

Chapter 7

Quantum Behavior of Atoms

Emission spectra and photons

In Chapter 4, we discussed how light (specifically infrared light) can be absorbed by molecules such as greenhouse gases. Compared to absorption, **emission** is the opposite process wherein energy is released from matter in the form of light. This occurs when matter that is oscillating (has energy) at a given frequency releases that energy (it changes oscillation frequency or stops moving). In molecules, this is seen through the change in oscillation in the bond as discussed in Chapter 4. For individual atoms, however, there are no bonds around which to oscillate. Despite this difference, when atoms release energy, they do so in the form of light at very specific frequencies (and therefore specific wavelengths). This was discovered by energizing low-density elemental gases (gases that contain single elements) to the point of glowing. When the light is observed, it was seen that different elements emitted different frequencies of light in a spectrum of *bright* lines. Only specific frequencies were observed instead of a continuous spectrum (as you would see with white light, rainbows, and the blackbody emission of Earth).

In the 1880's, Johann Balmer recognized that the visible light emission spectrum of hydrogen (see Figure 7.0), known by then to be the lightest and probably simplest element, follows a pattern in which the lines are more closely spaced at shorter wavelengths (i.e., from red to violet). Moreover, each chemical element has a distinctive pattern of colored emission lines (Figure 7.0), a sort of “fingerprint” of the element. For early spectroscopists this proved to be a difficult phenomenon to explain – why would an atom only emit a few, very distinct wavelengths of light? While it may have made sense that each element would have a unique emission spectrum, for a long time the exact frequencies of emitted light from each element proved impossible to predict or explain. These observations would be the basis on which physicists in the coming years (late 19th century into the early 20th century) would propose their atomic theories. They realized that any successful model of the atom must explain the patterns of wavelengths emitted by different elements.

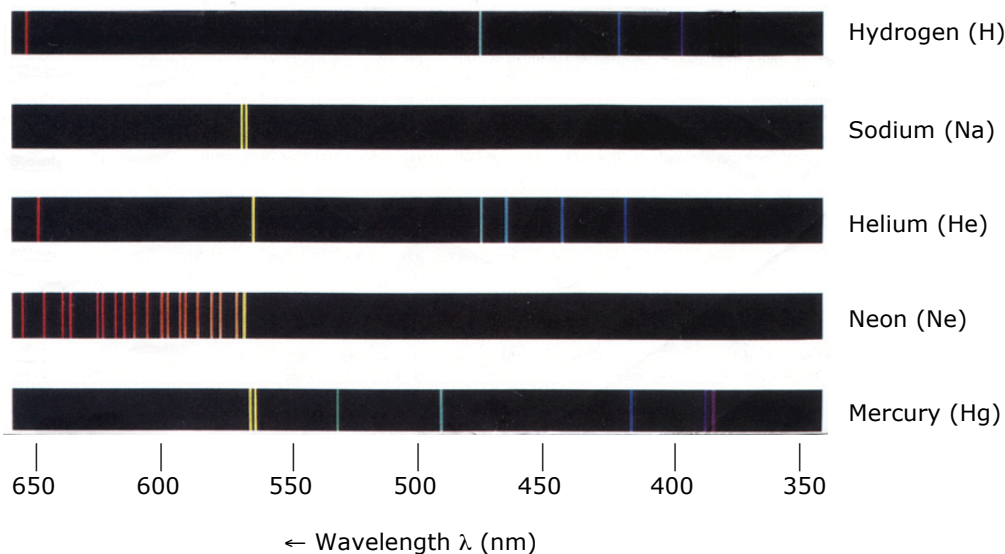


Figure 7.0: Emission spectra for various elements

It is important to note that when light is absorbed, the wavelength, frequency, and energy of that light are not changed. In actuality, it is the intensity of the light that decreases during absorption, which makes it dimmer. Lowering the intensity of a light wave results in a lower amplitude, but the frequency and wavelength of that wave remains the same. Every time light transfers energy *to* matter (read: is absorbed), it is transferring exactly $h\nu_{\text{light}}$. Similarly, every time light is released *from* matter (read: is emitted), it is released in multiples of $h\nu_{\text{light}}$. This is one of ways in which we ascribe “particle-like” nature to light – despite the fact that light is an electromagnetic wave (definitely not a particle), it does have the particle-like property of transferring fixed, discrete quantities of energy known as **photons**. The energy of a photon of light with given frequency ν is $E_{\text{photon}} = h\nu_{\text{photon}}$.

A photon is a **quantum** of light, meaning that it represents the smallest possible discrete “unit” of light. As a result, photons cannot be subdivided into smaller units and have discrete energies ($E_{\text{photon}} = h\nu_{\text{photon}}$). To be clear, a photon is not an object; rather, it is the total amount of energy (a quantum of energy) that is transferred between light and matter when light is absorbed by the matter or emitted from matter. This quantity is always the same (*quantized*) for light of a given frequency, ν_{photon} . As we saw in Chapter 4, it is the resonance between the oscillating frequency of the light and the matter (resonance) that leads to energy being transferred, and it takes many oscillations of the electric field for this energy to be transferred.

Quantum mechanics is the branch of physics that describes the nature and behavior of objects that, like photons, have quantized energy values. This is distinct from macroscopic objects and the world of **classical physics**, which have no limitations on the possible amount of energy they can carry. As we will see, the behavior of photons and subatomic particles (like electrons) differs in many fundamental ways from the behavior of the objects we interact with on a daily basis. For example, the interactions of light and matter may strike you as somewhat odd. Why would light only be absorbed by matter at certain resonant frequencies? Why do atoms only emit specific energies (and wavelengths) of light? Why is there such a big difference between the classical and quantized worlds? The first glimpse at answering these questions came from a set of experiments conducted between 1801 and 1927, and a phenomenon known as interference.

Wave interference

When rigid objects collide, energy is transferred between them, and often they bounce back after the collision. Waves, on the other hand, do not collide with other waves the way rigid objects do. Instead, waves interact through a phenomenon called **interference**. When two waves pass through each other, they interact through constructive and destructive interference. Constructive interference occurs when two waves are in phase (both have either positive or negative amplitudes). In such an occasion, the amplitudes of the two waves combine to create a wave with greater amplitude – either more positive or more negative (Figure 7.1 top). Destructive interference occurs when waves are in opposite phases and the amplitudes are subtracted from each other, resulting in a lesser amplitude wave (Figure 7.1 bottom).

