On the left, we've broken the Hamiltonian $\hat{H}$ into the kinetic energy part ($\hat{K}$) and the potential. Notice that in here, we don't have $V(x, y, z)$, but only $V(r)$. When we say r without the little vector arrow, we mean the distance from the origin, that is, $r = \sqrt{x^2 + y^2 + z^2}$. The potential here is *spherically symmetric*. Because it depends only on the origin, if you rotated the whole system through any angle, the potential would be no different.

If we substitute in the correct expression for the potential $V(r)$, this equation becomes:

$$\hat{K}\,\psi(\vec{r}) \;-\; \frac{1}{4\pi\,\epsilon_0}\frac{e^2}{r}\,\psi(\vec{r}) \;=\; E\,\psi(\vec{r})$$

As noted in the previous chapter, the potential is always negative. As r gets very large (i.e. the electron is very far away from the proton), the potential approaches zero. Again, this is just a convention; we could add any constant we wanted to the potential without changing the physics of what's happening. We've chosen this because it's convenient not to have to worry about the nuclei of atoms that are far away. The solution to this equation will be individual functions $\psi(\vec{r})$, each corresponding to a different allowed state, each with a corresponding energy level. The solutions that represent an atom— where the electron is bound to the proton— have $E < 0$. Classically, if a particle moves in this potential, that will set a maximum distance away from the origin that the particle could reach.

14.2 The Orbitals

The specific functions $\psi(\vec{r})$ (or $\psi(x, y, z)$, or $\psi(r, \theta, \phi)$ that work with the Schrödinger equation are the eigenfunctions of the Hamiltonian operator. Because we don't know necessarily when we start what those functions are, even though we've now specified the operator, we have to go through a process in order to figure out what the possible functions $\psi(\vec{r})$ are.[1] Therefore, we call those functions the "solutions" of the Schrödinger equation. The exact functional form of these solutions aren't particularly illuminating. However, they do have some general features, the existence of which underlie all of atomic structure. In the previous chapter, we talked about some solutions that could be described by energy levels. For instance, the solutions to the one-dimensional simple harmonic oscillator have evenly spaced energy levels indexed by an integer n. In three dimensions, it will take three different "quantum numbers" to index the solutions. The numbers we choose to represent the states are the ones that have a most direct physical interpretation.

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[1] That process is much more advanced than what could be covered here and involves differential equations.

We call the solutions "orbitals" rather than just energy levels. In Hydrogen, there are usually multiple orbitals that share the same energy. In other atoms, fewer orbitals will share the same energy. These orbitals represent states available to the electron. Each state has an energy, a total angular momentum, and a z component of orbital angular momentum associated with it.[2] Those three values are the observables for which the orbitals are eigenstates. It's not surprising that the orbitals are energy eigenstates, because we produced them by finding states represented by wave functions that solve the Schrödinger equation, which *is* the energy eigenfunction equation. It is less obvious why they would be angular momentum eigenstates. It turns out that it's possible to break the kinetic energy operator into two parts, a "radial" part and a part that *is* the orbital angular momentum operator. That means that the Schrödinger equation includes the orbital angular momentum eigenvalue equation inside it.

These orbitals are *not*, however, eigenstates for position or for momentum. In particular, not being position eigenstates, electrons in atomic orbitals do not have definite position. Rather, there is a probability density for them to be at different positions, just as an electron in the $|+z\rangle$ spin state is not in a definite state of x spin and has probabilities to be found with positive and negative x spin. While the name "orbital" suggests that the electron is circling the nucleus in a manner analogous to how the Earth circles the Sun, this is not what is happening at all. The electron doesn't follow any particular path through space around the nucleus. Instead, the orbital is a probability cloud representing the effective amplitude for the electron to be found in any one tiny region of space around the nucleus. One consequence of this is that the negative charge associated with the electron is spread throughout this cloud. Whereas the Earth's mass is always at the position the Earth is in its orbit at any given moment, there is no single position for an electron in an atom, so there's no single place where the electron's charge is. The charge of the electron is more diffuse. Additionally, the center of the cloud is right at the nucleus. For the ground state, where the probability distribution is spherically symmetric, to something "far" from the atom (i.e. far enough away that the probability for the electron being found that far away or farther is negligible) the atom acts as if it were entirely neutral, with the effective charge of the electron being at exactly the same place as the effective charge of the proton.

