Quantum aspects of atoms

Notes on General Chemistry

...[quote]...

We have learned how the de Broglie relations,

$$\boxed{\begin{aligned} \nu_{\text{matter}} &= E_{\text{matter}} / h \\ \lambda_{\text{matter}} &= h / p_{\text{matter}} \end{aligned}}$$

de Broglie relations.

together with the fundamental energy-balance relations of the light-matter interaction,

$$\boxed{\begin{aligned} E_{\text{matter},f} - E_{\text{matter},i} &= -\Delta E_{\text{light}} = E_{\text{photon}} = h\,\nu \ (\text{light absorption}) \\ E_{\text{matter},f} - E_{\text{matter},i} &= -\Delta E_{\text{light}} = -E_{\text{photon}} = -h\,\nu (\text{light emission}) \end{aligned}}$$

Light-matter interaction energy balance.

allow us in principle to account for the lines seen in the spectra of the matter.

There are two complementary ways to proceed.

From spectroscopy to matter energies: The first way is to use spectroscopy—detailed measurement of spectra—to determine the energies, $E_{\text{matter},j}$, that occur in a particular system. We will see how this is done, for the example of the spectra of one-electron atoms, using a separate computer-based activity

From matter energies to spectroscopy: The second way is to generalized the approach we used to treat a particle confined in one dimension, to treat electrons in atoms and combinations of atoms in molecules. We will learn about this approach here.

■ Determining wavefunctions and energies of electrons in atoms

We have seen how, without needing to use spectroscopic information, to calculate the possible energies and corresponding wavefunctions of a particle confined to a region but able to move freely in that region—the so-called particle in a box. Then we were able to use these energies to predict the spectrum of the system. This is an example of going from matter energies to spectroscopy.

We were able to do this is because, since the particle moves freely, we could write down the expression for its energy, namely it kinetic energy $m\,u^2/2 = p^2/(2\,m)$, and this kinetic energy remains constant for a given total energy.

More generally things are not so simple, in that particles are subjected to forces as they move and so the value of their kinetic energy is no longer is constant. The consequence is that a more sophisticated method is needed to determine their possible total energies and corresponding wavefunctions. Rather than describe this method, we will explore its results of electrons in atoms.

The method is based on the central equation of quantum mechanics, known as the *Schrödinger equation*. The Schrödinger equation is a relation between, on the one hand, how much the wavefunction at each point in space is curving and, on the other hand, the product of values of the kinetic energy and wavefunction of the particle at that point.

For a particle in one dimension, the Schrödinger equation is

$$\text{curvature of } \psi \text{ at } x = -\frac{2\,m}{\hbar^2} (\text{kinetic energy at } x \times \psi \text{ at } x)$$

Here are the four key consequences of this equation and how it determines possible energies and corresponding wavefunctions.

- First, the wavefunction curves a lot either when kinetic energy is high or the wavefunction magnitude is large; while it curves much less when kinetic energy is low or the wavefunction magnitude is small.

- Second, the curving of the wavefunction is *toward the axis*, and so the wavefunction *oscillates*, when kinetic energy is *positive*. This reflects the de Broglie relation that wavelength decreases when kinetic energy, $p^2 / (2\,m)$, increases.

- Third, the curving of the wavefunction is *away from the axis*, and so the wavefunction can grow to *infinitely large magnitudes* when kinetic energy is *negative*. If the wavefunction magnitude becomes infinitely large, we say such the wavefunction is *unphysical*, since then it cannot be meaningfully normalized to give a total probability of one.

- Fourth, the possible energies of the system are those special values for which the curving away from the axis is controlled so that the wavefunction does not become infinitely large.

In this way energies and wavefunctions of electrons in atoms can be determined. For our purposes what is important is to learn about these wavefunctions and their relative energies. A good way to do this is to look at the wavefunctions themselves.

■ Spherical polar coordinates: *r*, *θ* and *ϕ*

Since an electron in an atom can move in all three spatial dimensions, its wavefunction depends on three spatial coordinates. Since atoms are spherical, because the Coulomb attraction of an electron for the nucleus depends only on the distance, *r*, from the nucleus, the most natural spatial coordinates to use are *spherical polar coordinates*. Here is how to determine the spherical polar coordinates of a point, in terms of its *Cartesian coordinates*, *x*, *y*, and *z*.

The first coordinate, *r*, is the distance of the point from the origin. The second coordinate, *θ*, is the angle between the positive *z* axis and the line from the origin to the point; *θ* is in the range 0 to *π*. The third coordinate, *ϕ*, is the angle between the positive *x* axis and the line from the origin to the location in the *xy* plane intercepted by the line perpendicular to the *xy* plane and passing through the point; *ϕ* is in the range 0 to 2*π*. Note that in mathematics the definitions of *θ* and *ϕ* are reversed; the definitions given here are used in chemistry and physics.
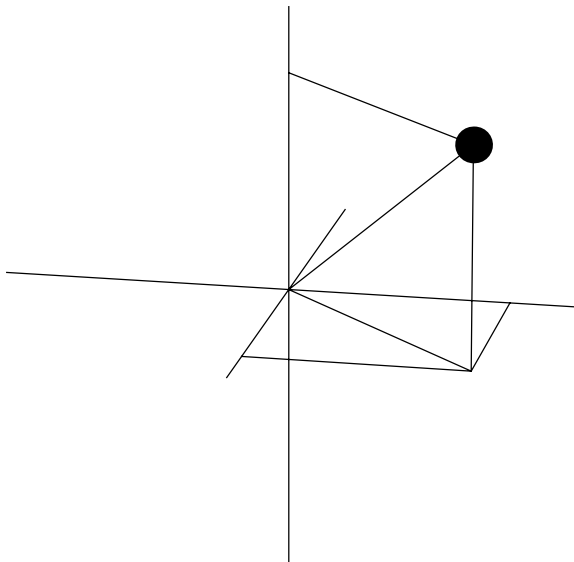
In the figure above, the positive z axis is up, the positive y axis is to the right, and the positive x axis is out of the plane of the paper. Label the angle θ, the angle ϕ, and the distance r of the point.

