

## Unit 12: Quantum Waves in Multiple Dimensions and the Hydrogen Atom

In this unit, we will begin to deal with real (and nearly real) quantum examples. The basic features you observed in the simple one-dimensional cases will still apply, though:

- More nodes in a wave function imply greater energy.
- A bound state requires the wave function to go to zero at the ends.
- One can characterize quantum states by the number of nodes in between the ends.
- Because the number of nodes is necessarily quantized, the resulting properties of the quantum state, such as energy and angular momentum, are also quantized.

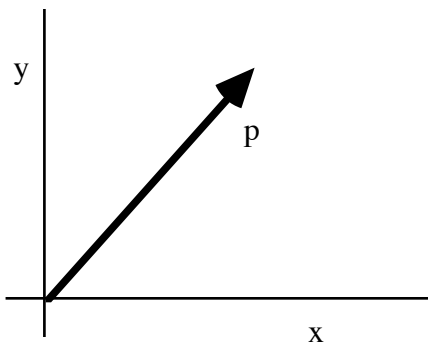
We will apply these concepts to the single multi-dimensional system that is easily calculated, the particle in a box. Then we will apply them qualitatively to systems with spherical symmetry, and look at wave functions associated with the electron in the hydrogen atom.

### Session 1: Particle in a Multi-Dimensional Box

Although this session will discuss the example that is called by physicists the multi-dimensional box, this is a bit redundant—of course a box has multiple dimensions. This notation is only meant to contrast it to the one-dimensional box, which isn't really a box at all! First we will consider a two-dimensional "box," and then generalize to three dimensions (and more, in principle). But before we do that, we need to make sure we understand how to relate momentum to energy in multiple dimensions.

#### *Guidebook Entry 12.1: Momentum and Energy in Two Dimensions*

Let's first think about a classical particle, which has a vector momentum  $\vec{p}$  composed of an x component  $p_x$  and a y component  $p_y$ . Sketch those components below.



How does the magnitude of the momentum  $p$  relate to the components  $p_x$  and  $p_y$ ? Express your answer as an equation.

The kinetic energy relates to the magnitude of the momentum in the same way as momentum and kinetic energy are related in one dimension. Find a mathematical expression for the kinetic energy in terms of the momentum components. You may need to recall the definitions

$$p = mv \quad \text{and} \quad E_{kinetic} = \frac{1}{2}mv^2.$$

Quantum mechanically, we can measure the momentum in a given dimension by observing how quickly the wave function oscillates up and down in that dimension. If we are lucky, it will oscillate sinusoidally, and therefore we just have to measure the wavelength, and use the Planck law  $p = h/\lambda$ . If there are different momentum components in the  $x$  and  $y$  dimensions, then there will be a different periodicity in that dimension, that is there will be different wavelengths, which we can call  $\lambda_x$  and  $\lambda_y$ . (While it is convenient here to think of wavelengths in each direction, remember  $\lambda$  does not make a good vector  $k=2\pi/\lambda$  is the proper vector quantity.) Derive an expression for the kinetic energy in terms of these two wavelengths.

This last activity gave us an important result, that the energy is just the sum of the energies associated with wave motion in each dimension. You should make sure that your result is equivalent to an expression like:

$$E = \frac{h^2 \pi^2}{2m L_x^2} + \frac{h^2 \pi^2}{2m L_y^2} = \frac{h^2 \pi^2}{2m} \left( \frac{1}{L_x^2} + \frac{1}{L_y^2} \right)$$

In the next activity, we will relate the wavelengths to the number of nodes in the different directions, which will allow us to relate the energy in these multi-dimensional systems to the number of nodes (which we will continue to refer to as quantum numbers). It is in fact easier to use the nodes as reference points to allow us to count the number of half-wavelengths fit in a given direction. Typically the energy formulae relate most simply to this number, the number of half wavelengths.

*Guidebook Entry 12.2: The Two-Dimensional Box*

Recall the ground state (lowest energy state) of the particle in the one-dimensional box. How many nodes were there between the two ends?