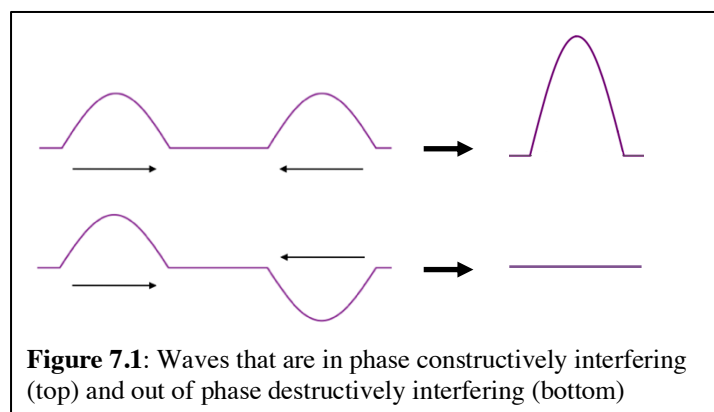


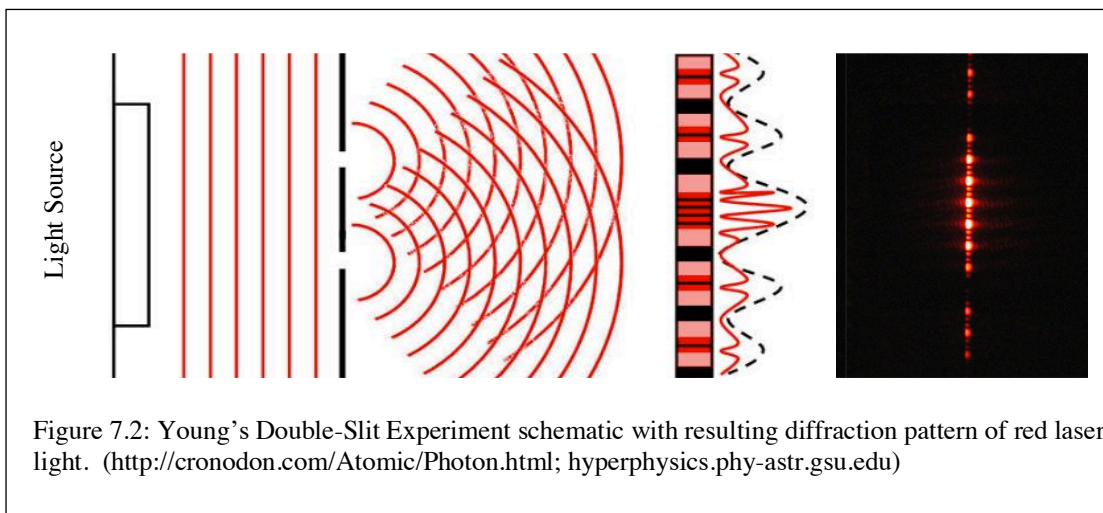
Figure 7.1: Waves that are in phase constructively interfering (top) and out of phase destructively interfering (bottom)

The waves in both cases then pass through each other and continue to propagate as they were before the interaction. The CDF player demonstrating constructive and destructive interference can be found here: <http://quantum.bu.edu/CDF/101/23-ElectronWaveInterference-1.cdf>

(Note: If you have not done so already, you will first need to download Wolfram CDF Player on your computer; select the “Student” option in the roll down menu on the website: <http://www.wolfram.com/cdf-player/>)

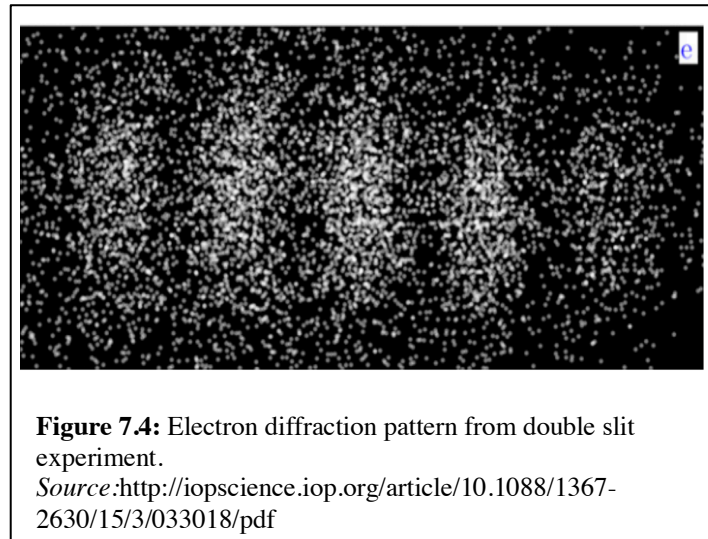
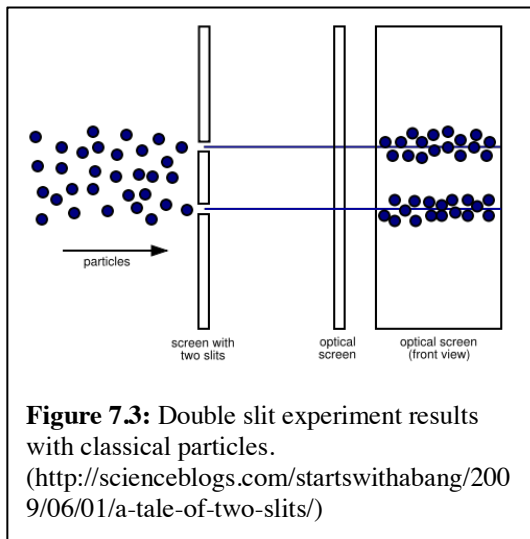
Double slit experiment for light

The question of the exact nature of light – whether it behaved as a particle or a wave – dates back at least 2000 years to the atomist Democritus. A few decades before Maxwell provided strong evidence in support the wave-like nature of light with his famous equations for electromagnetism, a scientist named Thomas Young conducted an experiment designed to test this question. In 1801, well before the conversation of quantum mechanics started in the scientific world, Young directed a light source at a screen that had two small slits cut into it (Figure 7.2). A screen then detected the pattern of the light after it passed through the slits. If light behaved like a particle, then the expected results would be two bright bands on the screen: one bright band for each of the slits. Instead, the results showed a **diffraction pattern** – a phenomenon that occurs when waves interact. Each bright spot on the screen (far right side of the figure) showed a peak in the amplitude due to constructive interference between the two radiating waves. Each dark spot represented destructive interference, where the amplitudes of the interfering waves cancelled (zero amplitude = zero intensity = dark). As such, Young concluded that the light acted as would be expected from a wave, not as particles.



Double slit experiment for electrons

In 1961, 160 years after Young's initial experiment, the double slit experiment was repeated using a beam of electrons instead of light. The expectation was that if electrons acted like particles, then the resulting screen would show two groups of electrons – those that passed through one slit or the other. Consider what would happen if you threw Ping-Pong balls at a screen with an opening just wide enough for a ball to pass through – the few that made it through would fly through and hit approximately the same location (Figure 7.3) The results of the experiment using electrons, however,



were the same as what was seen with the diffraction of light: wave-like diffraction patterns emerged, with multiple “bright” and “dark” bands (Figure 7.4). Initially, it was thought that the results were inaccurate, and that electrons might have been “hitting” or scattering each other as they passed through the slits, causing them to spread out. To test this concern, the experiment was repeated in 1974 with individual electrons being emitted one at a time to prevent any possible scattering. What they saw, however, was another diffraction pattern. The only way this pattern could be created was if individual electrons had wave-like properties similar those of light. A time-lapse video of these results can be found at <https://www.youtube.com/watch?v=ZqS8Jkk1HI>

Note that each dot captured on the screen represents a single electron signal after having passed through the slits. As time continues, these dots collect into groups, resulting in a diffraction pattern similar to that of light. One of the greatest implications of these findings was that the mass of an electron is spread out energetically in a wave, not localized in one point like a classical object. This is why we say that atoms have “electron waves”.

Observing the wave-like properties of electrons is the key to the quantized nature of light and light-matter interactions. Let’s take a look at how a classical example of waves gives us information about the quantized nature of matter. The images in Figure 7.5 show an example of a classic particle (a baseball) that is localized, and a classic wave (sound) that is delocalized.