Using trigonometry and the three-dimensional Pythagorean theorem, it is not too hard to get the following expressions for the spherical polar coordinates in terms of the Cartesian coordinates.

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

$$\theta = \text{ArcCos}(z/r), \text{ and}$$

$$\phi = \text{ArcTan}(y/x).$$

Note that in determining the value of ϕ using the arctan, you need to determine which quadrant ϕ is in. In particular, in $x < 0$, then you need to add π to the value of the arctan, and if $x = 0$, then $\phi = \pi/2$ when $y > 0$ and $\phi = -\pi/2$ when $y < 0$.

Here are some example points expressed in both Cartesian and spherical polar coordinates.

What values of the spherical polar coordinate correspond to the xy plane? Answer: $\theta = \pi/2$ and all values of r and ϕ.

What values of the spherical polar coordinates correspond to the yz plane? Answer: The positive y part of the yz plane corresponds to $\phi = \pi/2$ and all values of r and θ; the negative y part of the yz plane corresponds to $\phi = -\pi/2$ and all values of r and θ.

What values of the spherical polar coordinates correspond to the zx plane? Answer: The positive x part of the zx plane corresponds to $\phi = 0$ and all values of r and θ; the negative x part of the zx plane corresponds to $\phi = \pi$ and all values of r and θ.

What values of the spherical polar coordinates correspond to the $(x, y, z) = (1, 1, 1)$? Answer: $r = \sqrt{3}$, $\theta = \text{ArcCos}\left(1/\sqrt{3}\right)$ and $\phi = \pi/4$.

What values of the spherical polar coordinates correspond to the $(x, y, z) = (1, 0, 0)$? Answer: $r = 1$, $\theta = \pi/2$ and $\phi = 0$.

What values of the spherical polar coordinates correspond to the $(x, y, z) = (0, -1, 0)$? Answer: $r = 1$, $\theta = \pi/2$ and $\phi = -\pi/2$.

What values of the spherical polar coordinates correspond to the $(x, y, z) = (0, -1, -1)$? Answer: $r = \sqrt{2}$, $\theta = 3\pi/4$ and $\phi = -\pi/2$.

What values of the spherical polar coordinates correspond to the $(x, y, z) = (-1, 1, -1)$? Answer: $r = \sqrt{3}$, $\theta = \text{ArcCos}\left(-1/\sqrt{3}\right)$ and $\phi = 3\pi/4$.

What values of the spherical polar coordinates correspond to the $(x, y, z) = (1, 1, -1)$? Answer: $r = \sqrt{3}$, $\theta = \text{ArcCos}\left(-1/\sqrt{3}\right)$ and $\phi = \pi/4$.

What values of the spherical polar coordinates correspond to the $(x, y, z) = (1, -1, 1)$? Answer: $r = \sqrt{3}$, $\theta = \text{ArcCos}\left(1/\sqrt{3}\right)$ and $\phi = -\pi/4$.

What values of the spherical polar coordinates correspond to the $(x, y, z) = (-1, -1, -1)$? Answer: $r = \sqrt{3}$, $\theta = \text{ArcCos}\left(-1/\sqrt{3}\right)$ and $\phi = 5\pi/4$.

■ What wavefunctions of electrons in atoms look like

Let's denote the wavefunction of an electron in an atom as $\psi(r, \theta, \phi)$ in spherical coordinates and as $\psi(x, y, z)$ in terms of Cartesian coordinates. The numerical value of the wavefunction is the probability amplitude of the electron at the point $\{r, \theta, \phi\} = \{x, y, z\}$, and the corresponding probability density is $|\psi|^2$. The probability that the electron is in a small volume dV centered on the point is $|\psi|^2 dV$. The total probability of the electron being somewhere is $\int_V |\psi|^2 \, dV = 1$.

To visualize such wavefunctions and probability densities, we need three spatial dimensions and a fourth dimension for the value of the wavefunction. Since we live only in three spatial dimensions, we have to build up the visualization step wise, by holding one of the four dimensions constant.

One way to do this is by looking at "slices" of the wavefunctions. Each slice spans two of the three spatial dimensions, for a given fixed value of the third dimension. On each slice is displayed an image of the probability density corresponding to the wavefunction, with brightness proportional to density. By analyzing a series of parallel slices, we can get insight into the three dimensional structure of the wavefunction along the axes parallel to the slice plane. By repeating the analysis for different axes we can synthesize in our mind how the probability density is distributed throughout the space of the atom. This procedure is analogous to that used in medical whole body imaging used in computer aided tomography (CAT) scanning.

