

Atlas of electrons in atoms

Notes on Quantum Mechanics

<http://quantum.bu.edu/notes/QuantumMechanics/AtlasOfElectronsInAtoms.pdf>
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How we label wavefunctions of electrons in atoms

Because atoms are spherical, wavefunctions of electrons in atoms are most simply expressed mathematically in spherical polar coordinates. We have seen that these wavefunctions can be cataloged according to the number of radial loops, j , and the number of angular wavelengths, ℓ .

A quick way to determine the number of angular wavelengths is to look for surfaces cutting thorough the center of the atom on which the wavefunction vanishes *everywhere*. Such surfaces are called *nodal surfaces*. There is one nodal surface for each angular wavelength, and so in this sense the number of angular wavelengths and the number of nodal surfaces are synonymous.

The number of nodal surfaces (angular wavelengths) is usually expressed in terms of the following letter code: $\ell = 0 \rightarrow s$, $\ell = 1 \rightarrow p$, $\ell = 2 \rightarrow d$, and $\ell = 3 \rightarrow f$. If there are more than three nodal planes ($\ell > 3$), the code continues alphabetically, starting with g. The codes s, p, d, and f arose from the visual characterizations of lines in the spectra of atoms. These lines were eventually understood to involve wavefunctions with the corresponding number of nodal surfaces: s was associated with *sharp* lines, p was associated with *principal* (most intense) lines, d was associated with *diffuse* lines, and f was associated with *fine* (or perhaps faint) lines.

For an atomic electron wavefunction, the sum of the number of its radial loops, j , and the number of its nodal surfaces, ℓ , is known as its *principal quantum number*, $n = j + \ell$.

Wavefunctions are abbreviated by giving their principal quantum number and the code for the number of angular wavelengths. Here are some examples. A 5p wavefunction has $\ell = 1$ angular wavelength and $n - \ell = 5 - 1 = 4$ radial loops. A 3s wavefunction has $\ell = 0$ angular wavelengths and $n - \ell = 3 - 0 = 3$ radial loops. A 4f wavefunction has $\ell = 3$ angular wavelength and $n - \ell = 4 - 3 = 1$ radial loop.

- | How many radial loops does a 3p wavefunction have? Answer: two.
- | How many angular wavelengths does a 3d wavefunction have? Answer: two.
- | Give the abbreviation of a wavefunction with four angular wavelengths and two radial loops. Answer: 6g.

The reason the principle quantum number is important is that the energy of an electron in an atom is greater, the greater the principle quantum number of its wavefunction. The relative ordering of energy (lower energy, more stable to higher energy, less stable) is determined first by the value of n , and then, for a given n , by the value of ℓ , as follows:

$$1s < 2s < 2p < 3s < 3p < 3d < 4s < 4p < 4d < 4f < \text{etc. (atomic electron energy ordering).}$$

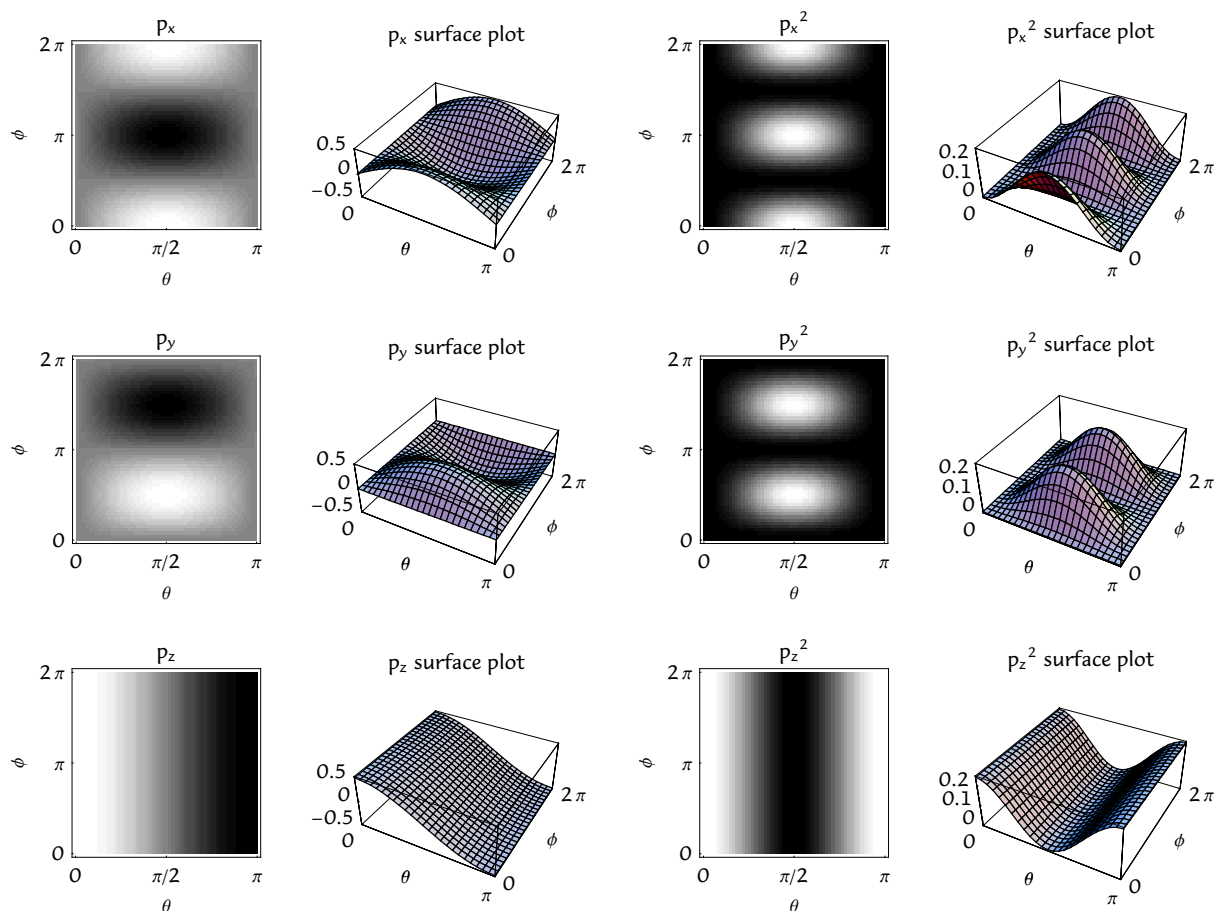
Soon we will learn about why this ordering is so, but for now it is good to memorize it.

Dissecting wavefunctions of electrons in atoms

A consequence of the spherical symmetry of atoms is that the wavefunction of an electron in an atom can be expressed in terms of how it changes with distance, r , from the nucleus—its *radial variation*—and how it changes with its angular position, θ and ϕ —its *angular variation*. The part of the wavefunction that changes with distance from the nucleus is known as the *radial wavefunction*. The radial wavefunction depends on the values of n and ℓ and is written as $R_{n\ell}(r)$. The part of the wavefunction that changes with angular position is known as the *angular wavefunction*. The angular wavefunction depends on the value of ℓ and on the value of second index, m , and is written as $Y_{\ell m}(\theta, \phi)$. It turns out that for a given value of ℓ there are $2\ell + 1$ angular wavefunctions, differing in the positions of their ℓ nodal planes. The index m labels these different locations.