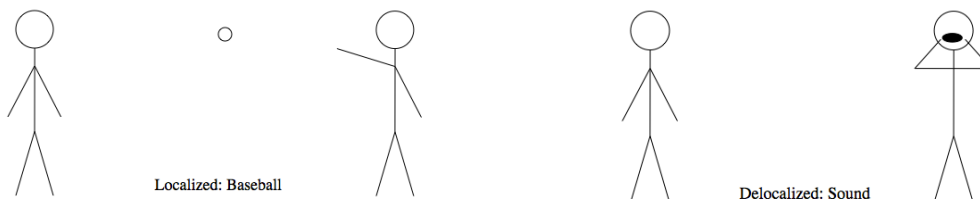


Figure 7.5: Localized versus delocalized behavior

In the localized example it is possible to circle the exact location of the baseball. That is because a classical object, or “particle”, is localized in space. With the sound example, however, it is not possible point to the exact location of the sound. This is because waves are delocalized, and are spread out in space. Based on the results of the double slit experiments, we can relate both light and electrons to the delocalized example because of their wave-like properties.

Remember, analogies are a good way to understand abstract topics, but they are limited. The analogies above do not give exact representations of electrons, but instead help to explain some of their more abstract behavior. The purpose of this example is to illustrate that the behavior of electrons in an atom is similar to that of delocalized waves spread out in space, not localized particles.

Matter waves and the de Broglie wavelength

The finding that electrons can behave as waves was a surprising one, and it raised new questions about the true nature of electrons. Louis de Broglie, a French physicist, wondered if electrons behaved as waves, does that mean one could calculate their wavelengths? It was already clear that electrons had momentum in the classical particle sense – i.e., the momentum of an electron was equal to its mass times its velocity ($p = mv$). The equation for the momentum of light, however, is different than for classical objects. For light, the momentum is defined as:

$$p_{\text{light}} = \frac{h}{\lambda_{\text{light}}} \quad [7.1]$$

where h is Planck's constant (6.626×10^{-34} J·s) and λ is the wavelength of the light. This now provides an interesting comparison between photons and electrons. Because electrons also have wave-like behavior, it stands to reason that they would also have a wavelength. De Broglie, having observed a diffraction pattern for electrons passing through crystal, made a logical leap that, if electrons were behaving in a wave-like manner similar to light, he could combine Einstein's formula for the momentum of light with the equation for momentum of a particle ($p = mv$) to find the wavelength of an electron ($\lambda_{\text{electron}}$):

$$p_{\text{electron}} = m_e v = \frac{h}{\lambda_{\text{electron}}} = \frac{h}{\lambda_{\text{db}}} \quad [7.2]$$

where m_e is the mass of the electron (9.109×10^{-31} kg), and $\lambda_{\text{electron}} = \lambda_{\text{db}}$ is the de Broglie wavelength of the electron wave. Rearranging this equation we can solve for the de Broglie wavelength:

$$\lambda_{\text{db}} = \frac{h}{p_{\text{electron}}} = \frac{h}{m_e v} \quad [7.2]$$

Worked Example 7.1: What is the de Broglie wavelength (in m) of an electron ($m = 9.109 \times 10^{-31}$ kg) moving at a speed of 5×10^5 m/s?

Solution: the de Broglie wavelength of an electron (9.109×10^{-31} kg) moving with speed of 5×10^5 m/s is computed with equation 7.2:

$$\lambda_{\text{db}} = \frac{h}{p} = \frac{6.626 \times 10^{-34} \text{ J} \cdot \text{s}}{(9.109 \times 10^{-31} \text{ kg})(5 \times 10^5 \text{ m/s})} = 1.5 \times 10^{-9} \text{ m}$$

Careful: units can be a problem here; the mass must be in kg (not g) because Planck's constant contains J.

Based on this equation, an electron traveling at a speed of 500 km/s would have a de Broglie wavelength of about 1.5 nm (1.5×10^{-9} m). While this seems small, it is significant compared to the size of an atom, which has a radius on the order of 1 Å ($= 10^{-10}$ m).

However, what would happen if we applied formula [7.2] to everyday objects? After all, according to de Broglie's equation, anything with a mass and a velocity would also have a wavelength. To answer this question, consider a baseball in worked example 7.2.

Worked Example 7.2: What is the de Broglie wavelength (in m) of a baseball ($m = 0.15$ kg) thrown at 90 miles per hour (40 m/s)? Does this baseball have a de Broglie wavelength? Why or why not?

Solution: the de Broglie wavelength of a baseball (0.15 kg) moving with speed 40 m/s is computed with equation 7.2:

$$\lambda_{\text{db}} = \frac{h}{p} = \frac{6.626 \times 10^{-34} \text{ J} \cdot \text{s}}{(0.15 \text{ kg})(40 \text{ m/s})} = 1.1 \times 10^{-34} \text{ m}$$

It is clear that we can calculate a wavelength for this *heavy* and *slow* classical object, such as a baseball thrown at 90 mph, but there is no real meaning to the value. Because the de Broglie wavelength is *much* smaller than the baseball, there are no wave-like properties ascribed to this object. However, objects with very small masses (like electrons) will often have measureable and meaningful de Broglie wavelengths. An important implication here is that the boundary between classical and quantum objects is perhaps fuzzier than we might imagine. At what point do we decide that a particle is acting like a wave?

Particle-in-a-box model

Up until now, we have considered electrons moving freely (outside of an atom). But what happens to an electron when it is bound to an atom? Does it remain a wave? To help us answer this question, let's start with a more familiar scenario that illustrates a wave between two boundaries. Suppose two people were to hold a spring or a jump rope at both ends and one person started shaking one of the ends. At first, waves would likely travel back and forth rather chaotically. But with continued shaking (and adjusting of the amount of energy supplied to the spring or rope), the two people would be able to create standing waves. The more energy put into the spring or rope, the more peaks the standing wave would have. If the two people moved farther away from each other, the spring or rope would be stretched out to fill the space, and the amplitude of the waves created would decrease. The activity below provides a CDF player to help you better understand this relationship with standing waves.

For classical standing waves (such as our example of the spring or jump rope), the number of loops is **quantized**. This means that there can only be specific values of wavelengths within these types of standing waves (i.e., whole number multiples of $\frac{1}{2} \lambda$). As we have seen, if the wavelength is quantized, then the energy of the wave is also quantized. This is an appropriate analogy to an electron inside an atom. Because the electron is attracted to the positive charge of the nucleus, it becomes bound to the atom. The electron wave disperses around the nucleus and forms a standing wave much like a spring or jump rope. The boundaries in the atom are therefore created by the energy of this attraction.

Activity: Standing Waves Simulation

Go to the following applet:

<http://quantum.bu.edu/CDF/101/09%20Standing%20Waves%20applet.cdf>

When this first opens, you will see two sliders at the top. The first, labeled *Barrier Separation* (L), indicates the separation between the two barriers. The second, labeled *loops* (n), indicates the number of loops (1 loop = $\frac{1}{2}$ of a waveform; one full wavelength is two loops) in the wave.

Exercise 1: Set the separation of the barriers (L) to 5 nm. Draw the wave for: $n = 1$, $n = 2$, $n = 3$, $n = 4$, and $n = 5$. Answer the following questions based on your drawings.