Of the three quantum numbers that represent the electron orbitals, the quantum number n, the principle quantum number, is sometimes called the shell number. The

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[2] Remember that if a system is in a definite state for the z component of angular momentum, it can not have a definite value for x and y angular momentum. This is true for orbital angular momentum as well as for the intrinsic spin of particles. Whereas in a classical system, x, y, and z components of angular momentum would give you three "degrees of freedom", three things that could be varied, the orthogonality of those observables in quantum mechanics means that you only have two: total angular momentum, and one component.

average distance of the electron from the nucleus is determined *primarily* by n. In a single-electron atom, to first order the energy of the atom is determined entirely by n. (There are second order effects, such as the magnetic interaction between the spin and orbit of the electron, that are beyond the scope of this class.) The ground state has $n = 1$, and higher shells have larger values of n.

The second quantum number, l, indexes the total orbital angular momentum of an electron in that state. It too must be a non-negative integer; that is, it can be 0 or a positive integer. The angular momentum represented by l does *not* include the spin angular momentum of the electron. Electrons remain electrons, and as such their total spin angular momentum is $\frac{\sqrt{3}}{2}\hbar$, and the possible projection along any axis is quantized to $+\hbar/2$ and $-\hbar/2$. The *total* angular momentum in the electron cloud of an atom depends on the orbital and spin angular momenta of all the electrons. Combining those angular momenta is fairly complicated, and involves taking into account the fact that electrons are indistinguishable particles. It turns out that for a given state, the angular momentum quantum number l must be less than the principle quantum number n. Thus, for the ground state, $n = 1$, we know that $l = 0$. The next shell out, $n = 2$, there are two possible values of l: $l = 0$ and $l = 1$. The orbital angular momentum associated with a given value of l is $\hbar\sqrt{l(l+1)}$. Notice that this means that the ground state orbital has zero orbital angular momentum! This highlights the degree to which these orbitals are not analogous to planets circling stars, for a planet circling a star assuredly does have orbital angular momentum.

The third quantum number, m, indexes the z projection of the angular momentum. Just as electron spin angular momentum is quantized, so is electron orbit angular momentum. However, there's a difference. Instead of having half-integral values, orbital angular momentum has integral values. As a spin-1/2 particle, we could say that the quantum number for the total spin of every electron is $s = 1/2$. The z projection, which we've called s_z, is then either $+\frac{1}{2}\hbar$ or $-\frac{1}{2}\hbar$. We could say that there are quantum numbers, perhaps m_s, associated with electron spin that give the electron two possible spin states, one with $m_s = 1/2$, the other with $m_s = -1/2$.

In electron orbits, the total angular momentum l is an integer. m can be either positive or negative (representing angular momentum that's in the positive or negative z directions). Unlike electron spin, m can also be zero. However, m cannot get any larger than l. Thus, for a given value of l, there are $2l + 1$ possible projections: $m = -1$, $m = -1 + 1$, …, $m = 0$, …, $m = l - 1$, $m = l$.[3] The z component of orbital angular momentum associated with an orbital with quantum number m is just $m\hbar$. Notice that, just as with electron spin, it's impossible to have a z component of angular momentum that is equal to the total angular momentum of the state. Just like electron spin, the x, y, and z components of angular momentum are all represented

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[3] So for $l = 1$, there are three possible values of m: -1, 0, and 1. For $l = 2$, there are five possible values of m: -2, -1, 0, 1, and 2. And so forth.

by non-commuting operators. That is, an orbital can only be in a definite state for one of them. Thus, while a classical particle would have multiple different states (effectively) for a given l and m (as there would be different x and y projections of angular momentum available), a quantum particle's orbit is *completely specified* by just the total angular momentum quantum number l, and the z projection quantum number m.