For an s electron there are no nodal planes and so the angular wavefunction is a *constant*, that is, there is no change in the electron wavefunction at a given distance from the nucleus for different angular positions.

For a p electron there is one nodal plane, and there the $2\ell + 1 = 3$ different orientations of the nodal plane. The angular wavefunctions are labeled p_x , p_y and p_z according which Cartesian axis is perpendicular to the nodal plane. Here are two representations of the p_x , p_y and p_z angular wavefunctions and their squares.



Two representations of the p_x , p_y and p_z angular wavefunctions (left two columns) and their square (right two columns). For each line, in the left most plot, bright areas are positive values and dark areas are negative values of the wavefunction; in the next plot, the values of the surface above zero are positive values and values of the surface below zero are negative values of the wavefunction; on the next plot, bright areas are large positive values and dark areas are small positive values of the squared angular wavefunction; finally, on the right most plot the height of the surface is the value of the squared angular wavefunction.

For which values of θ and ϕ does the p_x angular wavefunction have its largest positive value? Answer: $\theta = \pi/2$, $\phi = 0 = 2\pi$.

For which values of x , y and z does the p_x angular wavefunction have its largest positive value? Answer: $x > 0$, $y = 0$, $z = 0$.

For which values of θ and ϕ does the p_x angular wavefunction have its largest negative value? Answer: $\theta = \pi/2$, $\phi = \pi$.

For which values of x , y and z does the p_x angular wavefunction have its largest negative value? Answer: $x < 0$, $y = 0$, $z = 0$.

Essentially, the p_x angular wavefunction concentrates electron probability amplitude along the x axis.

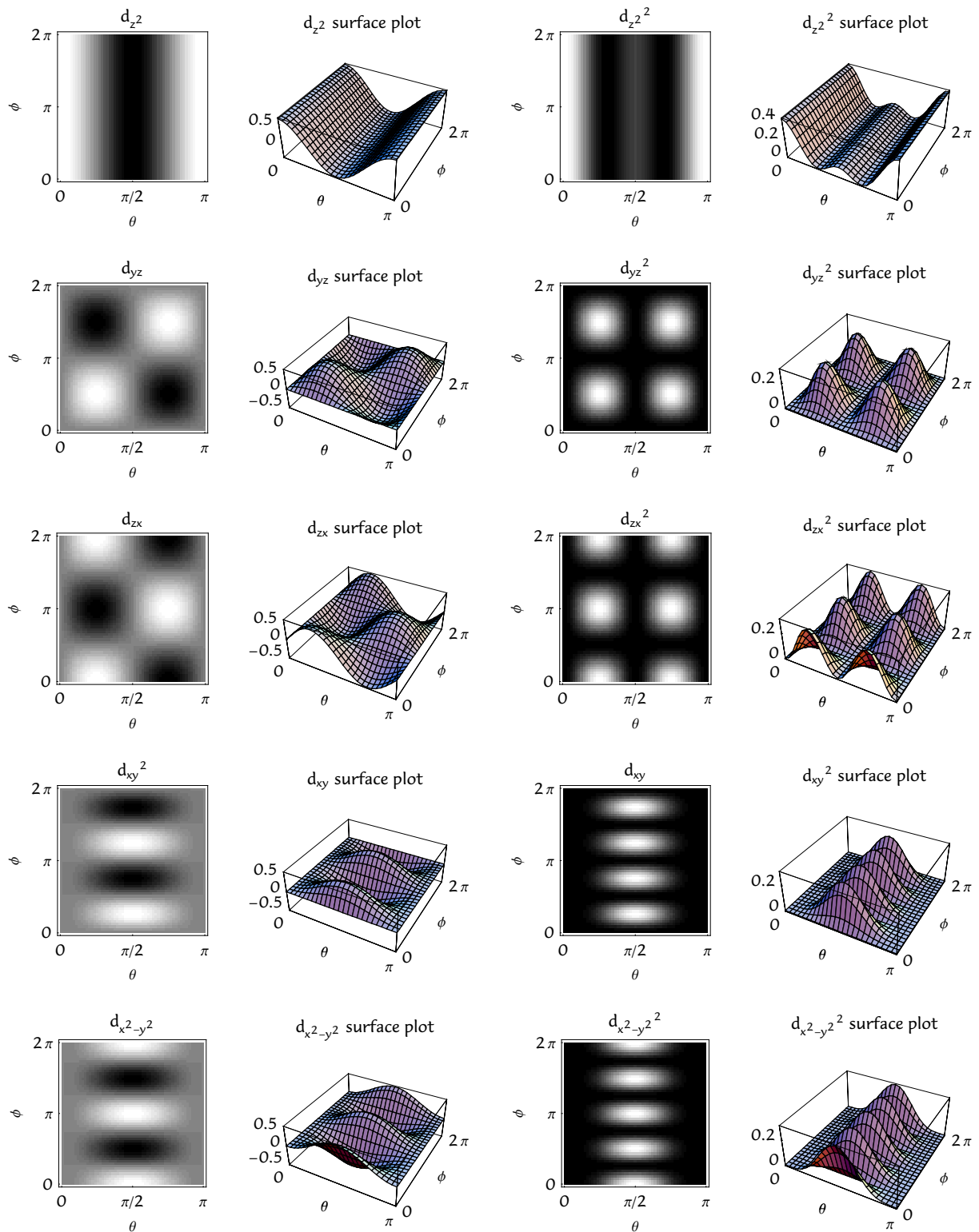
Along which direction does the p_y angular wavefunction concentrate electron probability amplitude? Justify your answer by answering the four questions asked above applied to the p_y angular wavefunction.

Along which direction does the p_z angular wavefunction concentrate electron probability amplitude? Justify your answer by answering the four questions asked above applied to the p_z angular wavefunction.

For a d electron there are two nodal planes, and there the $2\ell + 1 = 5$ different orientations of these nodal planes. The angular wavefunctions are labeled as follows

label	positions of nodal surfaces
d_{z^2}	two cones at 45° and -45° to the xy plane
d_{yz}	two planes perpendicular to yz plane containing y and z axes
d_{zx}	two planes perpendicular to zx plane containing z and x axes
d_{xy}	two planes perpendicular to xy containing x and y axes
$d_{x^2-y^2}$	two planes perpendicular to xy plane at 45° to x and y axes

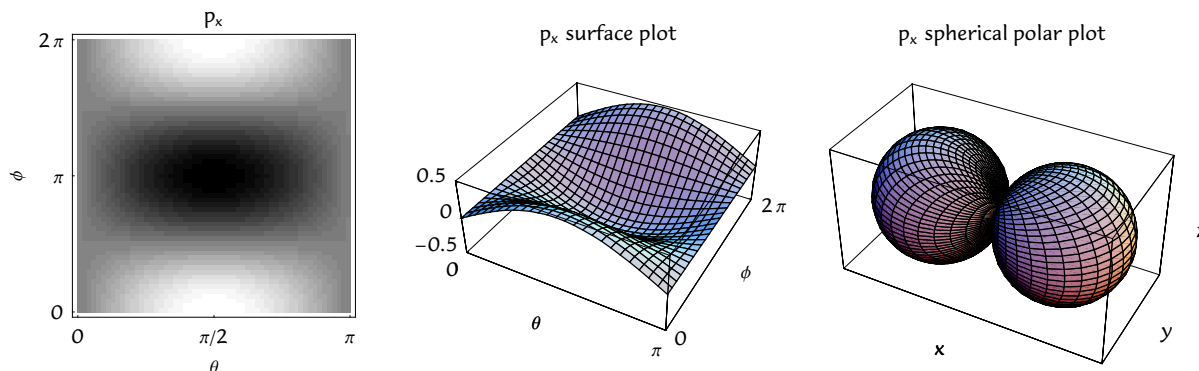
according which Cartesian axis is perpendicular to the nodal plane. Here are the two representations of the five d angular wavefunctions and their squares.



