

# Chapter 2, Quantum aspects of light and matter

Near the end of his life Albert Einstein wrote, "All the fifty years of conscious brooding have brought me no closer to the answer to the question: What are light quanta? Of course today every rascal thinks he knows the answer, but he is deluding himself." We are today in the same state of "learned ignorance" with respect to light as was Einstein. Arthur Zajonc, "Light Reconsidered," Optics & Photonic News, October 2003

## Atoms, light, and their interaction

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### ■ Light is as light does

Our world is bathed in light, and every aspect of the light we see traces to its interaction with the atoms and molecules that make up our world. Light, matter, and their interaction form the inseparable fabric of our visual world.

A good place to begin learning about this visual fabric is to understand just what light is. For our purposes, as Forrest Gump might say, light is as light does, and what light does is to rhythmically tug on electrical charges—it makes charges jiggle! The number of tugs in a second is called the frequency of the light. Turning this around, light is produced whenever electrical charges are set in rhythmic motion.

Visible, UV, and higher frequency light tugs primarily on the negatively charged electron clouds in matter. IR, microwave, and lower frequency light tugs primarily on the positively charged nuclei of matter.

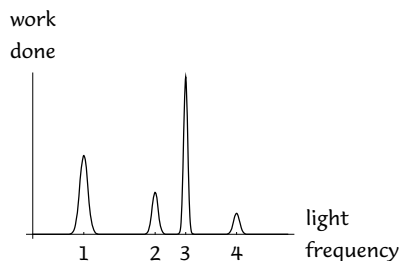
That we see different colors is because electron clouds in matter have particular frequencies that they jiggle at. These frequencies are called *resonance frequencies*. The more tightly an electron cloud is held (by positive charged nuclei), the higher its resonant frequencies.

If an electron cloud is tugged on at other than one of its resonant frequencies, it doesn't jiggle. Imagine a huge bowl of pudding. If we slowly move the bowl back and forth, the pudding is undisturbed. If we very rapidly jiggle the bowl, the pudding is not able to respond and so continues to remain undisturbed. But if we jiggle the bowl at just the right frequency, we can set the pudding to jiggle at just the same frequency. When we say something is *transparent* to light of a certain frequency range, we mean that light does not cause it to jiggle at those frequencies. The reason air is transparent to our eyes is because the electron clouds in nitrogen and oxygen molecule are held too tightly to be set jiggling by the frequencies of visible light.

Air contains about 1% argon. Predict whether the electron cloud in argon atoms jiggles at the frequencies of visible light.

### Spectra

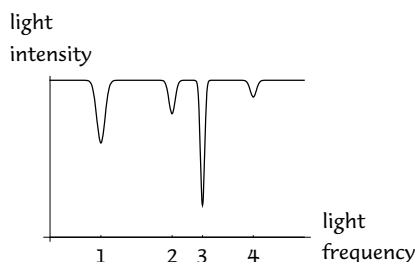
Since electron clouds have mass, it takes energy to make them jiggle. This means that if we monitor how much work is done by light, we'll find that work is done when light is tugging at resonant frequencies, but that no work is done otherwise. A *absorption spectrum* is a graph of the work done by light as a function of the frequency of its tugging on matter.



Spectrum showing the work done by light jiggling an electron cloud versus frequency. There labels number four resonance frequencies of the electron cloud.

### Absorption spectra

If we shine light on a sample, when the light frequency matches a resonant frequency and so does work, the energy expended appears as a drop in the intensity of the light. Here is a graph of light intensity versus frequency.



Absorption spectrum showing the reduction in light intensity by light jiggling an electron cloud versus frequency. There labels number four resonance frequencies of the electron cloud.

This way on probing the resonant frequencies of an electron cloud is called an *absorption spectrum*, because the energy expended by the light is *absorbed* by the atom into the jiggles of electron cloud.

Here is the absorption spectrum of hydrogen atoms in the visible wavelength range.

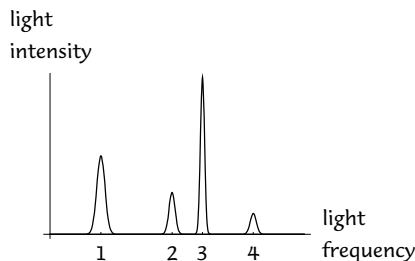


Absorption spectrum of gaseous hydrogen atoms at high temperature. Wavelength increases from 380 nm on the left to 740 nm on the right, and so frequency increases to the left.

The dark lines mark those wavelengths of the light that hydrogen atoms absorb. In the visible region of the spectrum there are only four such absorption lines for hydrogen atoms. Other atoms typically absorb light at many, many more different wavelengths. Absorption spectra are typically seen in light emitted from stars as it passes through interstellar clouds of atoms on its way to us. In the laboratory it is more typical to see emission spectra.