- How does the number of loops affect the wave?
- Will you ever have only part of a loop between the two barriers? What does this mean for the number of wavelengths you can have inside the barriers?

Exercise 2: Set $n = 1$. Change L and answer the following questions based on your observations.

- What happens to the amplitude of the wave as you change the separation of the barriers? What happens to the wavelength as you change the separation of the barriers?

To simplify and help visualize this phenomenon, a one-dimensional electron wave can be trapped in a “box” of energy barriers. The result is a one-dimensional standing wave, much like the analogy to a spring fixed at both ends, called the “Particle in a Box” model (Figure 7.6). The separation of these barriers (L) can be equated to the size of the atom. For bonding electrons in a molecule, this same concept applies. In this case, the separation between the barriers (L) represents the size of the molecule. A similar CDF applet to the one used in the standing wave example can be used to describe the Particle-in-a-box model:

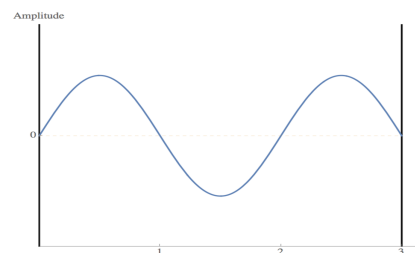


Figure 7.6: Particle-in-a-Box Model

<http://quantum.bu.edu/CDF/101/12-ParticleInABox-1.cdf>

The model is based on the following assumptions: (1) the particle – usually an electron – is confined to a one-dimensional box with length, L , which has a uniform and flat bottom (lower energy than the wave) inside the box; (2) the walls of the box will be infinite (infinite energy), which means that the particle/wave cannot escape and will have zero amplitude at the walls (creating nodes); and (3) only whole numbers of loops ($1/2$ wavelengths) can be found in the box.

Understanding the different energies (or “energy states”) of these standing waves gives insight into the quantized properties of electrons. We can demonstrate this by doing a little algebra. First, we can calculate the average energy of the particle trapped in the box by using the formula for kinetic energy and substituting p/m for v (from $p = mv$):

$$E = \frac{1}{2}mv^2 = \frac{p^2}{2m} \quad [7.3]$$

where m is the mass of the particle (usually an electron) and p is the momentum. Recall from de Broglie that the momentum of a matter wave is equal to h/λ for the wave (equation [7.2]). Substituting equation [7.2] into equation [7.3] gives us the energy of the matter wave in terms of the wavelength:

$$E = \frac{h^2}{2m\lambda^2}. \quad [7.4]$$

As you have seen in the standing wave activity above, the wave contained in the box must have a whole number of loops (n , or half-wavelengths). Therefore, the total length of the box, L , can be written as:

$$L = n \left(\frac{\lambda}{2} \right). \quad [7.5]$$

Rearranging equation [7.5] and substituting it into equation [7.4] gives the formula for the energy of a matter wave with mass, m , with n loops that is confined to a box of length, L :

$$E_n = \frac{n^2 h^2}{8m_e L^2}. \quad [7.6]$$

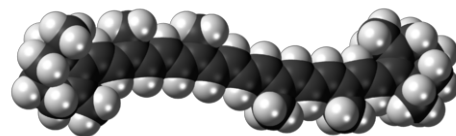
Because h and m_e (mass of an electron = 9.109×10^{-31} kg) are constants, we can further simplify this equation to:

$$E_n = \left(\frac{h^2}{8m_e} \right) \frac{n^2}{L^2} = K \frac{n^2}{L^2}$$

where K is a constant equal to 6.02×10^{-38} J²s²/kg.

Notice that equation [7.6] (the particle-in-a-box model) indicates that matter waves that are confined to one-dimensional boxes will have finite, discrete energies that are proportional to n^2 . That is, the two lowest energy wave states ($n = 1$ and $n = 2$) will have energies $E_1 = K/L^2$ and $E_2 = 2^2 K/L^2 = 4E_1$, but there will be no states possible between these two! (Because standing waves cannot have fractions of nodes/loops – n must be a positive integer). This result constitutes a huge leap in our understanding of the nature of electrons in atoms – specifically their quantized behavior. Of course, unlike our particle in a box model, the electron will be a 3-dimensional wave, which will require a little more investigation.

Worked Example 7.3: β -carotene (right) is a strongly colored orange pigment found in plants and fruits (e.g., carrots). The molecule is long and straight, so the electron waves of the molecule can be modeled using the particle-in-a-box model. β -carotene absorbs light most strongly around 470 nm (blue and green light), which means that the rest of the visible light shines through (is transmitted) or is reflected. As a result, your eye picks up the colors of visible light that are not absorbed, making it look orange-red. The absorption of blue light (470 nm) corresponds to a change in the electron waves from $n = 11$ to $n = 12$ due to the absorption of energy. Based on these observations, estimate the length of the molecule (the “box”) in nm.



Solution: Changes in electron waves (such as the absorption of light) involve two energy states. In this case, we are studying the change from $n = 11$ to $n = 12$, from the absorption of one photon of 470 nm light. First, we must calculate the energy of one photon with a wavelength of 470 nm using equations $c = \lambda\nu$ and $E_{light} = h\nu_{light}$.

$$\Delta E = h\nu = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{s})(3 \times 10^8 \text{ m/s})}{(4.7 \times 10^{-7} \text{ m})} = 4.23 \times 10^{-19} \text{ J}$$

Using equation [7.6] for the energy of each state, we get:

$$\begin{aligned} \Delta E &= E_{\text{final}} - E_{\text{initial}} = E_{12} - E_{11} \\ \Delta E &= \frac{(12)^2 h^2}{8m_e L^2} - \frac{(11)^2 h^2}{8m_e L^2} = (12^2 - 11^2) \frac{h^2}{8m_e L^2} \end{aligned}$$

Solving for the length of the box (L), we get:

$$\begin{aligned} L^2 &= (12^2 - 11^2) \frac{h^2}{8m_e \Delta E} \\ L^2 &= (12^2 - 11^2) \frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{s})^2}{8(9.109 \times 10^{-31} \text{ kg})(4.23 \times 10^{-19} \text{ J})} = (3.28 \times 10^{-18} \text{ m})^2 \\ L &= 1.81 \times 10^{-9} \text{ m} = 1.81 \text{ nm} \end{aligned}$$

If we assume that the electron wave that we are modeling is delocalized over the length of the entire molecule (it is), then we estimate that the molecule is approximately 1.8 nm long.

Standing waves on a spring are a good analogy for electron waves

As we saw, standing waves with specific energies and wavelengths can be produced on a spring (or rope) by applying the right amount of energy. Because we are producing standing waves, only specific waves with are possible: 1 loop (half-wavelength), 2 loops, 3 loops, etc. In the language of quantum mechanics, we would call the spring itself the “*field*” and the waves that are produced on this spring are the “*excitations*.”

Electrons are also excitations of a field: the *quantum field*. All space is permeated with the quantum field, and electrons are specific excitations of that field. Similar to the excitations of waves on a spring, the electron excitations of the quantum field are also limited to being 1 loop, 2 loops, 3 loops, ..., n loops. These are what we will refer to as electron waves.