The solution to the Schrödinger equation provides a dazzling wealth of orbitals available to the electron in the Hydrogen atom. Strictly speaking, we've solved for the orbitals as energy eigenstates. This means that if an electron is in one of those states, in the absence of observations or interactions it will stay in that state. (If it's in an indeterminate energy state, if you somehow manage to measure the energy of the atom you will collapse the atom's wave vector and it will drop into an eigenstate.) However, observationally, atoms that are in excited states do not stay there forever. After a while, they will spontaneously decay, with the electron dropping down to a lower state, and eventually with the electron reaching the ground state (which *is* stable. This would imply that the atom must somehow be interacting with something, if it is able to change from one eigenstate to another. Indeed, it does; it is interacting with the electromagnetic field. Even if there isn't any light (i.e. any "excitations of the electromagnetic field") around us, the field is always there. What's more, there are always virtual photons, as a result of the energy/time version of Heisenberg's Uncertainty Principle (Section 11.4.1). The interaction of the atom with the electromagnetic field yields a probability in any given time interval that the atom may emit a photon and drop to a lower energy state. The energy of that photon corresponds exactly to the difference in energy between the upper and lower states of the transition.

14.3 Visualizing Orbitals

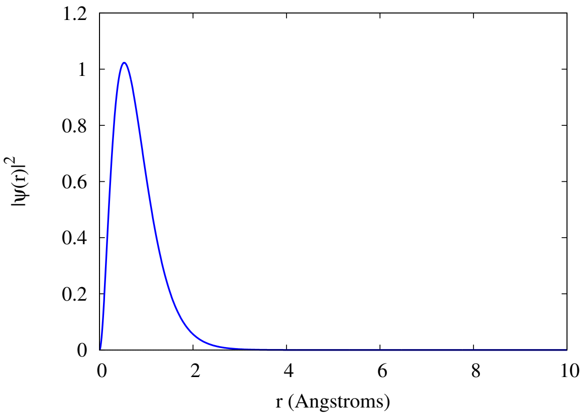
Historically, the energy available orbitals in an electron were identified by observing the wavelengths of light that would be emitted as the electron changed energy levels. Until we understood that light was quantized in photons, it was difficult to explain this as different energy levels. However, it was recognized that there were specific spectroscopic "lines" (i.e. wavelengths associated with a given transition) for each atom. The nomenclature that grew up around these lines is what gives us the nomenclature that we use today to name the various orbitals. Alas, the reasons for the letters that we use have little to do with the physics of the atom and everything to do with how the spectroscopic lines looked to the scientists who identified them. Each orbital is indicated by a form nx, where n is the principle quantum number and x is a letter corresponding to the angular momentum quantum number l. That letter is s for orbitals with $l = 0$; it is p for orbitals with $l = 1$; it is d for orbitals with $l = 2$;

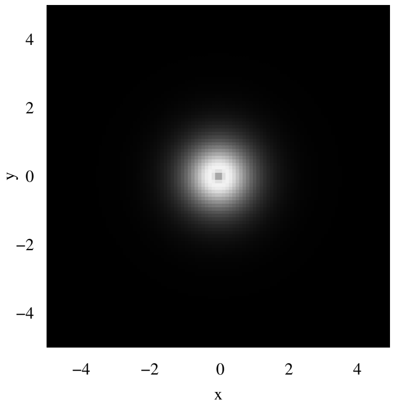
and it is f for orbitals with $l = 3$.

14.3.1 s Orbitals

Orbits with $l = 0$ are called s orbitals. Although this is not where the letter comes from, it's useful to think of these as "spherical" orbitals, because they are spherically symmetric. However, they aren't just spheres! Again, remember that the probability cloud for the electron is a fuzzy ball around the nucleus, representing where the electron is likely to be found.

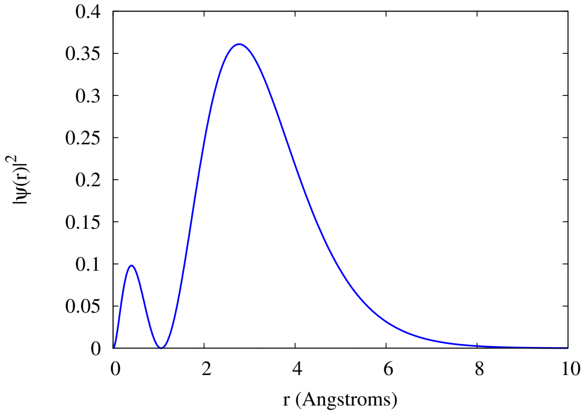
The plot below shows two visualizations of the 1s orbital. On the left is a plot of $\Psi^*(r)\Psi(r)$. This gives the *probability density* for the electron to be found at radius r. That is, you must pick a small range dr around the r you're interested in, and multiply this probability density by that dr. You then get the probability for finding the electron with that dr of your chosen r. On the right is a cut through the $x - z$ plane showing the probability density as a function of position. Lighter colors mean more probability of finding the electron at that position. Notice that there is a darker spot at the center. This corresponds to the probability dropping to zero at $r = 0$, as seen in the left plot. In both cases, distances are plotted in terms of Angstroms; one Angstrom is 10^{-10} m which, as you can see from the plot, is about the size of an atom.