To illustrate how slices look, here are the results of one of the possible hydrogen atom probability densities (there are many different possibilities) in the xy plane ($z = 0$) for five different resolutions.
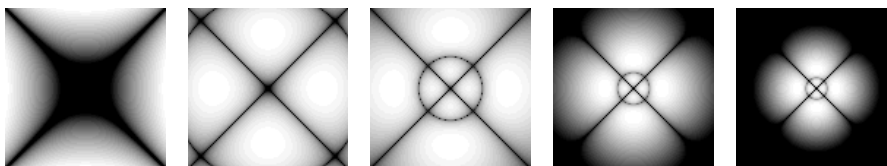
An example hydrogen atom probability density in the *xy* plane. Positive *x* is to the right, positive y is up. The nucleus is at the center. From left to right, the width and height are 1, 10, 30, 60 and 100 a_0 = 0.529 Å. The brightness of the display is proportional to the probability density.

In each case the nucleus is at the center. The figures differ on the area spanned by the slice. From left to right, the width and height are 1, 10, 30, 60 and 100 a_0 = 0.529 Å (a_0 is the classical radius of the hydrogen atom in its lowest energy state). The brightness of the display is proportional to the probability density.

We have learned for the one-dimensional example of a free particle confined to a region that wavefunctions have loops, and between loops the wavefunction vanishes. This means that there are regions where the probability density vanishes. The slices above show that there are also loops and so regions of vanishing probability density in three dimensions.

There are two important features of loops in three dimensional wavefunctions. First, because atoms are spherical, there are separate sets of loops in the radial direction (going out from the nucleus) and in the angular directions (going around the nucleus at fixed distance *r* from it). Second, because the angular wavefunction repeats after a full circle, angular loops must meet smoothly after at the close of the circle. This means that angular variations must have an integer number of wavelengths and so always *an even number of loops*.

> For the *xy* slices above, how many radial loops (going out from the nucleus) are there? Answer: two.

> For the *xy* slices above, how many angular loops are there? Answer: four.

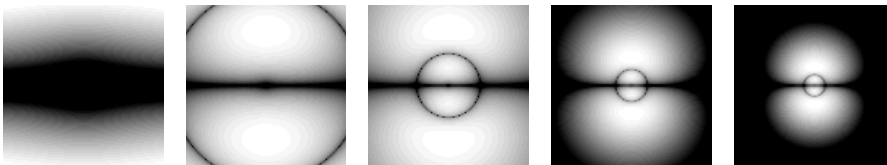> For the *xy* slices above, how many angular wavelengths are there? Answer: two.

Here are the results for the same hydrogen atom probability density but in the *yz* plane (*x* = 0).
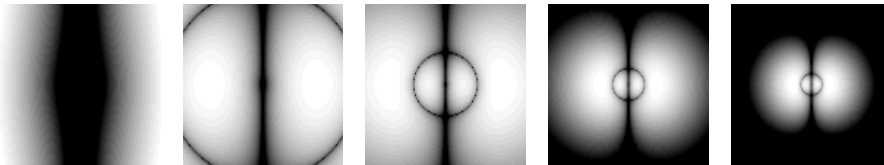
An example hydrogen atom probability density in the *yz* plane. Positive *y* is to the right, positive *z* is up. The nucleus is at the center. From left to right, the width and height are 1, 10, 30, 60 and 100 a_0 = 0.529 Å. The brightness of the display is proportional to the probability density.

> For the *yz* slices above, how many radial loops (going out from the nucleus) are there? Answer: two.

> For the *yz* slices above, how many angular loops are there? Answer: two.

> For the *yz* slices above, how many angular wavelengths are there? Answer: one.

Finally, here are the results for the same hydrogen atom probability density but in the *zx* plane (*y* = 0).

An example hydrogen atom probability density in the *zx* plane. Positive *z* is to the right, positive *x* is up. The nucleus is at the center. From left to right, the width and height are 1, 10, 30, 60 and 100 a_0 = 0.529 Å. The brightness of the display is proportional to the probability density.

> For the *zx* slices above, how many radial loops (going out from the nucleus) are there? Answer: two.

> For the *zx* slices above, how many angular loops are there? Answer: two.

> For the *zx* slices above, how many angular wavelengths are there? Answer: one.

These slices perpendicular to the three Cartesian axes illustrate that while the number of radial loops does not change, no matter which slice through the nucleus is made, the number of angular loops can be different. This difference in angular loops is a key to forms a three dimensional image in our mind of the probability density.

A nice way to visualize how such three dimensional images look is to construct what is known as an *isosurface*. An isosurface of a function *f*(*x*, *y*, *z*) consists of all of those particular values of the independent variables *x*, *y*, and z for which the function *f* has the *same* value, known as the *isovalue*.