Caution: Spherical polar representation of angular wavefunctions are misleading

We have seen that to understand the distribution of wavefunctions of an electron in an atom we need to use the value of the angular wavefunction along a particular direction as a scale factor to adjust the value of the radial wavefunction. In this regard we have seen two representations of the angular wavefunction, as a density plot and as a surface plot, as a function of the angles θ and ϕ .

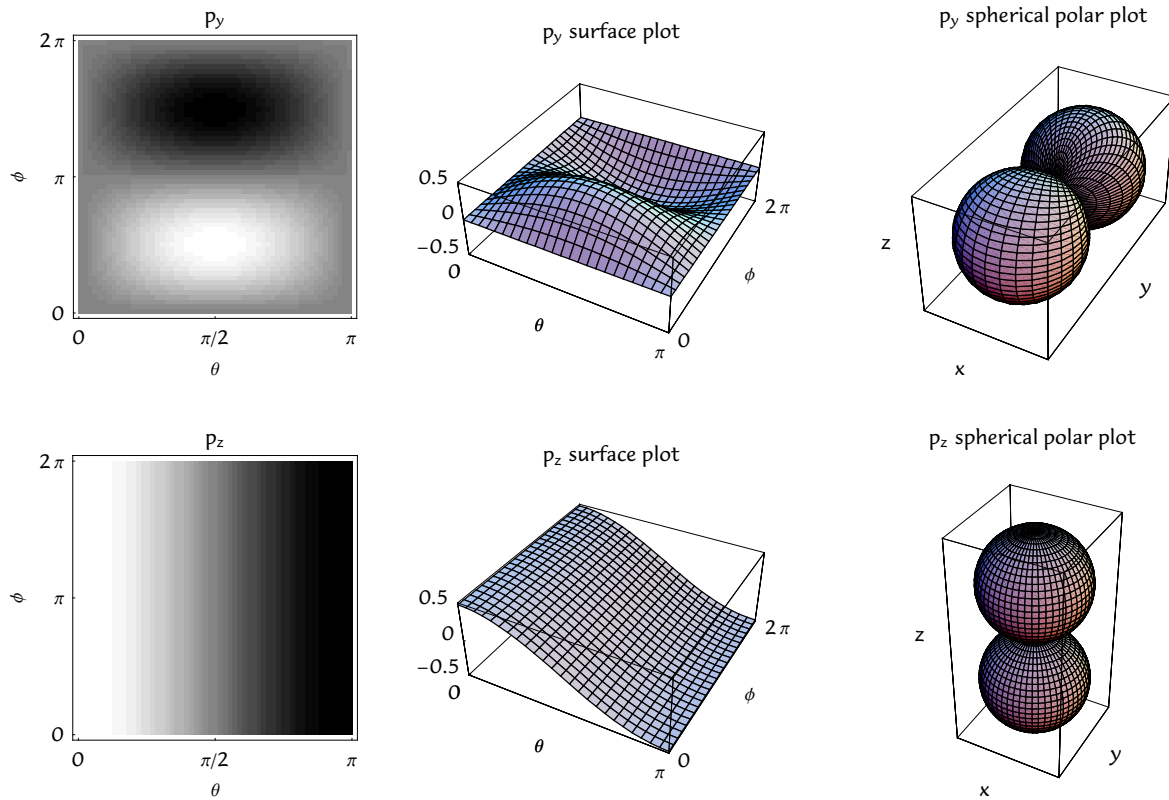
In textbooks a third representation of angular wavefunctions is used, known as a spherical polar plot. A spherical polar plot is a surface whose distance from the origin along a particular direction is the magnitude (that is, the value without sign) of the angular wavefunction along that direction. If the value of the angular wavefunction is positive, a + sign is placed near that part of the surface, and if the value of the angular wavefunction is negative, a - sign is placed near that part of the surface. As an example, here are the two representations we have used of the p_x angular wavefunction together with the spherical polar representation.



Density, surface and spherical polar plots of the p_x angular wavefunction. The positive x lobe of the spherical polar plot is + and the negative x lobe is -.