While it helps to think about quantized electron waves as being similar to the one-dimensional (1D) standing waves on a spring, they are actually three dimensional (3D) inside an atom. The 3D electron wave is often referred to as an “electron cloud” around the nucleus. While “cloud” is a helpful name for visualizing the electron, remember that it is just an analogy – an electron is a single delocalized wave in three dimensions. Just like the one-dimensional particle-in-a-box model, there are a finite number of energy states that a three-dimensional electron can occupy in an atom. In the next section we will explore the nature of the 3D electron waves.

Three-dimensional electron waves

In the 1920s, the Austrian physicist Erwin Schrödinger developed an equation that can be used to find the energy states of electron clouds. While the mathematics of the Schrödinger equation are far beyond the scope of this course, we can discuss some of the different ways that electrons can exist in three-dimensions. Just like adding more energy to a jump rope will increase the number of loops in one dimension, adding more energy to an electron will increase the number of “loops” that it has in three dimensions. When describing the energy states of electrons in three dimensions, we will run into two types of loops called **radial loops** and **nodal planes**. As we will see, the number of radial loops and/or nodal planes influences the shape of the electron cloud.

Radial loops

Radial loops form concentric spheres around the nucleus and are the reason why it is most appropriate to visualize atoms as being, for the most part, spherical. Let’s investigate these radial loops and learn how to identify the number of radial loops (3D loops) an electron cloud has by looking at it. Moving forward, we will indicate the number of *radial loops* by the letter “*j*”.

Figure 7.7 shows the lowest energy electron wave that has only a single radial loop ($j = 1$). Electron waves with this shape (spherical) are called “s” orbitals. An **orbital** is the electron cloud energy states. Note: the term “orbital” is somewhat problematic when it comes to describing the behavior of electrons, as it suggests an “orbit” or a planetary model of the atom. Instead, “orbitals” describe electrons as *waves* – it is important to keep in mind that nothing is actually “orbiting.” Since the electron wave in Figure 7.7 only has a single loop, we call it the **1s orbital**. Figure 7.8 shows the second lowest energy electron wave that has two radial loops ($j = 2$). You can see there is a node (black ring) between the two loops, much like where a standing wave passes through a zero point. This electron wave is still spherical, but because of the two loops we call it the **2s orbital**.

As the number of radial loops increases, so does the total number of loops in the electron wave. As we have seen, the more loops present in a wave, the smaller the wavelength and the greater the energy. Therefore, the 2s electron wave is higher in energy (more loops, more energy) than the 1s electron wave.

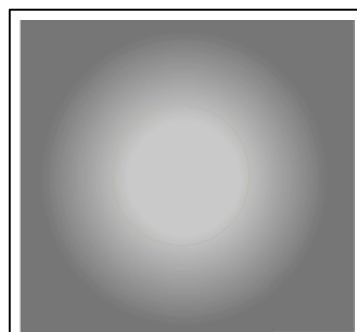


Figure 7.7: 2D representation of a 1s electron cloud

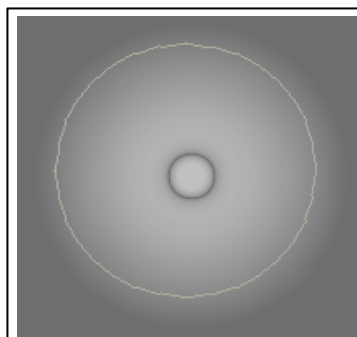


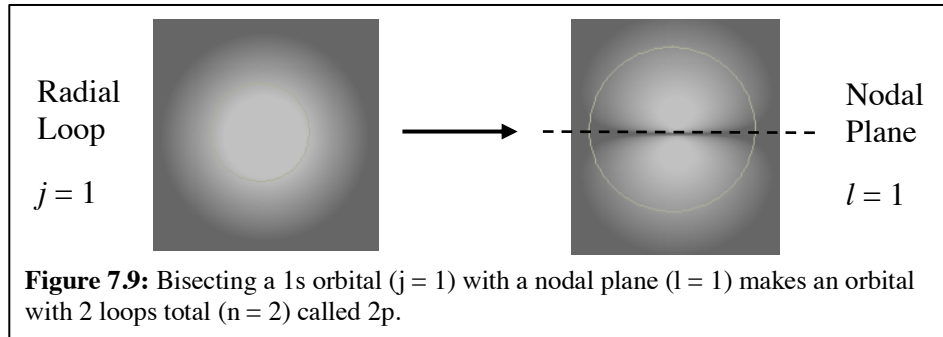
Figure 7.8: 2D representation of a 2s electron cloud

Nodal planes

In addition to having multiple radial loops, many electron clouds are broken up by nodal planes. Much like a node in a standing wave (where the energy is zero), nodal planes will result in two-dimensional areas where the electron density of an orbital is zero. In this section we will investigate nodal planes in an electron cloud. The example provided in Figure 7.9 shows the difference between an electron orbital with one radial loop and no nodal planes (Figure 7.9 on the left), versus an electron orbital with




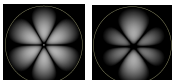
one radial loop and one nodal plane (Figure 7.9 on the right). Note that the addition of a nodal plane has changed the shape of the orbital from a sphere into more of a “dumbbell” shape.

If an electron orbital with one radial loop is cut by two perpendicular nodal planes, the resulting shape is a 3d orbital (see table below). The number of nodal planes in an electron wave are indicated using the letter “ l ”, known as the **angular quantum number**.



The 1s orbital has an l value of 0, meaning there are no nodal planes in this orbital, whereas the 3d orbitals have an l value of 2, meaning that there are two nodal planes in each of these orbitals. A summary of the different types of orbitals and their shapes is presented in Table 7.1.

Table 7.1: Shapes and names of atomic orbitals with various values of l

l	Name	General shape of the electron wave	Image
0	s	Spherical, no nodal planes	
1	p	Dumbbell shaped, 1 nodal plane	
2	d	Cloverleaf shaped, 2 nodal planes	
3	f	More complex shapes (see visualization activity)	

As the number of nodal planes in a wave increases, the energy of the electron wave also increases in a manner similar to the increase in energy with increasing radial loops. The total energy of an electron wave is thus calculated as the sum of the radial loops (j) and nodal planes (l):

$$j + l = n$$

where “ n ” is the **principal quantum number**. For example, the electron orbital with two radial loops and no nodal planes has $j = 2$, $l = 0$, and $n = 2$, and is called the 2s orbital.

The two remaining quantum numbers: m_l and m_s

In addition to the principal quantum number (n) and the angular momentum quantum number (l) that describe the *energy* and *shape* of electron clouds, there are two additional quantum numbers (variables) that describe electron cloud configurations. The first of these is called the **magnetic quantum number** (m_l), which describes the *orientation* of a given electron cloud in three-dimensional space. For example, an “s” orbital ($l = 0$) can only have one configuration in three dimensions because it is a sphere. Therefore, there is only one value of m_l for any “s” orbital ($m_l = 0$). For a “p” orbital ($l = 1$), however, there are multiple orientations. Each of these orientations results in a different possible electron cloud. For example, the 2p electron clouds (Figure 5.9) have three possible orientations – the nodal plane can be located along the x-, y-, or z-axis. Therefore, the electron cloud 2p has three possible values for m_l .

You will notice that each of these orientations is an individual orbital. That is because while they each have the same energy value (because they have the same n and l values) each one is a separate orbital. This quantum number is written as subscripts on each orbital label to indicate the difference in orientation (e.g., $2p_x$, $2p_y$, $2p_z$).