Here is the isosurface of the hydrogen atom probability density shown above for the isovalue of $0.001/a_0{}^3$.
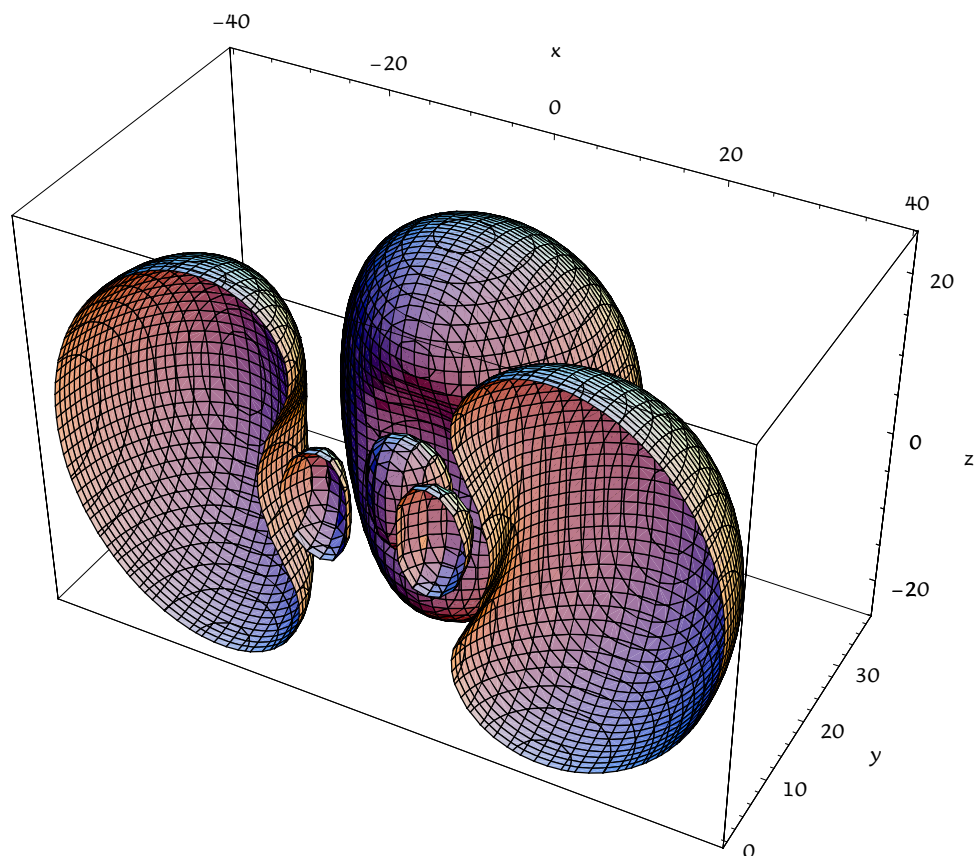
Isosurface of a hydrogen atom electron probability density for the isovalue of $0.001/a_0{}^3$. Values of x, y, and z are in $a_0 = 0.529$ Å.

> On the isosurface figure, sketch the xy plane. Your sketch should look like the figure below. Does the way the plane slices the isosurface match the xy slices shown earlier?
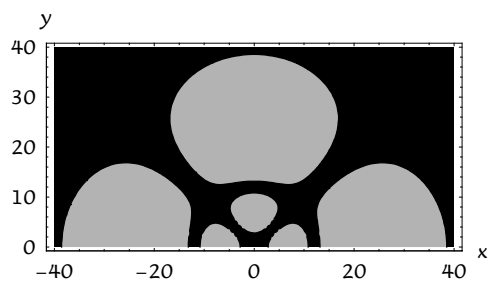
On the isosurface figure, sketch the *yz* plane. Your sketch should look like the figure below. Does the way the plane slices the isosurface match the *yz* slices shown earlier?
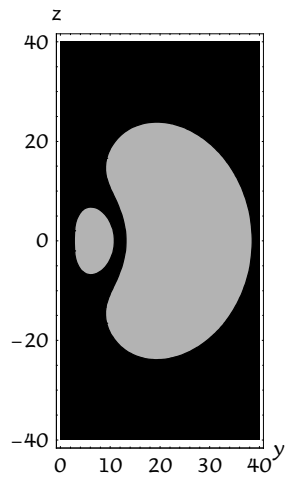
On the isosurface figure, sketch the *zx* plane. Your sketch should look like the figure below. Does the way the plane slices the isosurface match the *zx* slices shown earlier?
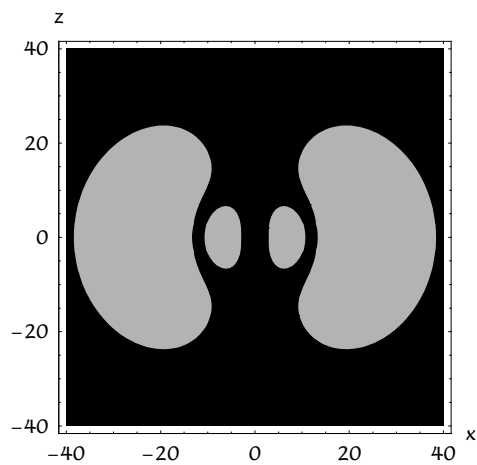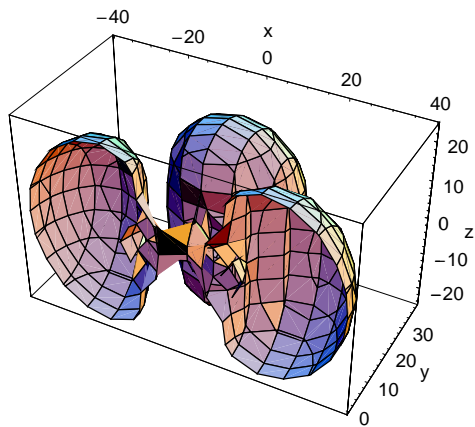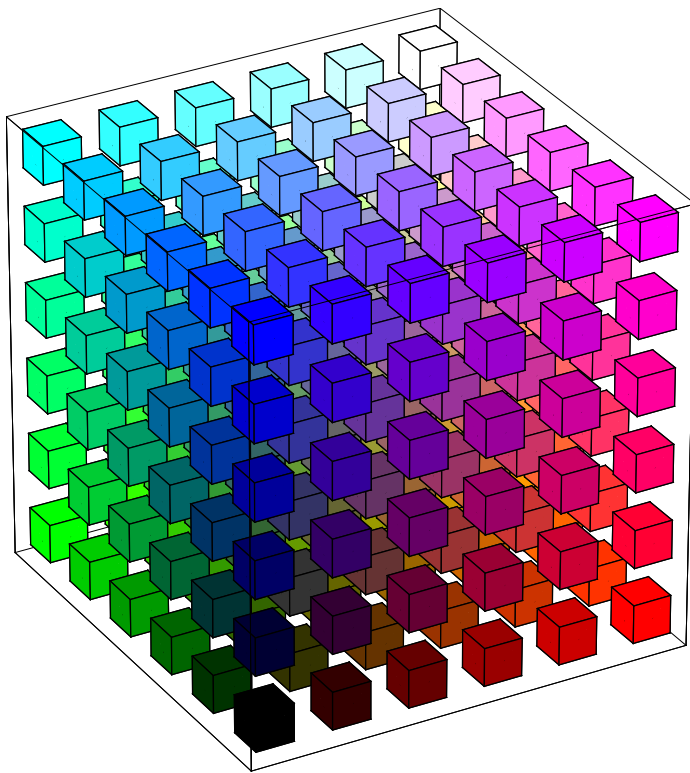