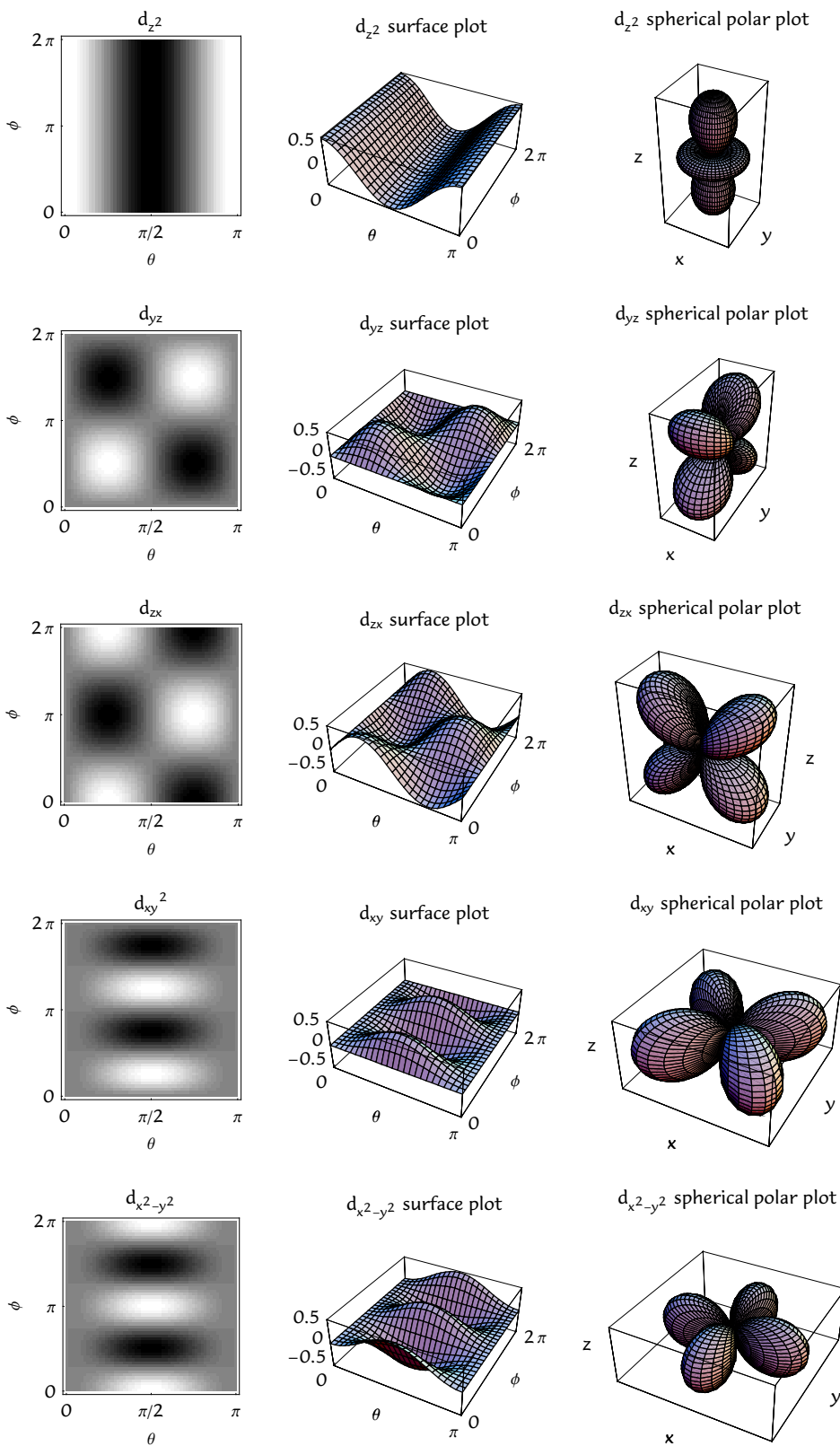
The coordinates x , y and z on the spherical polar plot serve *only* to fix the coordinate system used to define the angles θ and ϕ in the other two plots. In particular, these x , y and z coordinates are *not* the coordinates used to define the location of the electron in space. It is absolutely crucial that you understand this. The reason is that in the spherical polar plot the distance from the origin along a particular direction is *not* the distance of the electron from the nucleus along that direction; rather this distance is the numerical value of the angular wavefunction along the particular direction.

Here are the two representations we have used of the p_y and p_z angular wavefunctions together with their spherical polar representations.



Density, surface and spherical polar plots of the p_y and p_z angular wavefunctions. The positive y lobe and positive z of the spherical polar plots are + and the negative y and negative z lobes are -.

Finally, here are the two representations we have used of the five d angular wavefunctions together with their spherical polar representations.



Density, surface and spherical polar plots of the five d angular wavefunctions. The signs of the lobes on the spherical polar plot alternate, according to whether the corresponding surface value is positive or negative.

Notice how the angular wavelengths shift from the θ dimension to the ϕ dimension.

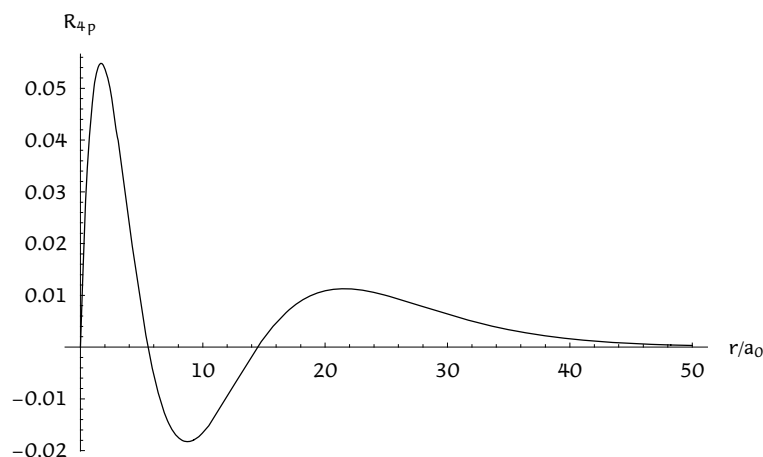
Which angular wavefunction has the *least* excitation in the θ dimension? Answer: Both $d_{x^2-y^2}$ and d_{xy} have no excitation in the θ dimension; that is, all angular excitation is in the xy plane, in the ϕ dimension.

Which angular wavefunction has the *most* excitation in the θ dimension? Answer: Both d_{z^2} the most excitation in the θ dimension, and there is no excitation in the ϕ dimension.

It is a general feature of angular wavefunctions that they differ in the amounts of excitation in the θ and ϕ . For a given ℓ there will always be just one angular wavefunction with excitation *only* in θ and there will always be two angular wavefunctions with excitation only in ϕ .

Constructing wavefunctions of electrons in atoms

The full, three dimensional electron wavefunction is the product $\psi_{n\ell m}(r, \theta, \phi) = R_{n\ell}(r) Y_{\ell m}(\theta, \phi)$ of the radial and angular parts. To learn how the two parts of the wavefunction combine to determine how the wavefunction varies throughout space, let's analyze as example the $4p_x$ wavefunction. Here is the $4p$ radial wavefunction.



Hydrogen atom $4p$ radial wavefunction.

Does this radial wavefunction have the correct number of loops?

Why do you suppose the wavelength increases as the distance from the nucleus increases?

One way to understand the three dimensional distribution of the $4p_x$ wavefunction, is to pick a direction θ, ϕ , and then multiply the radial wavefunction by the value of the angular wavefunction along that direction.

The value of the angular wavefunction along the positive x axis is $\sqrt{3/\pi}/2 = 0.49$. This means that along the positive x axis the $4p_x$ wavefunction is

$$\psi_{4p_x}(r, \theta = \pi/2, \phi = 0) = R_{4p}(r) p_x(\theta = \pi/2, \phi = 0) = R_{4p}(r) \times 0.49.$$

The value of the angular wavefunction along the negative x axis is $-\sqrt{3/\pi}/2 = -0.49$. This means that along the negative x axis the $4p_x$ wavefunction is

$$\psi_{4p_x}(r, \theta = \pi/2, \phi = \pi) = R_{4p}(r) p_x(\theta = \pi/2, \phi = \pi) = -R_{4p}(r) \times 0.49.$$

For which values of θ and ϕ does the p_x angular wavefunction have value zero? Answer: $\theta = 0$ and $\theta = \pi$ and, for all values of θ , $\phi = \pi/4$ and $\phi = 3\pi/2$.