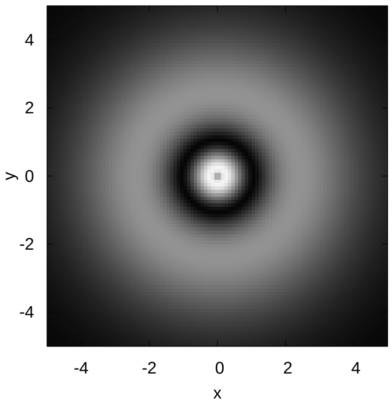




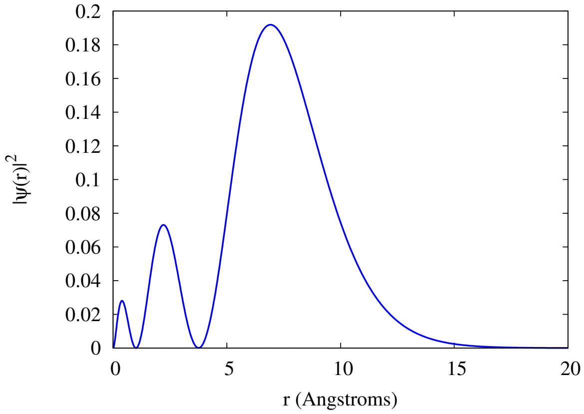
If you go to the 2s orbitals, an additional bump is added to the radial wave function. Also, the average distance the electron is from the center of the atom gets larger. While the probability clouds for a 1s and 2s orbital overlap, most of the probability for a 2s electron is outside most of the probability for a 1s electron. This means that to some extent, when working out the properties of an atom with two electrons in the 1s shell and one 2s electron (that would be Lithium), we can treat the nucleus plus the 1s shell as a single spherical ball of net charge +1. While this isn't perfect, this does lend some support to the approximation we'll make for multi-electron atoms that each electron is moving in a nuclear potential and not interfering too much with other electrons.

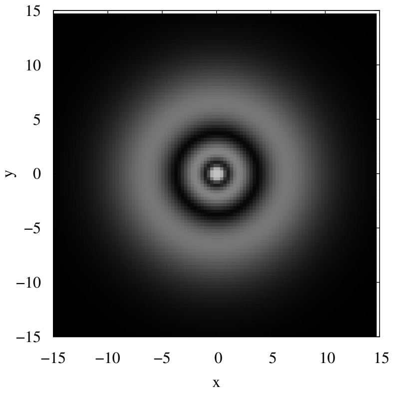
Below are the same two plots for the 2s orbital. The scale of the axes is the same as the scale used previously in the 1s orbital, so that you may compare the plots directly.





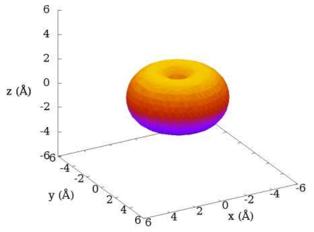
As we move to the 3s orbital, we have to expand the limits of our plots, as the electron is starting to have more and more probability to be at greater radius. In the plots below, you can see that the electron cloud still has reasonable probability density at a radius of 15 Angstroms. You can also see that the 3s orbital is three concentric fuzzy spherical shells; equivalently, the radial function has three bumps. Again, sizes are in Angstroms.