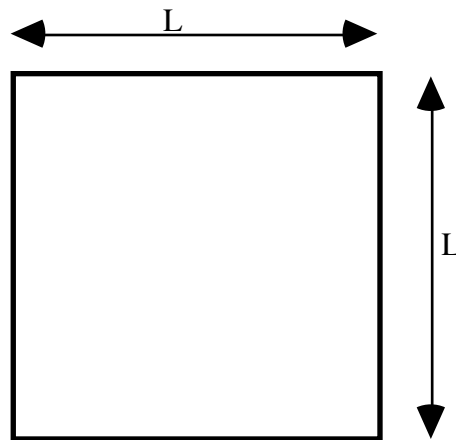
We can consider trying to fit waves into a two dimensional region, with the requirement that the waves go to zero at the boundaries. How many nodes do you expect to see between the boundaries for the ground state? How many half-wavelengths across does this correspond to? Explain.

If this region is rectangular or square, then the waves can be purely sinusoidal in either direction. In our color analogy, this would mean for the ground state the wave would be bright in the center and black at the borders. If you preferred to think of the rope analogy, you might think of this case as a sheet held fixed at the edges, but allowed to flap up and down in the middle.

If the region is a square with sides of length  $L$ , what are the wavelengths in each direction, that is  $L_x$  and  $L_y$ ?

What is the energy of this ground state? How does it compare to the energy of the ground state of a *one-dimensional* box of the same length  $L$ ?

Now imagine that there is a single node in the  $y$  direction—that is, I am fitting two half-wavelengths in between  $y=0$  and  $y=L$ . The node is no longer a point in space, but is rather a line. Draw this nodal line in the box region below.

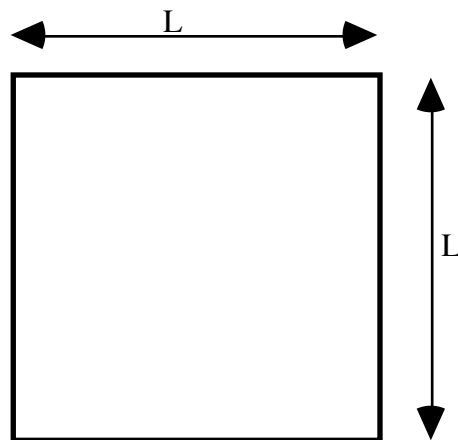


Open the file "2 D Quantum Box" from your hard disk. Give the program the values of  $n_y=2$  and  $n_x=1$ . Describe what you see. Does it agree with your prediction for nodal lines?

What is the energy associated with this state?

Let's use the quantum number  $n_x$  to give the number of half wavelengths fitting in the x direction (which is the number of nodes between the boundaries in that direction plus one), and a similar  $n_y$  in the y direction. For example, this gives us a ground state with  $(n_x, n_y) = (1, 1)$ . Derive an expression for the energy in terms of the quantum numbers  $n_x$  and  $n_y$ .

Just for practice, sketch your prediction for the nodes for the  $(n_x, n_y) = (2, 3)$  state, and find the energy. The energy should be 6.5 times that of the ground state.



Change the  $n_x, n_y$  values in the upper left corner of the Excel sheet, and wait for the chart to update. Does this agree with your prediction?

How would the general energy expression change if the lengths of the sides of the box are different from one another? Let the sides be given by  $L_x$  and  $L_y$ .

How would you generalize the energy expression to a *three*-dimensional box, with sides each of length  $L$ ?

If you have time, play a bit with the Excel sheet so you get used to identifying the quantum numbers from the wave functions by trying a variety of [small]  $n_x$  and  $n_y$  values.