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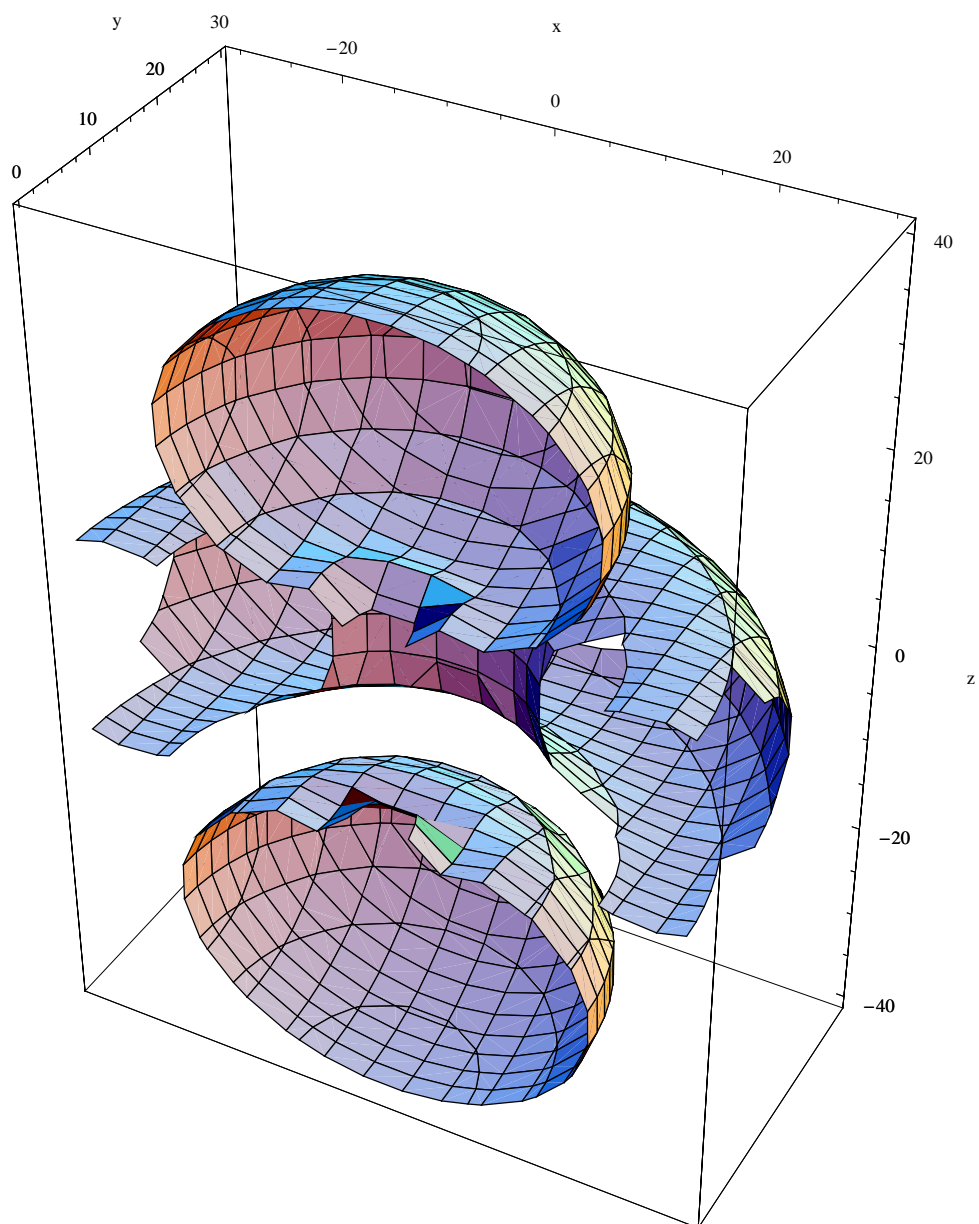
F:\Dan\Notes on General Chemistry\Mma\03 Atomic structure\Isosurfaces