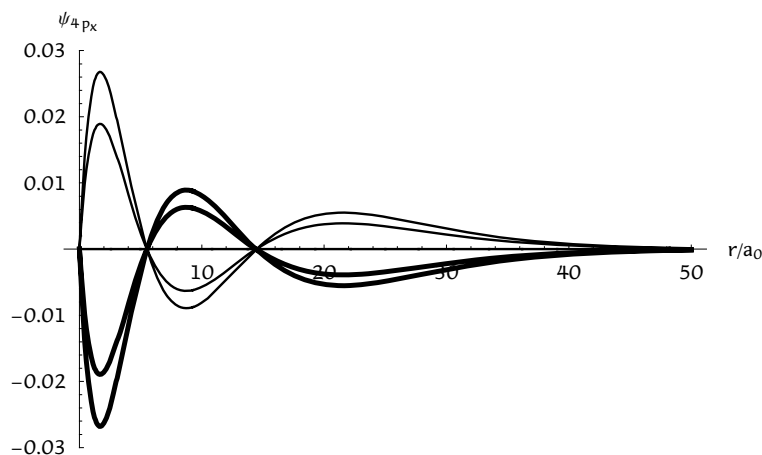
For which values of x , y and z does the p_x angular wavefunction have value 0? Answer: $x = 0$, $y \neq 0$, $z \neq 0$, that is, the yz plane.

The value of the angular wavefunction in the yz plane is zero. This means that in the xy plane the $4p_x$ wavefunction vanishes,

$$\psi_{4p_x}(r, \theta, \phi = \pi/4 \text{ and } 3\pi/4) = R_{4p}(r) p_x(\theta, \phi = \pi/4 \text{ and } 3\pi/4) = R_{4p}(r) \times 0 = 0.$$

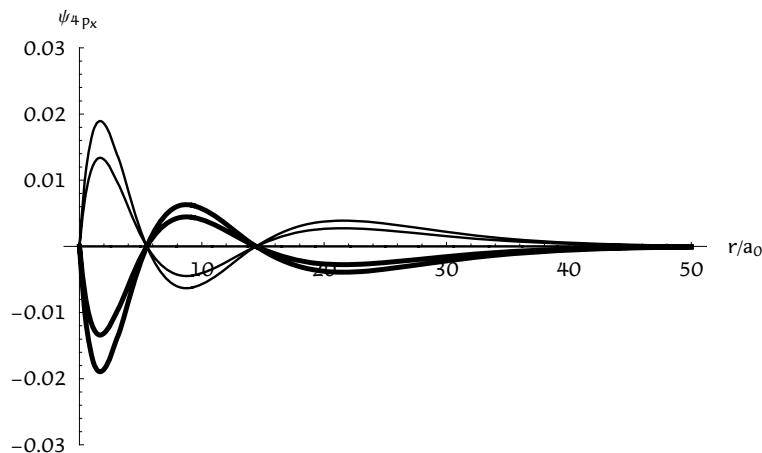
For directions away from the x axis but on the positive x side of the yz plane, the value of angular wavefunction will be between 0.49 and zero, and so the $4p_x$ wavefunction will look the same as along the positive x axis except that its maximum and minimum oscillations will not be as great. Similarly, for directions away from the x axis but on the negative x side of the yz plane, the value of angular wavefunction will be between -0.49 and zero, and so the $4p_x$ wavefunction will look the same as along the negative x axis except that its maximum and minimum oscillations again will not be as great. Finally, along *all* directions in the yz plane, the $4p_x$ wavefunction will be zero, since the angular wavefunction is zero there.

Here is a plot of the $4p_x$ wavefunction for $\theta = \pi/2$ and five equally spaced values of ϕ between 0 and π .

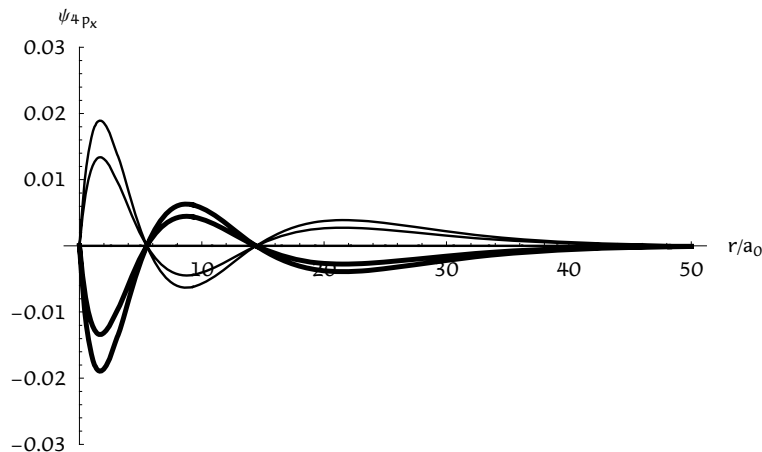


The hydrogen atom $4p_x$ wavefunction for $\theta = \pi/2$ and five equally spaced values of ϕ between 0 and π . Wavefunctions for $\phi > \pi/2$ are shown as heavier lines.

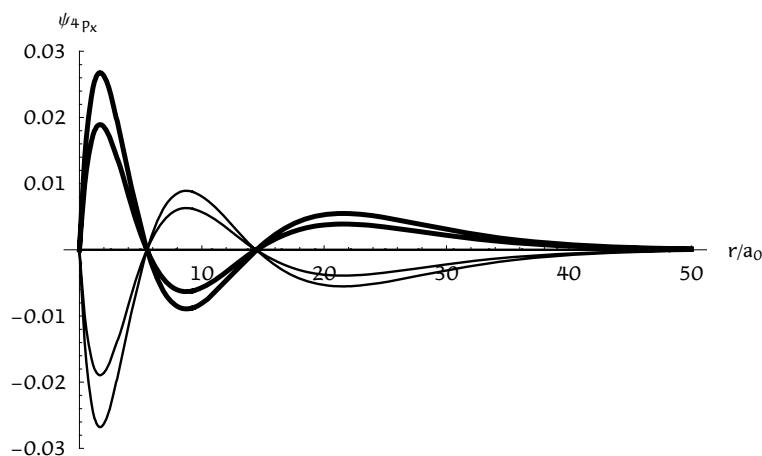
How would the $\theta = \pi/2$ plot change if the value of θ were $\pi/4$? Answer: Results for $\phi > \pi/2$ are shown as heavier lines.



How would the $\theta = \pi/2$ plot change if the value of θ were $3\pi/4$? Answer: Results for $\phi > \pi/2$ are shown as heavier lines.



How would the $\theta = \pi/2$ plot look if the values ϕ were between π and 2π ? Answer: Results for $\phi > 4\pi/3$ are shown as heavier lines.



Shell amplitudes and shell densities

Now that we have some experience interpreting the wavefunction of an electron in an atom, $\psi_{n\ell m} = R_{n\ell}(r) Y_{\ell m}(\theta, \phi)$, in terms of how it changes throughout the space surrounding the nucleus, let's see how we can understand the probability density corresponding to such a wavefunction. We know that probability density is defined as

$$|\psi_{n\ell m}|^2 = R_{n\ell}(r)^2 |Y_{\ell m}(\theta, \phi)|^2.$$

This expression has the units probability/volume. In spherical polar coordinate a small element of volume is

$$dV = r^2 dr \sin(\theta) d\theta d\phi$$

in terms of a small radial range dr and small angular ranges $d\theta$ and $d\phi$. As usual, to determine the probability of an electron being in a region of space centered at r, θ, ϕ we need to specify the volume enclosing this point,

$$|\psi_{n\ell m}|^2 dV = R_{n\ell}(r)^2 |Y_{\ell m}(\theta, \phi)|^2 r^2 dr \sin(\theta) d\theta d\phi.$$

This expression is just a numerical value, with no units, since it is a probability.