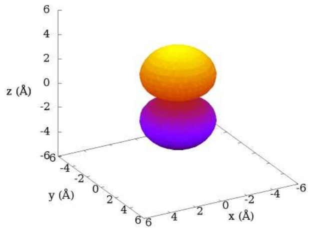


14.3.2 p Orbitals

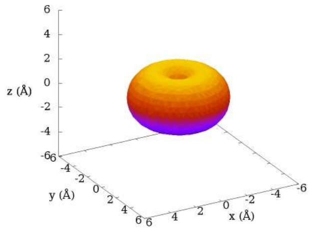
Orbitals with total angular momentum quantum number $l = 1$ are called p orbitals. Remember that l must always be less than n. As such, the first shell has no p orbitals; it only has s orbitals. This means that you can only put two electrons (with opposite spin) in the first shell. In the second shell, you can put eight total electrons. You can put two electrons in the 2s orbital, and six in the 2p orbital. Why six? For $l = 1$, there are three possible values for m, the quantum number that indexes the z component of angular momentum: $m = 1$, $m = 0$, and $m = -1$. Below is three plots showing what the $2p$ orbitals look like.



$m = +1$

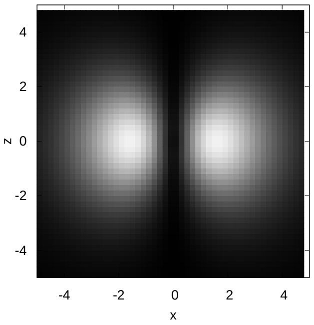


$m = 0$

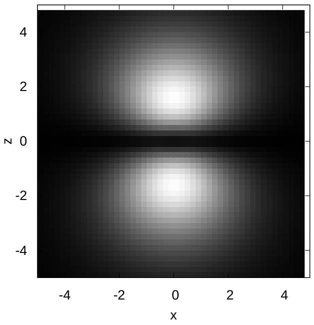


$m = -1$

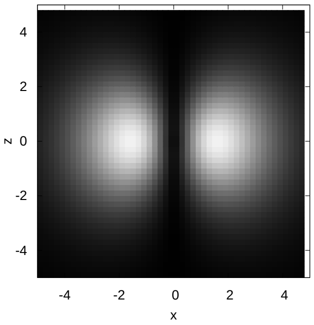
What we've drawn here is a surface of constant probability. In reality, the p-orbitals aren't hard shells, as this picture would seem to indicate. Rather, just as with the s-orbitals, they're fuzzy, with higher probability towards the "center" of the distribution (which may not be at the origin!) and less probability away from it. As a way of visualizing this, the plots below show a cut in the $x - z$ plane of the three orbitals depicted above:



$m = +1$



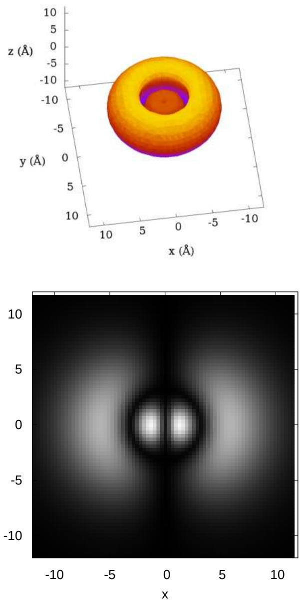
$m = 0$



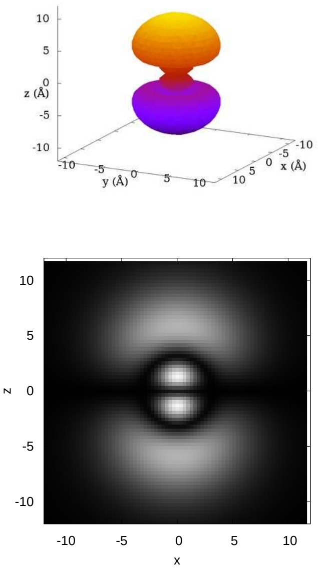
$m = -1$

Notice that the $m = +1$ and $m = -1$ $2p$ orbitals look identical. If you imagine rotating the plot around a vertical axis through the center of the plot, both of those orbitals look like two lobes, one over the other. The $m = 0$ orbital looks different, however. If you imagine rotating it around a vertical axis, you get an orbital that looks like a thick donut.