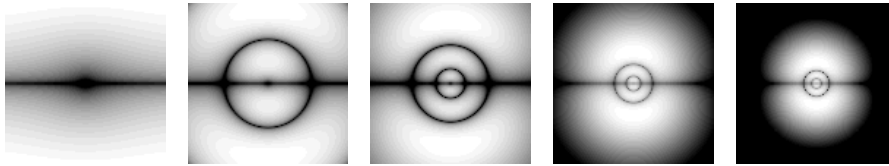Very nice plot of $\Psi_j(\alpha)$
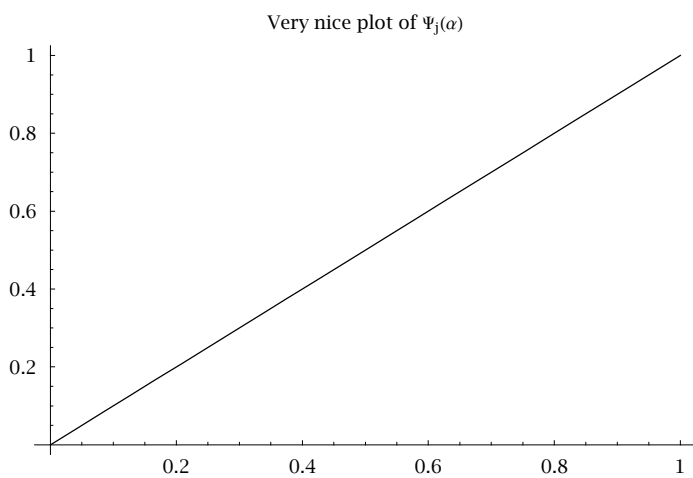
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■ A taxonomy of atomic wavefunctions