Since atoms are spherical, it is helpful to analyze probability in terms of spherical regions. In particular, the *shell probability* is the probability that an electron is *somewhere in the shell of radius r and thickness dr surrounding the nucleus* is

$$\text{shell probability} = \int_0^\pi \sin(\theta) d\theta \int_0^{2\pi} d\phi \left| \psi_{n\ell m} \right|^2 R_{n\ell}(r)^2 r^2 dr.$$

Now, a property of the angular wavefunctions is that the sum of their squared modulus over a spherical surface is one, and so we can write the shell probability as

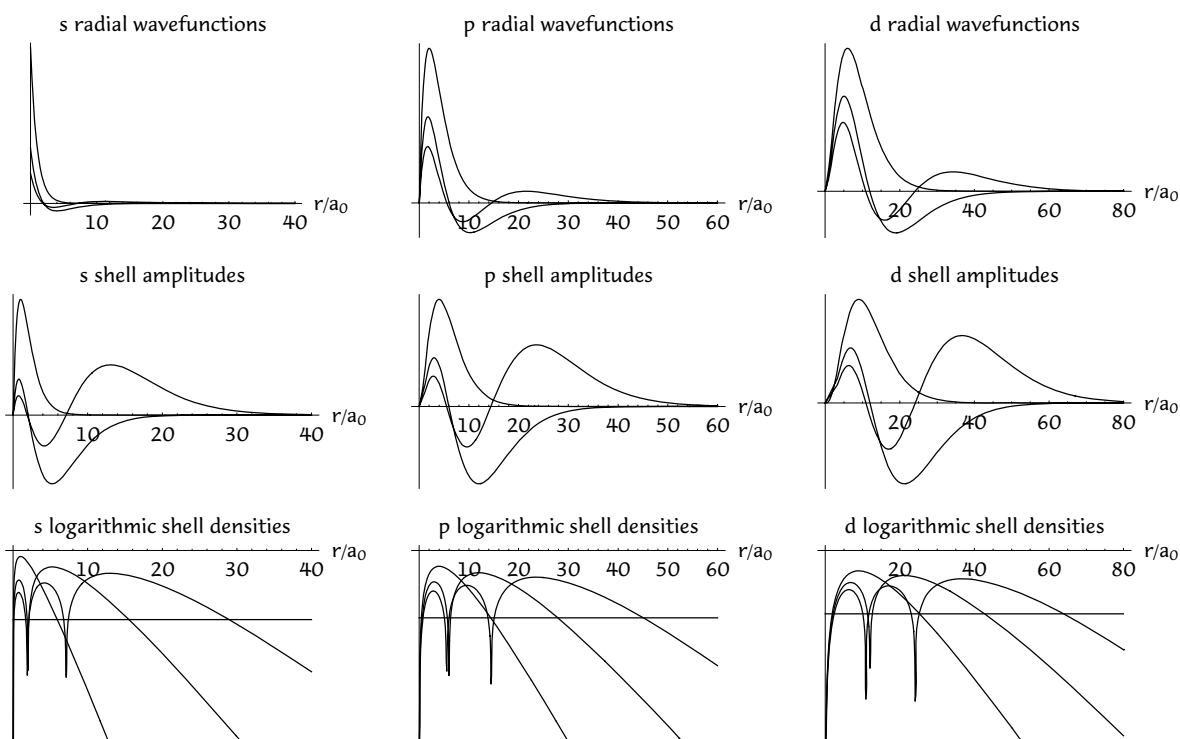
$$\text{shell probability} = R_{n\ell}(r)^2 r^2 dr.$$

The quantity $R_{n\ell}(r)^2 r^2$ has the units probability/length and it is known as the *shell density*. The quantity

$$P_{n\ell}(r) = R_{n\ell}(r) r$$

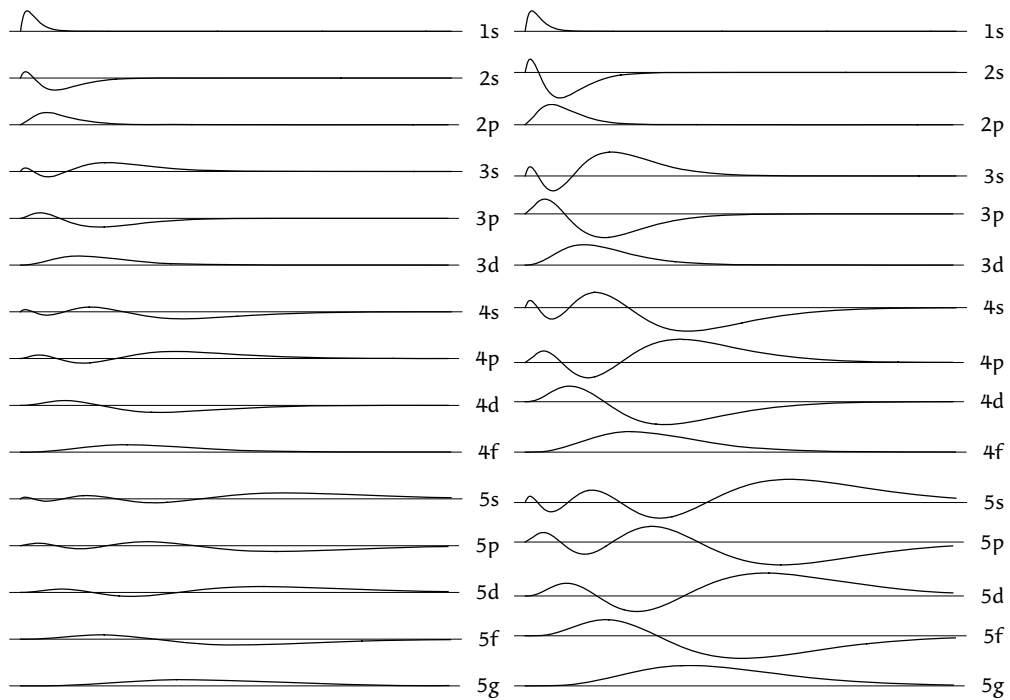
is known as the *shell amplitude*, by analogy to probability amplitude, in the sense that the square of the shell amplitude is the shell density.

Here are the three lowest energy (most stable) radial probability amplitudes (radial wavefunctions), shell amplitudes and shell density for s, p, and d electrons in hydrogen atom.



Three lowest energy (most stable) hydrogen atom, radial probability amplitudes (radial wavefunctions), shell amplitudes and shell density for s, p, and d electrons in hydrogen atom. The shell densities are shown on a logarithmic scale, with a reference line at value $10^{-3}/a_0$.