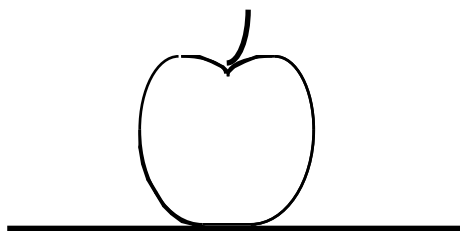
## Session 2: Looking at Hydrogen Atoms

In this session, we will look at color pictures of quantum wave functions (which were programmed by Rachel Wood '93) for the hydrogen atom. Since hydrogen atoms are three dimensional structures, and we only have the two dimensions of the computer screen available for representing these atoms, we need first to develop a convention for how we look at them. Once we have this, we will be able to categorize all of the possible wave functions of the hydrogen atom, and see how this relates to the atomic quantum numbers ( $n, l, m_l$ ) that you may have learned about in introductory chemistry.

### *Guidebook Entry 12.3: Slicing Apples*

In this exercise, you will start with a real three dimensional object, an apple to be specific, and figure out how to represent its structure, both internal and external, by looking at slices of it. Each slice will be a picture that we can represent easily on a two dimensional surface.

The apple looks something like the figure below, where I am imagining the apple sitting on a table, in the same orientation as it might have been when it was hanging from a tree.



Take a paring knife, and cut an apple with a horizontal slice, that is, parallel to the surface of the table. Sketch what this slice looks like below. [Sketch only the two dimensional surface that is the intersection of the knife cut with the apple; don't try to give any perspective sketch of the rest of the apple.]

If you were to show your sketch above to someone who had never seen an apple before, what aspects of the shape of an apple would *not* be communicated by your sketch?

Take another apple. Make a different cut that reveals the most additional information you can about the shape of an apple. Describe that cut, and show it below.

Now, eat as much of the apples as you would like. Someone in your group probably missed breakfast anyway.

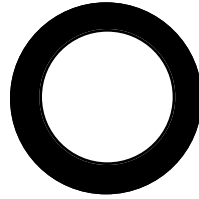
The programs that we have developed for looking at hydrogen atom wave functions show two different slices of the wave function: one made by a horizontal cut (like the first apple cut), and one by a vertical cut (which I guess many of you did as your second cut). To give you some practice recognizing an object from these two cuts, I have sketched some cuts from common objects, and you need to guess what these objects are.

*Guidebook Entry 12.4: Guessing Objects from Slices*

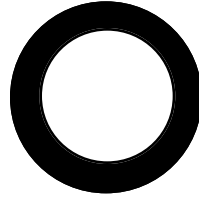
In each of the following sketches, you are given a vertical and a horizontal slice, and you need to describe what the object looks like in three dimensions.

What is this three-dimensional object?

Horizontal cut:

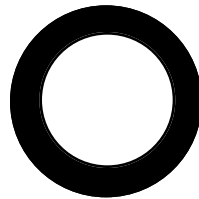


Vertical cut:



What is this three-dimensional object?

Horizontal cut:



Vertical cut:

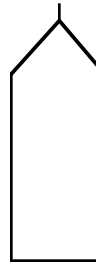


What is this three-dimensional object?

Horizontal cut:

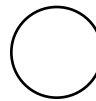


Vertical cut:

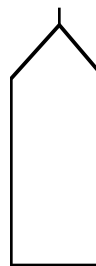


What is this three-dimensional object?

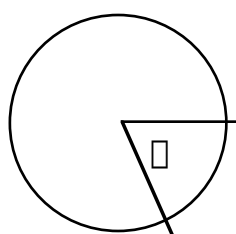
Horizontal cut:



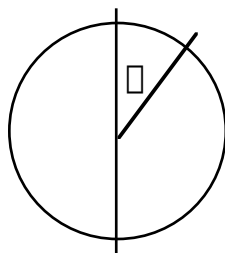
Vertical cut:



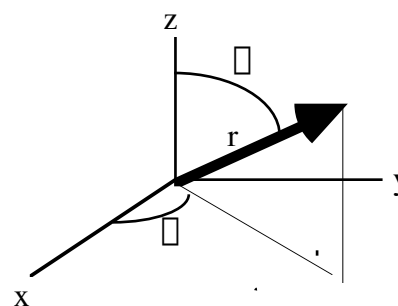
In all of our examples, we have assumed that there are some symmetries in our objects; otherwise there would be no hope of predicting the shape of the object without a complete set of slices spaced very close to one another. These symmetry assumptions will be valid for the hydrogen atom wave functions, but this means we must choose the axis which defines the symmetry. In practice, for real hydrogen atoms floating freely in a vacuum, this axis is chosen by the direction of whatever magnetic field happens to be present, provided perhaps by a laboratory magnet, or perhaps by the earth's magnetic field. We will assume that this axis is vertical and that it corresponds to the z-axis in cartesian coordinates. The natural coordinate system to use in this case is spherical coordinates, where the three coordinates that describe a point in space are no longer x, y, and z, but rather r (the distance from the center point), and two angles. The first of these is usually symbolized by  $\theta$ , and represents the angle relative to the vertical symmetry axis, as shown in the vertical cut below. The second is symbolized by  $\phi$ , which represents the angle about the horizontal, as shown in the horizontal cut below. Although we won't do much quantitatively with these, it is important to separate these different directions as we attempt to fit an integral number of nodes in each of them.



Horizontal cut



Vertical cut


 relationships among  
spherical and cartesian  
coordinates

The purpose of the next few sections is simply to develop an intuition for how one can fit nodes in the r,  $\theta$ , and  $\phi$  directions.

All of the computer displays must be calculated as they go along, so they take a while to produce (about a minute or two). The top half of the screen shows the horizontal cut, the lower half of the screen the vertical cut. The left half of the screen shows the "color values" of the wave function, the right half shows just the amplitude squared, which is proportional to the probability of finding the electron at that location. Once the figure is completely drawn, it is animated so that you can see the time dependence. The wave functions are in the Workshop Data folder in a folder labeled H Atoms 12.2. Each of the wave functions is labeled by a series of numbers that indicate the number of nodes in the r,  $\theta$ , and  $\phi$  directions.

*Guidebook Entry 12.5: Fitting Nodes in the Radial Direction*

The radial coordinate can run from zero to infinity, and is not sensitive to the direction away from the center. Nodes in the radial direction must therefore reflect this symmetry.

The ground state has no nodes. The program for this is labeled H000. Run this program, and describe what the function looks like. Pay attention to the colors that you see.

A node on a one dimensional wave function is a point, on a two dimensional wave function, it is a line or curve. What sort of geometric object should a node in a three dimensional wave function look like?

Run the program that has one radial node, H100. Describe the resulting wave function, and what the node looks like. Before the display starts to be animated, make particular note of what colors you see.

What do you expect the wave function with two radial nodes to look like?

Run the program H200. Does it agree with your prediction?

*Guidebook Entry 12.6: Fitting Nodes in the  $\phi$  Direction*

The  $\phi$  coordinate can run from zero to  $\pi$ . It does not need to run more than half a rotation, since the other side is accessible by changes in the  $\theta$  coordinate. Nodes in the  $\phi$  direction must therefore be reflected on the opposite side as well.

Run the program that has one  $\phi$  node, H010. Describe the resulting wave function, and what the node looks like.

What do you expect the wave function with two  $\phi$  nodes to look like? Can you guess what the colors should be before the display is animated?

Run the program H020. Does it agree with your prediction? You should be able to describe the nodes in terms of cones; check with an instructor if that doesn't make sense.

*Guidebook Entry 12.7: Fitting Nodes in the  $\phi$  Direction*

The  $\phi$  coordinate can run from zero to  $2\pi$ . Since it runs a full  $2\pi$ , it comes back on itself. This means that the quantization in this direction is just like the quantization for a particle confined to a hoop. The "nodes" in this direction are not actually nodes, but full wavelengths through the color spectrum.

Run the program that has one  $\pi$  node, H001. Describe the resulting wave function, and what the "node" looks like.

Notice there is also a zero at the center of the wave function. Why must this be? [Hint: Imagine that it was not zero at the center. What color would it be?]

What do you expect the wave function with two  $\pi$  nodes to look like?