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An electron in an atom can have almost limitless variations in its probability densities, depending on what energy level it is in. Here are representations of a different atomic probability density in the *xy* plane for five different resolutions.
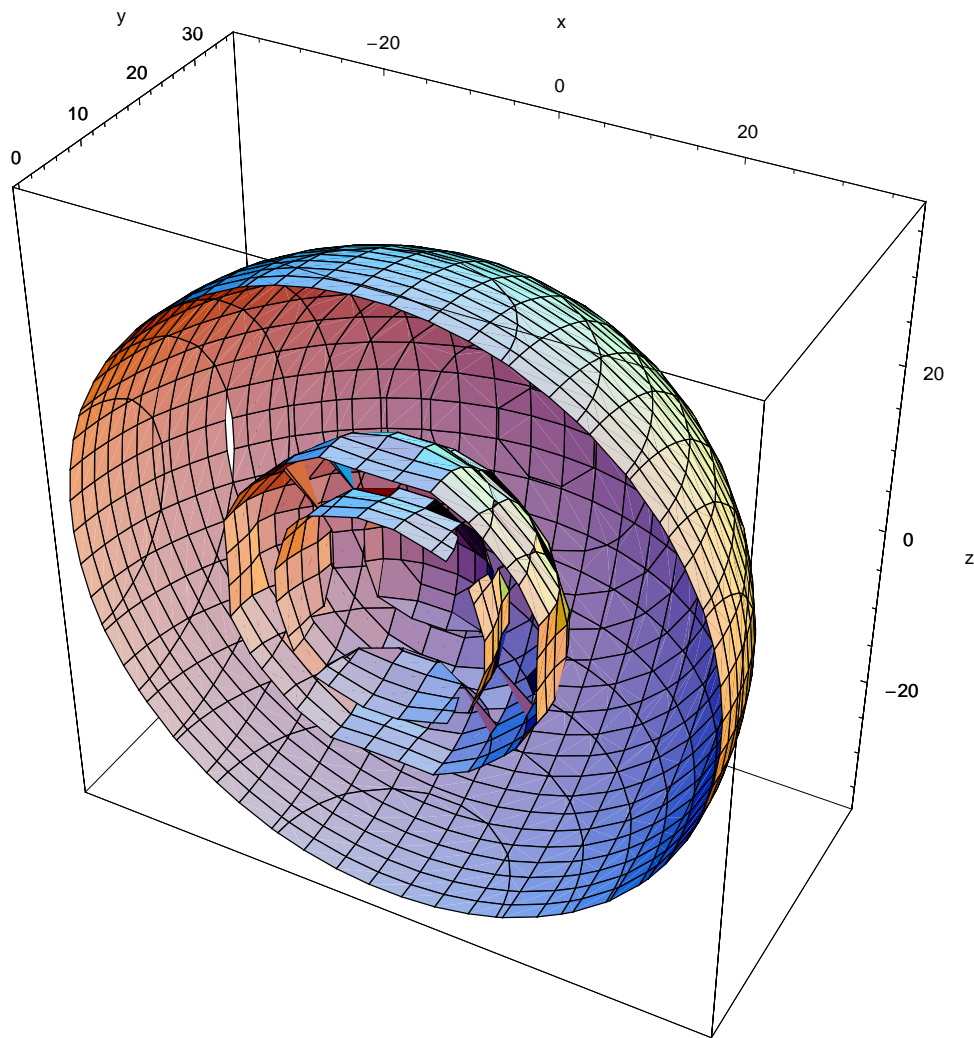
A second example hydrogen atom probability density in the *xy* plane. The nucleus is at the center. From left to right, the width and height are 1, 10, 30, 60 and 100 $a_0 = 0.529$ Å. The brightness of the display is proportional to the probability density.
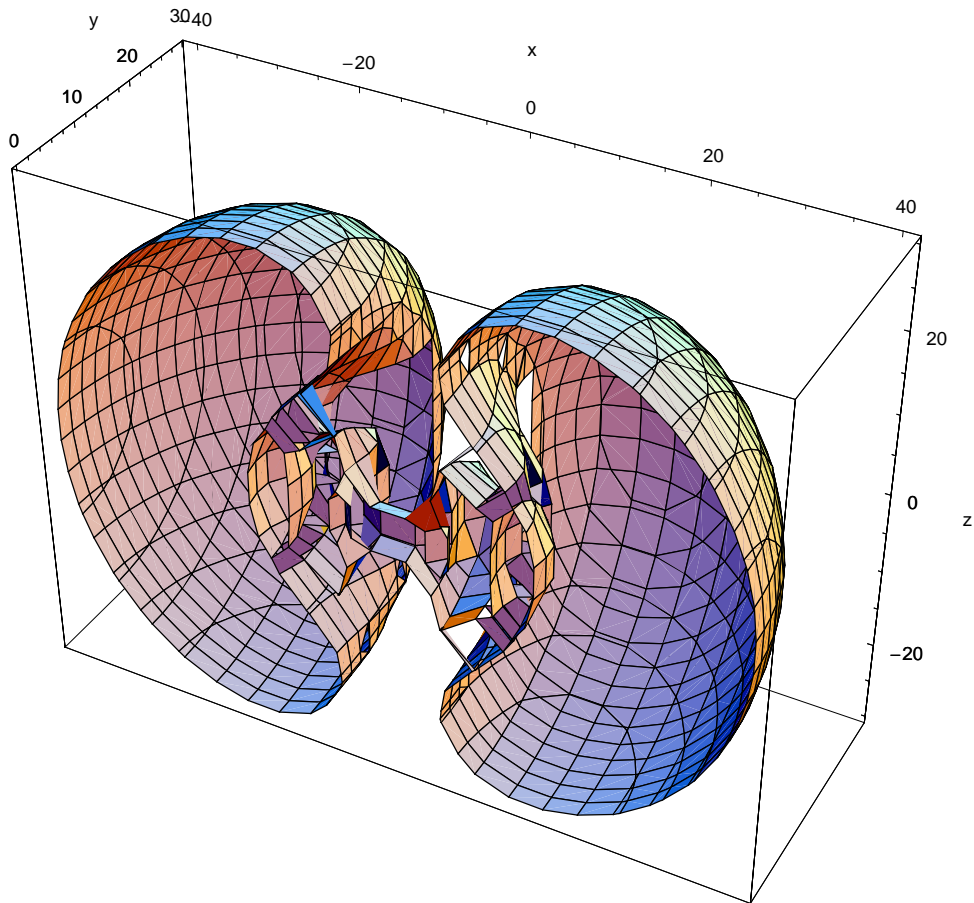
And here are representations of a third atomic probability density in the *xy* plane for five different resolutions.

A third example hydrogen atom probability density in the *xy* plane. The nucleus is at the center. From left to right, the width and height are 1, 10, 30, 60 and 100 $a_0 = 0.529$ Å. The brightness of the display is proportional to the probability density.

To allow you to explore the three dimensional structure of atomic wavefunctions, we have created the interactive software tool, *Tomograph2d*, to make slices through different hydrogen atom probability densities, perpendicular to each of the three Cartresian axes, for different values of coordinate perpendicular to the slice. (The 2d in the name Tomography2d refers to the fact that each slice spans two of the three spatial dimensions.)

Tomograph2d allows you to select the number of radial loops and the number of angular wavelengths (one angular wavelength equals two loops). It turns out that in addition if there are ℓ angular wavelengths, then there are $2\ell + 1$ *different* probability densities with the same number of radila loops and angular wavelengths, and so Tomorgraph2d allows you to specify these alternatives. Finally, there is a slider that allows you to move the slice plane along its perpendicular axis, so that you can see how the probaiblity density changes when it does not contain the nucleus.

Here are a series of explorations you can do with Tomograph2d to learn how atomic wavefunctions are distributed in space, and to sort them out into families.

Three dimensional structure

We have created the interactive software tool, *Tomograph2d*, to learn about the three dimensional citriculture of atomic wave functions. The tool works by making slices through a wavefunction to display the relative probability density in the plane of the slice. By analyzing a series of parallel slices, we can get insight into the three dimensional structure of the wavefunction. This procedure is analogous to that used in medical whole body imaging used in computer aided tomography (CAT) scanning.

Relative energies

We have learned for the one-dimensional example of a free particle confined to a region that the wavefunction for the lowest possible energy has one loop, that the wavefunction for the second lowest possible energy has two loops, and one loop is added for each higher energy.