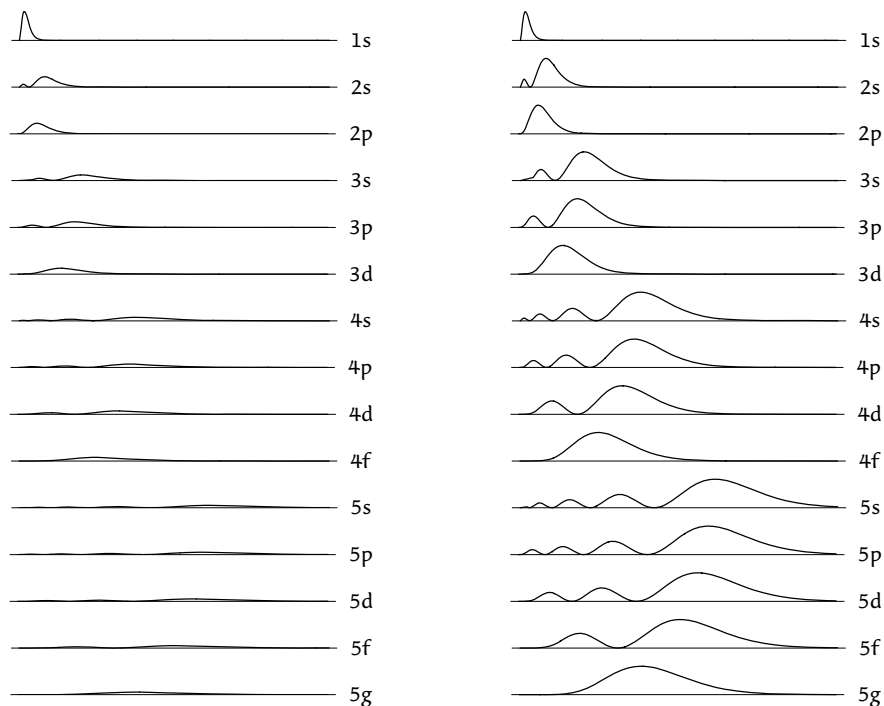
Here are the 1s through 5g shell amplitudes, on an absolute scale (left column) and scaled to a common maximum amplitude (right column).



Hydrogen atom shell amplitudes $P_{nl}(r) = r R_{nl}(r)$. The left column has a common vertical scale; the right column has a vertical scale adjusted so that each amplitude has the same maximum value. The horizontal axis is r , in units of a_0 .

- | Characterize the difference between the 2s and the 2p shell amplitudes.
- | Characterize the difference between the 3s, 3p and 3d shell amplitudes.
- | Explain whether the number of peaks in the 5f shell amplitude are correct.

And here are the 1s through 5g shell densities, on an absolute scale (left column) and scaled to a common maximum amplitude (right column).



Hydrogen atom shell densities $P_{nl}(r)^2 = r^2 R_{nl}(r)^2$. The left column has a common vertical scale; the right column has a vertical scale adjusted so that each density has the same maximum value. The horizontal axis is r , in units of a_0 .

Based on the 3s, 3p and 3d shell densities, for which case is there the greatest electron density close to the nucleus?
Answer: 3s.

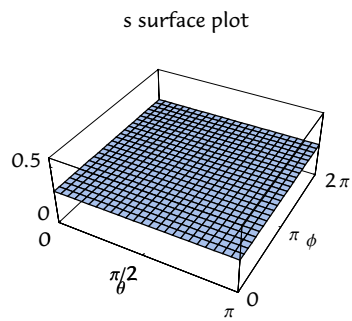
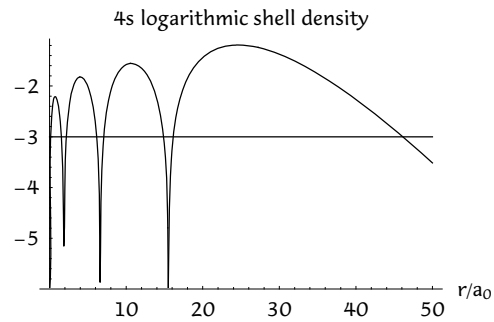
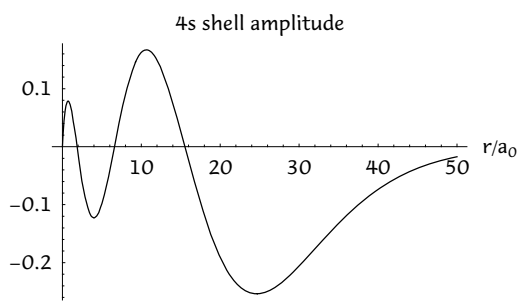
Based on the 3p and 3d shell densities, for which case is there the greatest electron density close to the nucleus? Answer:
3p.

Based on the 3s, 3p and 3d shell densities, for which case is there the greatest electron density far from the nucleus?
Answer 3s.

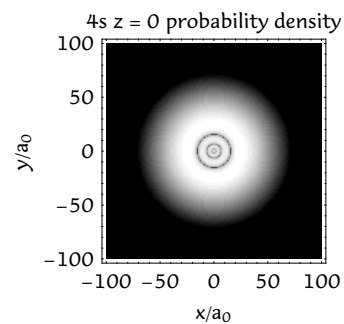
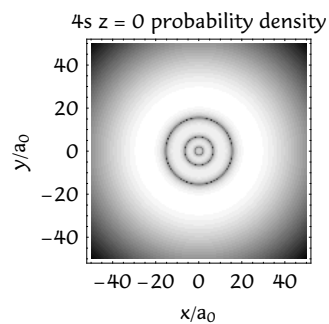
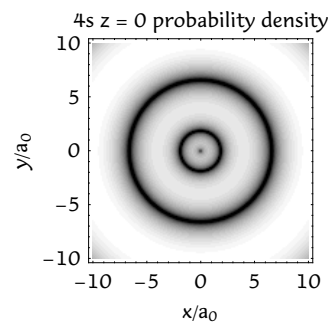
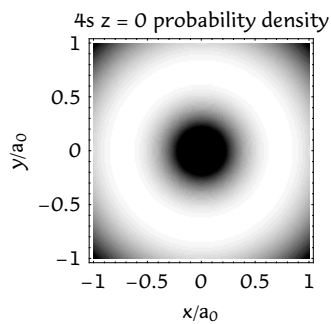
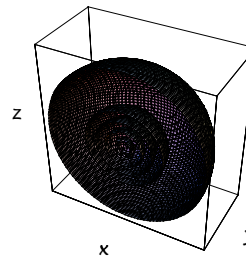
4s shell amplitude, angular wavefunction, shell density and probability density

Now that we understand that the full, three dimensional wavefunction of an electron in an atom is the product of its radial wavefunction and its angular function, lets see some example visualization of these three dimensional wvafuncions.

Here are the radial and angular components, shell density, and xy plane slices of the three dimensional probability density of the hydrogen atom 4s electron.