Run the program H002. Does it agree with your prediction?

### Session 3: Quantum Numbers, Energies, and Bigger Atoms

In this session, we will make connection with the conventions used commonly by physicists and chemists to describe atomic wave functions. We will also touch base with how energies of these atoms depend on the quantum numbers, and then talk briefly about how we can use these basic concepts to understand the fundamentals of the structure of multi-electron atoms.

In this first activity, you will demonstrate your understanding of the hydrogen atom wave functions by making your own 3-D models with one of our favorite scientific tools, Play-Doh. We then will look at wave functions with nodes in several dimensions at the same time. In looking at these functions, recall our convention for the sequence of quantum numbers:  $r$ ,  $l$ , and then  $m$ .

#### *Guidebook Entry 12.8: Combining Nodes*

To make sure that you are interpreting the computer models correctly, I want each of you to make your own Play-Doh model of the hydrogen atom wave function that has two  $l$  nodes. First, start up the computer model for the 020 wave function which we saw in the last session--make sure you are starting the correct one! While this is starting up, select some good colors of Play-Doh, and if you recall what the wave function looked like (you might check your last activity guide), start making models. After you each have a model, see if they look like one another. Then check with an instructor.

We can also have combinations of node structure in more than one of the dimensions. Let's imagine we have one radial node, and one  $l$  node. Make a model of what you expect this will look like. Sketch your model below.

Now what does the computer model look like of H110? Does it agree with your model? If you are unsure of any discrepancies, check with an instructor.

Now look at a couple more computer models. As a test of your understanding, write down the number of nodes for each wave function.

H Test 1: r nodes:

nodes:

nodes:

H Test 2: r nodes:

nodes:

nodes:

H Test 3: r nodes:

nodes:

nodes:

Now, you may check your results with the answers on the last page of this session. Discuss any discrepancies with an instructor. If you have any notes or hints you'd like to remember for identifying nodes, write that below.

The conventional quantum numbers, while they contain the same information as the number of nodes, contain that information in a different combination, which is described in the next exercise. It will be your job to establish the mathematical relationships between the two systems.

*Guidebook Entry 12.9: Standard Quantum Numbers, Energy, and Angular Momentum*

Because the energy is dependent to considerable accuracy on just the total number of nodes in the wave function, the so-called principle quantum number  $n$  is equal to the *total* number of nodes in the wave function *plus one* (this way the lowest state is labeled  $n=1$ , which makes the energy expression simpler than for other choices). Given this, write an expression that relates this quantum number  $n$  to the number of radial nodes  $n_r$ , the number of  $\phi$  nodes  $n_\phi$ , and the number of  $\theta$  nodes  $n_\theta$ .

The total energy (kinetic plus potential) of an electron in a hydrogen atom is given by the following expression:

$$E = -\frac{2.2 \cdot 10^{-18} \text{J}}{n^2}.$$

While it is a bit beyond what we can do right now, this constant in the numerator can be found easily; I did it on an envelope to check my recollection. It depends only on such constants as the mass of the electron, the charge of the electron, and Planck's constant. It is an accidental result that all nodes "cost" the same amount of energy, but makes for a particularly simple result.

Does the total energy increase or decrease with increasing number of nodes? Discuss your answer with an instructor.

Using this energy rule, find the energies for transitions between  $n=2$  and  $n=3$ , 4, and 5.

$\Delta E$  for  $3 \rightarrow 2$ :

$\Delta E$  for  $4 \rightarrow 2$ :

$\Delta E$  for  $5 \rightarrow 2$ :

Using  $h = 6.6 \times 10^{-34}$  J sec and the speed of light  $c = 3 \times 10^8$  m/sec, find the wavelengths of these three transitions. What colors of light do they correspond to? Are they the colors you saw with the diffraction grating looking at the hydrogen discharge? (You will need to look at a chart of the visible spectrum, available in most intro texts.)