Here is how to extend this idea of the number of loops reflecting relative energy to three dimensions. First, because atoms are spherical, there will be separate sets of loops in the radial direction (going out from the nucleus) and in the angular directions (going around the nucleus at fixed distance from it). Second, because the angular wavefunction at $\theta = 0$ is as $\theta = 2\pi$, angular variation must meet smoothly after one full cycle in θ. This means that the lowest energy angular variation must have one full wavelength (that is, two loops rather than one loops), and each increase in angular excitation must be accompanied by the addition of another full wavelength.

With this background, lets sort out atomic wavefunctions in families according to the number of wavelengths moving around the nucleus at fixed distance from it, and then, within a family, the according to the number of loops radially outward from the nucleus.
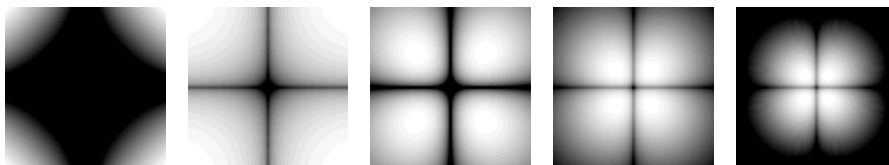
Here are the probability densities in the *xy* plane of the simplest members for the family of hydrogen atom wavefunctions with zero, one, and two angular wavelengths.
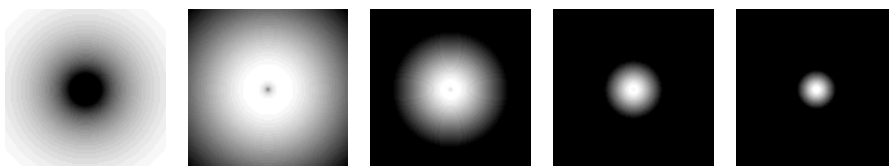
Probability density in the *xy* plane of the simplest member for the family of hydrogen atom wavefunctions with zero angular wavelengths. The nucleus is at the center. From left to right, the width and height are 0.5, 5, 15, 30 and 50 a_0 = 0.529 Å. The brightness of the display is proportional to the probability density.
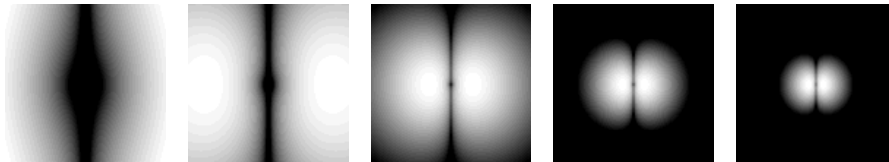
Probability density in the *xy* plane of the simplest member for the family of hydrogen atom wavefunctions with one angular wavelength. The nucleus is at the center. From left to right, the width and height are 0.5, 5, 15, 30 and 50 a_0 = 0.529 Å. The brightness of the display is proportional to the probability density.

Probability density in the *xy* plane of the simplest member for the family of hydrogen atom wavefunctions with two angular wavelengths. The nucleus is at the center. From left to right, the width and height are 0.5, 5, 15, 30 and 50 a_0 = 0.529 Å. The brightness of the display is proportional to the probability density.

■ Electron kinetic and potential energy in atoms

In chemistry to central example of this is the one-electron atom. With respect to the nucleus of such an atom, which is so heavy that we can assume its motion is negligible compared to that of the electron, the electron experiences the force

$$F_{\text{Coulomb}} = \frac{(+Z\,e)\,(-e)}{4\,\pi\,\epsilon_0\,r^2} = -\frac{Z\,e^2}{4\,\pi\,\epsilon_0\,r^2}$$

due to the Coulomb attraction of the electron, with charge $-e$, to the nucleus, with charge $+Z\,e$. (The constant $\epsilon_0 = 8.85419 \times 10^{-12}$ $C^2\,J^{-1}\,m^{-1}$ is the vacuum permittivity.) This force means that the electron experiences a potential energy

$$V_{\text{Coulomb}} = -\frac{Z\,e^2}{4\,\pi\,\epsilon_0\,r}$$

This potential energy becomes increasingly negative as the separation r between the electron and the nucleus becomes smaller. On the other hand, the potential energy rises to zero in the limit that the electron is infinitely far away from the nucleus.

> Calculate the potential energy, in eV, of an electron in hydrogen atom ($Z = 1$) for electron-proton distance $r = 1.00$ Å. Answer: -14.4 eV.

> Calculate the potential energy, in eV, of an electron in hydrogen atom ($Z = 1$) for electron-proton distance $r = 100.$ Å. Answer: -0.144 eV.

Since total energy is the sum of kinetic and potential energy, the presence of the Coulomb attraction between the electron and the nucleus means that for a given total energy, the kinetic energy of the electron will be different for different distances of the electron from the nucleus.

> Assume the electron in hydrogen atom has total energy -1.00 eV. Calculate the kinetic energy of the electron at the following distances from the nucleus: 10.0 Å, 5.00 Å, 1.00 Å, 0.500 Å, and .100 Å. Answer: 0.440 eV, 1.88 eV, 113.4 eV, 27.8 eV, and 143 eV.

This problem shows that, for a given total energy, the kinetic energy increases as the electron is closer to the nucleus. This is equivalent to saying that the electron moves faster.

> Calculate the speed u, in m/s, of the electron in hydrogen atom corresponding to the kinetic energies of the previous problem. Answer: 197,000 m/s, 407,000 m/s, 1,090,000 m.s 1,560,000 m/s, and 3,550,000 m/s.