The final quantum number, m_s , is called the “**spin**” quantum number. This title can be very confusing (and *misleading*), because there is nothing here that is actually spinning (remember, we are talking about a 3D wave, not a particle). What this term represents is an *intrinsic magnetic property* of electrons. Based on this property, electron clouds can have two different orientations of “spin”: “spin up” and “spin down”. The “spin up” magnetic property has a slightly lower energy than “spin down”. This property results in the following rules of electron configuration in an atom:

1. The two different spin orientations allow two electron clouds to exist in a single orbital (one “spin up” and one “spin down”) without cancelling each other out.
2. While electrons may repel each other through the electromagnetic force (two negative charges will repel), it is more energetically favorable for two electrons to occupy orbitals with a specific number of loops (n) before creating an orbital with a greater number of loops (because a higher n is a higher energy).
3. Within a single energy level (set of orbitals with the same value of n and l) electrons will spread out within the orbitals before pairing up due to their repulsion.

Together, these form the **Aufbau Principle** for electron configurations. The box diagram on the right (Figure 5.10) shows an example of how electrons would fill energy levels by using boxes to represent orbitals. The single box on the left represents an s orbital (such as 2s), while the three boxes on the right represent three p orbitals (such as $2p_x$, $2p_y$, $2p_z$). The electrons are drawn as arrows to represent either “spin up” or “spin down”. Note that due to the Aufbau Principle, the two 2p orbital electrons will have different orientations.

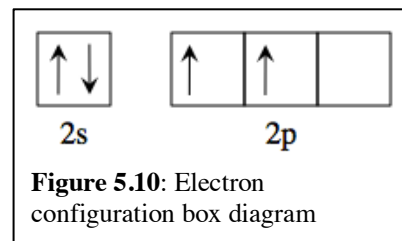


Figure 5.10: Electron configuration box diagram

Please take a moment to note that box diagrams are easy to misinterpret. Remember that electrons are not particles that are “in” orbitals – the electrons **are** the orbitals.

Activity: Exploring Hydrogen Atom Electron Clouds

1. s orbitals

Go to the following applet (Java-based, you may need to Google how to enable Java in your browser): <http://www.bu.edu/dbin/quantumconcepts/Hybridization/explorers.html>

Select the “**Hydrogen Explorer**” from the radio buttons on the screen. Next, select the “**Slice**” radio button. You can switch between the “**Slice**” or “**3D**” radio buttons on the right. The “**Slice**” view will allow you to look at any cross section of the orbital where the “**3D**” view will allow you to rotate and see the shape of the orbital. Next, select the “**Density**” radio button on the bottom right of the screen. You will see an energy diagram on the left hand side of the screen, and a view box on the right hand side. The view box will initially be blank because no energy level has been selected. Once you select an energy level, you will be able to see a 3D rendition of the electron cloud on the right. You can also click on this image and drag to rotate the view of the electron cloud.

Finally, select the “**View All Orbitals**” radio button at the top left of the screen. As you hover your mouse over each energy level, the energy value will be displayed on the left. What you will notice is that there are multiple lines drawn for many of the energy values, or orbitals.

Select the “1s” orbital. The image you see on your screen should match the image given below. This cloud shows only a single sphere, indicating that it has one radial loop ($j = 1$).

Exercise 1: On the energy diagram on your screen, select 2s. You should see an image that matches the image given below. How many radial loops does this image have? Indicate where the loops are on Figure 7.8.

Exercise 2: Select 3s. Sketch the 3D shape in your notes. How many radial loops does this orbital have?

Exercise 3: Based on the two sketches above, see if you can predict what 4s electron cloud would look like by sketching its 3D shape. Give an explanation for your drawing, and then check your work using the applet.

2. Nodal Planes

Select the “**Hydrogen Explorer**”, “**3D**”, “**Density**” and “**View All Orbitals**” radio buttons at the top left of the screen. Select the 1s electron orbital. Now, imagine that a nodal plane bisects this orbital. The resulting shape can be seen below ($l = 1$, and $j = 1$). This results in a 2p orbital. Select the 2p orbital and compare the shapes.

Exercise 1: If a 1s electron orbital is cut by two perpendicular nodal planes, the resulting shape is a 3d orbital. Select the $3d_{x^2 - y^2}$ orbital and sketch the shape. Indicate on your drawing where the nodal planes are located.

Exercise 2: Select the 2s electron orbital. Predict what the shape will look like when it is bisected by a nodal plane. Sketch this in your notes and check your work by selecting the 3p orbital.

Exercise 3: Select the 3s electron orbital. Predict what the shape will look like when it is bisected by two nodal planes. Sketch this prediction in your notes. What electron orbital does this represent?

Rydberg, Bohr, and other models of the hydrogen atom

The story behind our understanding the modern electron cloud of the hydrogen atom is a long and difficult one. While it begins in the 1880's with the experimental observations of the emission spectrum of hydrogen by Johann Balmer and some mathematical work by Johannes Rydberg, it is Bohr that is the real “hero” in the story – or perhaps the unwitting villain. In 1913 Bohr proposed the most famous – and categorically **incorrect** – model of the hydrogen atom: the Bohr model. Bohr was a genius and probably did more for the furthering of atomic physics than any one other person in history. That doesn't mean that he was right. **He wasn't, but his result is still important.**

The best guess at the time was that negatively charged electrons orbit the positively charged nucleus (this is not true, but let's see where he was going). The energies involved in the orbits would naturally depend on the strength of the attractive electric force between each electron and the nucleus, which in turn would depend on the number of protons and hence the atomic number of the element. There were two other major clues:

1. Electrons orbiting the nucleus should lose energy by making light. This would cause them to spiral into the nucleus in only a millionth of a second. Something must prevent them from doing so.
2. The pattern of wavelengths of emission lines is always the same for each element. The visible-light spectrum of the hydrogen atom (below) is particularly simple, with 3 (or 4 for people whose eyes are sensitive to deep-violet light) lines that are closer together at shorter wavelengths.



Visible light emission spectrum of hydrogen.

Bohr's solution was to combine the orbit model with the finding that light transfers energy in quantized amounts called photons. Bohr applied the concept of quantized energies to the orbits of electrons in an atom. The key idea was that an electron bound to an atom could only have certain discrete energies (for some reason that was unclear to him at the time). These energies are traditionally given as negative values, because electrons are bound to the atoms by the electric attraction to the nucleus (which, by convention, makes them negative). The lowest (most below zero) energy is called the ground state, while the higher (closer to zero) bound states are called excited states.

In Bohr's model, each excited state has a definite energy that is greater (closer to zero) than that of the ground state. If an electron absorbs a photon of just the right energy — exactly equal to the energy difference between two states — then the electron “jumps” up to the higher energy level and the photon of light is completely used up. On the other hand, an electron that is already in an excited energy state will spontaneously “jump” to a lower (more deeply negative) energy level. It does this in a small fraction of a second. This downward jump causes light to be emitted in the form of a photon with energy exactly equal to the difference between the energies of the two states.

Bohr's model thereby explained why the emission of light from atoms in a gas occurs in the form of lines: the atoms of a given element can only emit photons that have very specific energies and therefore very specific wavelengths. Each gaseous element has its own characteristic pattern of

emission lines. But could Bohr's model explain the values of the wavelengths of the emission lines? It is (by far) easiest to consider the hydrogen atom, since it contains only one electron.