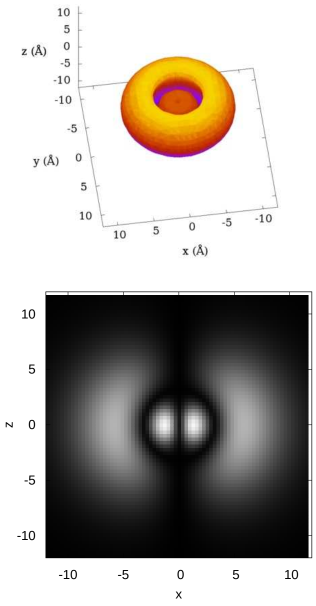
The p orbitals for higher values of n get more interesting. Just as the s orbitals become versions of themselves nested inside each other, the same thing happens with the p orbitals. Below are the three $3p$ orbitals:



$m = +1$



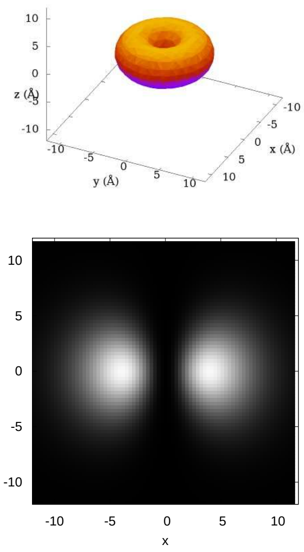
$m = 0$



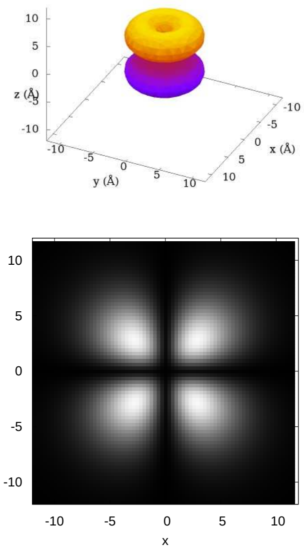
$m = -1$

14.3.3 *d* Orbitals

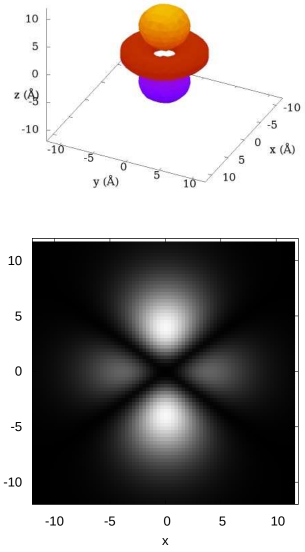
When $l = 2$, the orbitals that are the solutions of the Hydrogen atom Schrödinger equation are called d orbitals. These orbitals only exist for shells with $n = 3$ and greater, again because l must be less than n. As we saw with the p orbitals, the probability density for the electron in space is the same for $+m$ and $-m$. As such, we'll only plot the positive-m versions of the orbitals. As before, in addition to a 3d plot showing "shells" at a constant probability level, there is a 2d plot showing a cut in the x-z plane.



$m = 2$

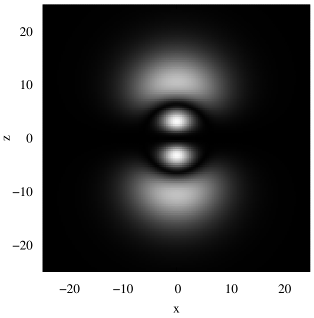


$m = 1$

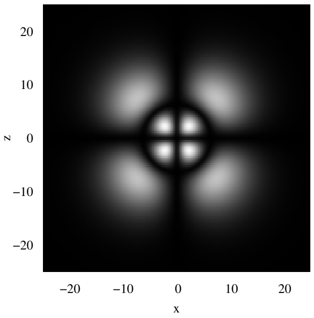


$m = 0$

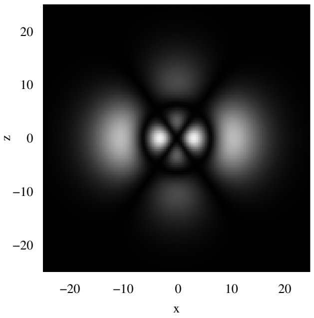
As with the p orbitals, as we go to the d orbitals in higher shells they get more interesting. Plotted below are the cuts through the x-z plane for the $4d$ orbitals:



$m = 2$



$m = 1$



$m = 0$