$\ell$  for  $3 \rightarrow 2$ :

$\ell$  for  $4 \rightarrow 2$ :

$\ell$  for  $5 \rightarrow 2$ :

The total number of angular nodes (both  $\ell$  and  $m$ ) gives the total angular momentum of the wave function, such that

$$L^2 = \frac{\ell(\ell + 1)\hbar^2}{(2\ell)^2} = \ell(\ell + 1)\hbar^2$$

where  $\ell$  is the total number of angular nodes, and is always non-negative. In the second version of this expression, I have used the symbol  $\hbar$ , defined as  $\hbar \equiv \frac{h}{2\pi}$ . Relate the quantum number  $\ell$  mathematically to  $n$  and  $m$ .

Finally, the angular momentum component along the pole (usually termed the z direction) is given by

$$L_z = n_{\ell} \frac{h}{2\pi} = m_{\ell} \frac{h}{2\pi} = m_{\ell} \hbar.$$

In this equation, we have implicitly defined both  $m_{\ell}$  and  $\hbar$ . The latter is especially common throughout all quantum mechanical calculations. Since the angular momentum component can be positive or negative,  $m_{\ell}$  can also be positive or negative.

Given these definitions of  $n$ ,  $\ell$ , and  $m_{\ell}$ , it is easy to see what restrictions there are on certain combinations of these quantum numbers. The next couple of questions lead you through the arguments; you may need to refer back to the definitions!

If  $n$  is 3, how many nodes total are there in the wave function?

What is the maximum number of angular nodes that are possible for  $n=3$  quantum states?

Express a general limit on the value of  $\ell$  for a particular  $n$  value.

Write a similar restriction on  $m_{\ell}$  based on a particular value of  $\ell$ .

Now comes the question of what happens when we build larger atoms. In other words, if we increase the charge of the atomic nucleus, we can then attach more electrons to the atom. But how do these electrons interact with one another? Since they have the same charge, they repel each other by the electrostatic force, but even more significantly, there is a purely quantum mechanical effect that causes some types of particles (electrons, protons, and neutrons to name a few) to refuse to get close to other identical particles. This same effect causes other types of particles (photons are the only common ones) to like to get close to one another. In the case of photons, this makes the laser possible. In the case of electrons in an atom, this gives rise to the Pauli Exclusion principle, which demands that no two electrons find themselves in the exact same quantum energy level. This is complicated by the fact that the electrons themselves have an intrinsic angular momentum, called spin. This spin, like all angular momenta, is quantized, with two possible values. The net result is that for the  $n=1$  level in a hydrogen-like atom, one can put *two* electrons, one with each spin value. The next exercise uses this fact to allow us to see where the natural breaks, based on chemical properties, occur in the periodic table of the elements.

*Guidebook Entry 12.10: Pauli and the Periodic Table*

How many different combinations of nodes are possible for an  $n=2$  level in the hydrogen atom? Check your answer with an instructor.

How many electrons can be put into the  $n=2$  level? (For all of the following exercises, you may assume that the negative charge of all of these electrons is balanced by an appropriately positively charged nucleus, such that the atom remains electrically neutral. Discuss this with your instructor if in doubt on this exercise.)

What element does this correspond to?

Do you know what the chemical properties of this element are?

How do these properties compare to those of an atom with a filled  $n=1$  level (i.e. with only two electrons)?

Although the energy levels depend only on  $n$  for the hydrogen atom, putting many electrons in an atom causes a significant difference between different  $\ell$  values with the same  $n$  value. As a result, there are a variety of smaller breaks as different levels are filled. But as you can see on the periodic table, there are groupings across that are two wide (corresponding to filling an  $\ell=0$  level), that are six wide (corresponding to filling an  $\ell=1$  level), that are ten wide (corresponding to filling an  $\ell=2$  level), and that are fourteen wide (corresponding to filling an  $\ell=3$  level). Since the chemical properties of atoms depend most heavily on the outermost electrons, the chemical properties of atoms with similarly partially filled outermost levels tend to be similar.

Answer Key for Guidebook Entry 12.8

H Test 1: 101  
H Test 2: 011  
H Test 3: 002