Bohr started with the Rydberg equation, multiplied by hc to get the formula in terms of energies, and broke up the formula into a "change" from one state to another:

$$\Delta E_{\text{atom}} = -\Delta E_{\text{light}} = -Rhc \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \quad [7.7]$$

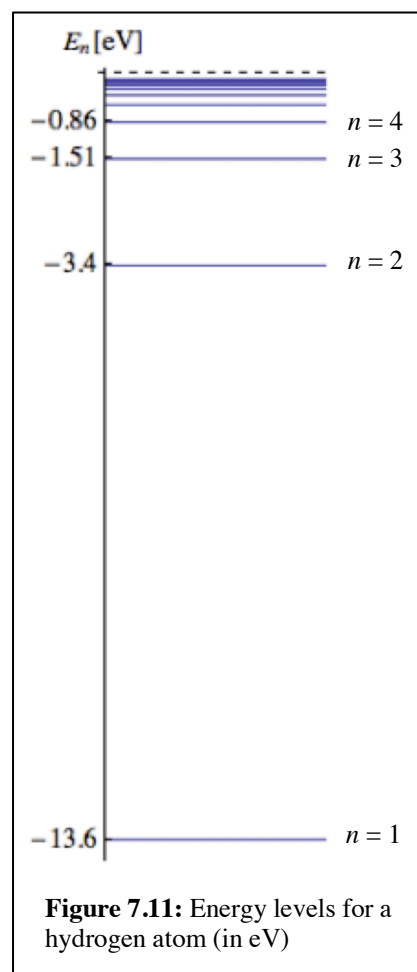
where n_f and n_i correspond to the final and initial states of the electron, R is the Rydberg constant ($1.097 \times 10^7 \text{ m}^{-1}$), h is Planck's constant ($6.626 \times 10^{-34} \text{ J}\cdot\text{s}$), and c is the speed of light ($3 \times 10^8 \text{ m/s}$). Bohr's model, therefore, is the assignment of energies to the different possible "levels" of the electron in the hydrogen atom:

$$E_n = -Rhc \left(\frac{Z^2}{n^2} \right) \quad [7.8]$$

where Z is the nuclear charge ($Z = 1$ for the hydrogen atom), n is the "level" of the electron (and must be a positive integer), and $Rhc = 13.6 \text{ eV} = 2.18 \times 10^{-18} \text{ J}$. As a result, we can plot the energy values for the hydrogen atom for each value of n (Figure 7.11). You will notice that the energy values are negative (based on equation [7.8]). Therefore, as the value of n increases, the energy becomes closer to zero (increases to be less negative). What we see is that as we increase in energy (as n increases), the energy values become closer together. Thinking back to chapter 4, this means that the greatest energy of light that could be absorbed or emitted would be between the two energy states with the greatest separation. For two consecutive energy levels, this would be between $n = 1$ and $n = 2$.

Although his model was based on the wrong picture of the atom — the electron is not like a tiny charged ball orbiting the nucleus — Bohr's equation is exactly right for computing the energies of all single-electron atoms. The biggest comedy of this story is that it is right, but for the wrong reasons — i.e., the model works to compute the energies of the electron, but it has **nothing to do with orbits!** As we know, n does not refer to an orbit, but rather the number of loops in the electron wave. So when an electron absorbs light it isn't moving anywhere, rather it is transforming from a wave with some number of loops into a wave with more loops. Conversely, when an electron wave with many loops becomes a wave with fewer loops that causes the emission of light. For example, we can model an electron that transitions from $1s$ ($n = 1$) to $2p$ ($n = 2$) or $2p$ ($n = 2$) to $3d$ ($n = 3$) using the following CDFs:

<http://quantum.bu.edu/CDF/101/1sTo2pTransition.cdf>
<http://quantum.bu.edu/CDF/101/2pto3dTransition.cdf>



Bohr insisted that the mathematical equations that he proposed (based on Rydberg and Balmer's works) have a certain philosophical meaning; moreover, he was insistent that the meaning be

attributable to the more classical physics of the 18th and 19th centuries, rather than the newer physics that was emerging. This is one the *dangers* in making models and using analogies. As new information became prevalent in the search for a quantum model of the atom, the desire to hang onto inaccurate classical examples was (and still is) very common. Wolfgang Pauli, a theoretical physicist studying the quantum nature of the atom once said, “It’s much easier to find one’s way if one isn’t too familiar with the magnificent unity of classical physics” (Lindley, 2008, p. 76). This quote illustrates the danger in being unwilling to let go of the common experiences of classical physics because it obscures the true nature of the atom.

Later, Bohr did come around to the idea of matter waves and was a leader (if not *the leader*) in the march toward the quantum mechanical model of the atom. We’ll never know if events would have played out differently if de Broglie and Schrodinger had preceded Bohr. What we do know, is that the model Bohr is perfect for *calculating energies*, but has *no physical meaning whatsoever* in regards to the nature of the atom.

Worked Example 7.4: Using the Bohr model, calculate the longest wavelength (in nm) of the light that will be absorbed by a helium ion (He^+) in its ground state ($n = 1$).

Solution: the longest wavelength corresponds to the lowest energy. Since we are talking about a helium ion ($Z = 2$) originally in its ground state ($n = 1$), then the final state is $n = 2$. If the state were any other value of n , then the energy difference between the two states would be higher (see Figure 5.11). The energy change in the atom is therefore:

$$\Delta E = E_{\text{final}} - E_{\text{initial}} = E_2 - E_1$$

$$\Delta E = -Rhc \left(\frac{2^2}{2^2} \right) + Rhc \left(\frac{2^2}{1^2} \right) = -Rhc + 4Rhc = 3Rhc$$

The energy associated with this change (according to the Bohr model) is $3Rhc$, which will correspond to light with wavelength:

$$\lambda = \frac{hc}{E_{\text{light}}} = \frac{hc}{3Rhc} = \frac{1}{3R} = \frac{1}{3(1.097 \times 10^7 \text{ m}^{-1})} = 3.04 \times 10^{-8} \text{ m} = 30.4 \text{ nm}$$

Photoelectric effect and photoionization

We have seen how different frequencies (and energies) of light can be absorbed by matter from low energy IR being absorbed by molecules, to the absorption of higher energy visible light by individual atoms. We have also seen that the frequencies (and energies) of light must be resonant with matter in order to be absorbed. However, what happens when light with even higher energies interact with matter? What happens with the higher values of n in an atom (the top of figure 7.11)?

In 1921 Albert Einstein received the Nobel Prize in Physics for “his services to Theoretical Physics, and especially for his discovery of the law of the photoelectric effect.” Sixteen years earlier, Einstein had published a paper wherein he describes how light with sufficiently small wavelength can cause electrons to become ejected from the surface of metals.

Bohr's model of the atom provides us a perfect way to understand how photoionization occurs. In the Bohr model, electron clouds gain energy as they absorb light. The frequencies that are absorbed are only those that cause the mixing of two different states of the electron cloud (i.e., two different number of loops, n). Notice, however, that the theoretical maximum value of n (positive integers) is infinity (the dotted line at the top of Figure 7.11). What does $n = \infty$ look like? A wave that has an infinite number of loops, with infinitely small wavelengths – such a wave doesn't look very much like a wave at all. In fact, it isn't. It would be an unbound electron – a particle.