4s 10^{-3} probability density isosurface

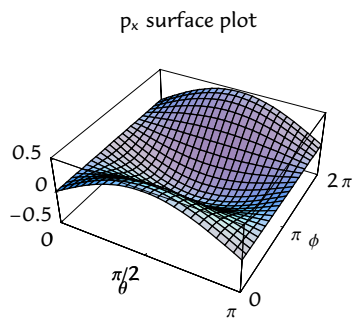
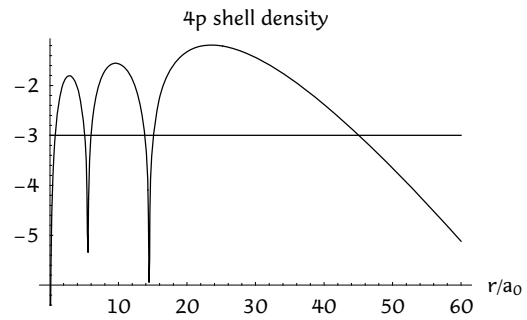
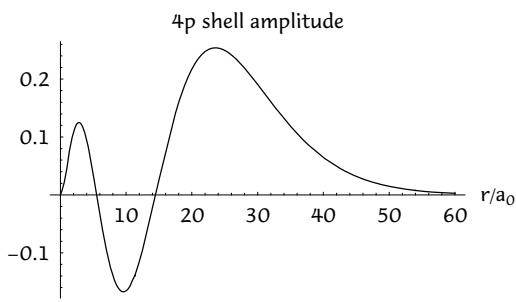


Hydrogen atom 4s electron radial and angular components, shell density, and xy plane slices of the three dimensional probability density.

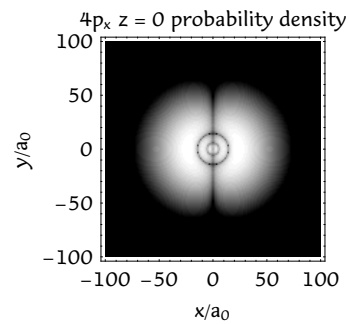
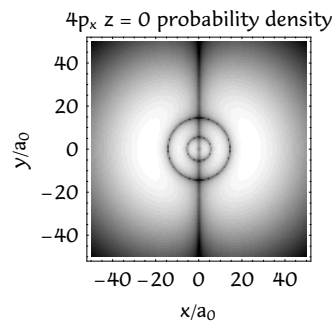
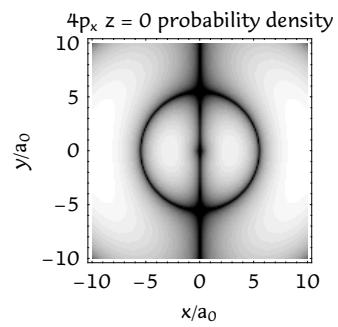
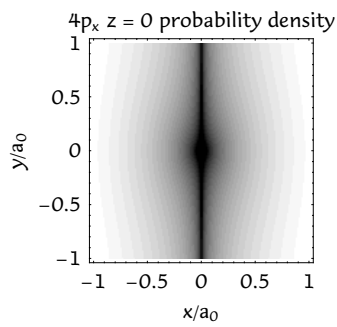
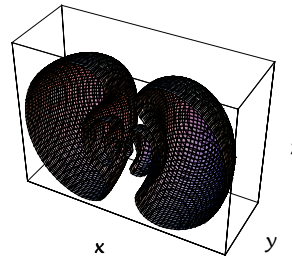
Sketch how this figure would look for the 3s wavefunction.

4p_x shell amplitude, angular wavefunction, shell density and probability density

Here are the radial and angular components, shell density, and xy plane slices of the three dimensional probability density of the hydrogen atom 4p_x electron.



$4p_x \cdot 10^{-3}$ probability density isosurface

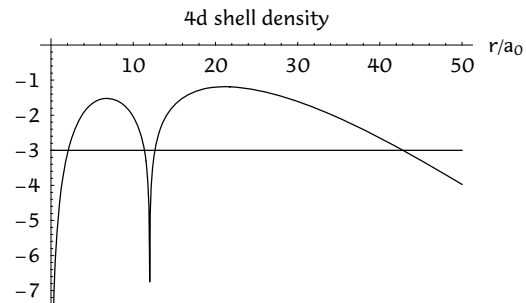
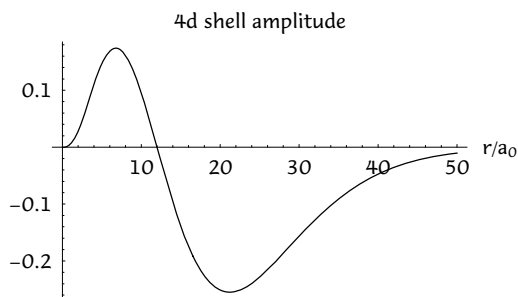


Hydrogen atom $4p_x$ electron radial and angular components, shell density, and xy plane slices of the three dimensional probability density.

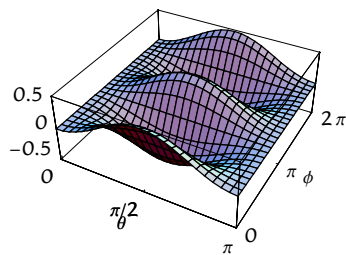
Sketch how this figure would look for the $3p_y$ wavefunction.

$4d_{x^2-y^2}$ shell amplitude, angular wavefunction, shell density and probability density

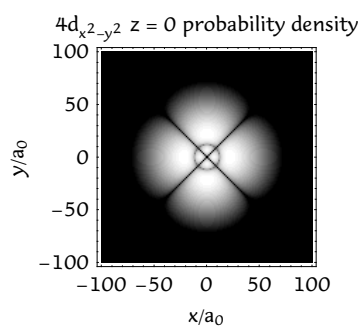
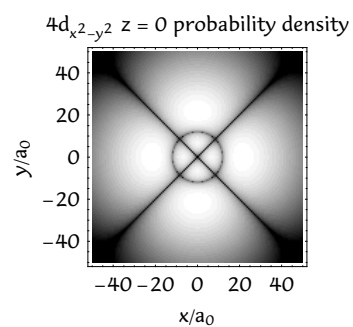
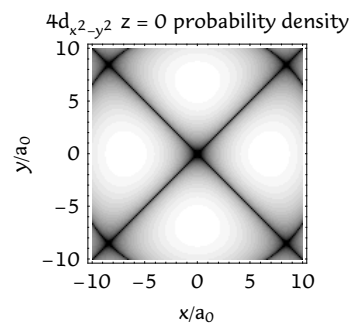
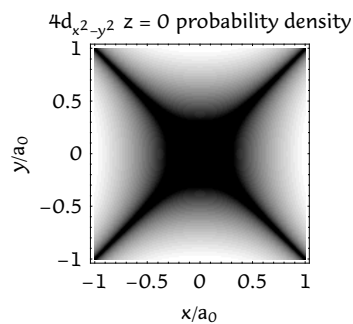
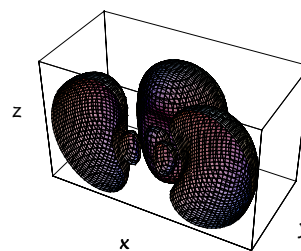
Here are the radial and angular components, shell density, and xy plane slices of the three dimensional probability density of the hydrogen atom $4d_{x^2-y^2}$ electron.



px surface plot



$4d_{x^2-y^2} 10^{-3}$ probability density isosurface



Hydrogen atom $4d_{x^2-y^2}$ electron radial and angular components, shell density, and xy plane slices of the three dimensional probability density.

| Sketch how this figure would look for the $3d_{xy}$ wavefunction.