The ionization energy, the energy that involves mixing the current state of the electron cloud with the $n = \infty$ electron cloud, is required for an electron to become detached (ionized) from the atom. For an electron cloud initially in the n^{th} state, the ionization energy is $IE = E_{\text{final}} - E_{\text{initial}} = E_{\infty} - E_n = -E_n$.

For a hydrogen atom in the ground state, this is $IE = 0 - (-Rhc) = 13.6 \text{ eV}$. That means that a photon of light that delivers more than 13.6 eV to the atom will cause the electron to be ejected from the atom, and the “excess” energy that is not required for the ionization becomes the kinetic energy of the ejected electron.

Worked Example 7.5: What is the kinetic energy (in eV) of an electron ionized from the helium ion ($Z = 2$), originally in the ground state, by light with photon energy 60 eV?

Solution: first, we calculate the ionization energy of the helium ion:

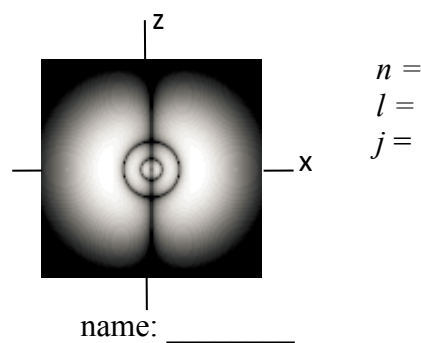
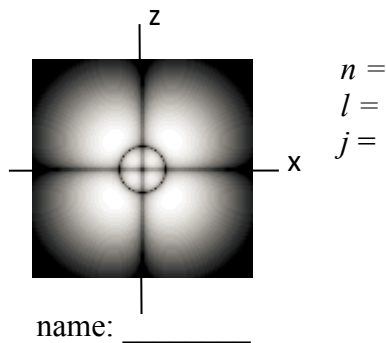
$$IE = E_{\infty} - E_1$$

$$IE = -Rhc \left(\frac{2^2}{\infty^2} \right) + Rhc \left(\frac{2^2}{1^2} \right) = 4Rhc = 54.4 \text{ eV}$$

Since it takes 54.4 eV to ionize the helium ion, and the light can transfer 60 eV, the electron will be ionized and will have kinetic energy $60 - 54.4 = 5.6 \text{ eV}$.

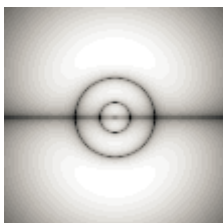
Practice Problems

1. What is the de Broglie wavelength of an electron traveling at $0.1c$?
2. Now that you know that you must have only whole numbers of loops in the Particle in a Box model (contained in an atom), what does it mean to say that the electron energy is quantized? (Hint: *remember the relationship between wavelength and energy*).
3. How fast (v) does a neutron have to travel so that its de Broglie wavelength is 1 \AA ($= 10^{-10} \text{ m}$)? The mass of a neutron is $1.6 \times 10^{-27} \text{ kg}$.
4. How fast would a beam of neutrons have to go in order for the neutrons to diffract through a sample of solid NaCl in the same way that light of 2 \AA ($2 \text{ \AA} = 2 \times 10^{-10} \text{ m}$) would diffract through the sample?
5. Estimate the size of the molecule (L) for which absorption of yellow light of 500 nm causes mixing of the ground and first excited state. (*Remember, a molecule can be considered a "box"*).
6. Which of the orbitals $4s$, $4p$, and $4d$ is the largest, that is, has the electron density distributed over the greatest volume?
7. Which of the orbitals $4s$, $4p$, and $4d$ is has the largest number of total loops?
8. For the two hydrogen electron clouds below identify the quantum number " n ", the nodal planes " l ", the number of radial loops " j ", and the specific name of the orbital. Which of these has more energy?

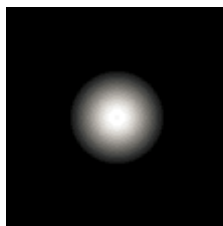


9. Shown below are displays of the *density* in the xy plane of an electron in several hydrogen atom orbitals. The brightness of the displays is proportional to the probability density. For each display, correctly name the orbital, for example, $1s$, $2p$, etc.

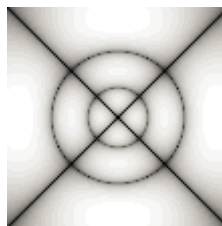
Display A: _____



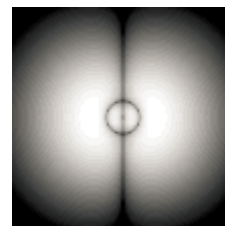
Display B: _____



Display C: _____

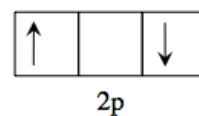
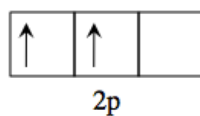
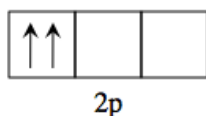
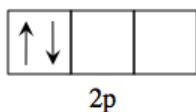


Display D: _____



10. An atom's emission spectrum contains lines of red light and green light (and nothing else). The reason why there is no orange light in the spectrum is because ...
- The atom would need more energy to emit orange light
 - The atom does not have an energy level corresponding to that of an orange light
 - The atom is not resonant with the orange light
 - Atoms always only can give off two lights

11. Circle the correct configuration, and indicate why the others are incorrect.



12. What electron cloud energies account for the line corresponding to the wavelength 434 nm in the gas discharge spectrum for the Balmer series of H atoms? (Choose one)
- Only the $n = 3$ cloud energy
 - Only the $n = 4$ cloud energy
 - Only the $n = 5$ cloud energy
 - The $n = 2$ and $n = 4$ cloud energies
 - The $n = 2$ and $n = 5$ cloud energies
13. Consider the ionization of a hydrogen atom originally in its ground state ($n = 1$). What energy would be required to ionization this hydrogen atom?
14. How would the energy required to ionize a hydrogen atom in the first excited state ($n = 2$) compare to your answer in problem (13)?
15. What is the expression for the energy (in J) for the ground state of an electron cloud in Li^{2+} ?
16. Calculate wavelength (in nm) of the light corresponding to the Li^{2+} electron cloud resulting from mixing a 3 loop electron wave with a 1 loop electron wave?
17. In terms of the variables R , h , and c , what is the smallest possible wavelength of light that will be emitted by a He^+ atomic ion, starting with the energy corresponding to level 6 loops?
18. The work function (ionization energy), of chromium metal is 7.2×10^{-19} J.
- What is the kinetic energy of an electron ejected from chromium by light of $\lambda = 250$ nm?
 - What happens to (i) the speed and (ii) the quantity of the ejected electrons if the wavelength of the light increases?
 - What happens to (i) the speed and (ii) the quantity of the ejected electrons if the wavelength of the light decreases?
19. For the two hydrogen electron clouds in problem (8), which has the largest ionization energy?
20. Photons of energy 13.6 eV are able to ionize the hydrogen atom in its $n = 1$ energy level. Are photons of this energy are able to ionize He^+ in its $n = 2$ energy level?

21. The figure shows three H atom electron clouds. Write down the numerical expression that when evaluated gives the value in eV of smallest ionization energy of these three clouds.