### Emission spectra

Light is not the only way to make jiggling electron clouds. When a beam of electron collides with atoms or molecules (such as happens when lightning passes through air, or a beam of electrons is created in a gas discharge tube), the resulting jiggles appear as light is given off. Such a spectrum is called an *emission spectrum*.



Emission spectrum showing the reduction in light intensity by light jiggling an electron cloud versus frequency. There labels number four resonance frequencies of the electron cloud.

An emission spectrum looks similar to the spectrum shown above of work done by light on an electron cloud, since the light given off can do work on *other* electron clouds.

Here is a representation of the emission spectrum of hydrogen atoms in the visible wavelength range.



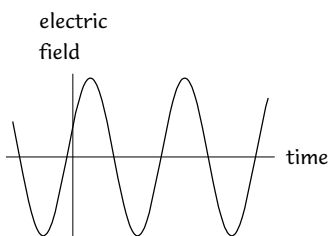
Emission spectrum of gaseous hydrogen atoms at high temperature. Wavelength increases from 380 nm on the left to 740 nm on the right, and so frequency increases to the left.

A nice display of the emission spectrum of the Sun and the atomic absorption spectra of hydrogen, helium, mercury and uranium is at <http://quantum.bu.edu/images/atomSpectra.jpeg>.

Spectra allows us determine resonant frequencies. Everything we know about the interior structure of atoms and molecules traces to understanding their resonant frequencies. Our plan, then, is to first learn how to characterize light, and then to learn how to account for the resonant frequencies of electron clouds.

## ■ Properties of waves

Light alternately tugs electric charges one way and then the opposite way. The tugging is due the effect of the electric field of the light on electric charges. If we plot the strength and direction of the electric field tugging on the electron cloud, it looks like a wave.



Electric field tugging on an electron cloud. The tugs are perpendicular to the direction of the light beam. The peaks corresponds to greatest tug in one direction, and the troughs correspond to greatest tug in the opposite direction. The axis of the tugs is known as the *polarization* of the light.

In addition to the oscillation of the electric field, there is a matching oscillation of a magnetic field. Their oscillation is perpendicular to one another and also to the direction of travel of the light. The magnetic field has a negligible effect on atoms compared to the electric field and this is why we focus our attention on the oscillations of the electrical component of light.

Because of the simultaneous presence of oscillating electric and magnetic fields, light is also called *electromagnetic radiation*. Sometimes, too, the term light is used to mean just

the visible range of light. We will use light to mean electromagnetic radiation, independently of whether it is visible to our eyes.

To see how to characterize the oscillations of the electric field, we need to describe how waves are represented mathematically. A *wave* is the oscillatory variation of *some property* in time and in space. If we focus on a particular point in space, the value of the changing property—the numerical value (amplitude) of the wave—is seen to oscillate about some average value. If instead we focus on a particular part of the wave, such as one of its crests—a point of maximum amplitude—the wave is seen to move through space.

Examples of waves are

Wave Type	Change of ...	With respect to ...
water	height of water	calm water
sound	density of air	ambient pressure
light	electric (and magnetic) fields	zero fields
chemical	concentration	reference concentration

### Representing wave properties mathematically

Waves can be expressed mathematically in terms of sine or cosine curves. The value of the curve at a particular time and location represents the amplitude of the wave at that time and location. For example, to represent a sound wave with a sine curve, the value of the sine curve at a given time at each point in space corresponds to the pressure, relative to ambient pressure, at that time and location.

What does the amplitude (value) of a sine curve represent for a water wave? Answer: The height of the water relative to calm water.

What does a sine curve represent for the electric field part of a light (electromagnetic) wave? Answer: The size and direction of the electric field.

The most striking feature of waves is that they move through space (standing waves, which oscillate in place, are a special case). To keep things as simple as possible, let's assume we have a wave only along one direction, which we call  $x$ . If we look at a wave at a particular instant in time, it is a sine curve, say. If we look at it a moment  $\Delta t$  later in time, it is still a sine curve, but the whole curve has shifted by an amount  $\Delta x$ .

It is probably not immediately obvious, but the way such a sine wave changes with position and time can be expressed as

$$\psi(x, t) = a \sin[2\pi(x/\lambda - t/\tau)].$$

The numerical value of this expression—the value of the changing property, such as the height of the water in a water wave, or the electric field in light—is called the *amplitude* (often represented by the Greek letter  $\psi$ , pronounced "psi"). To understand this expression it is helpful to analyze separately how it changes as position and time change.

Let's consider first how a wave looks for one particular time; this is like studying a photograph of the wave. To fix time, let's set the time  $t$  equal to zero. The expression for the wave when  $t = 0$  is

$$\psi(x, 0) = a \sin(2\pi x/\lambda).$$

As we have seen, the value of a sine function repeats every time its argument (which is called its *phase*) changes by  $2\pi$ . The phase changes because  $x$  changes. Let's see how much the phase changes if  $x$  changes by the amount  $\lambda$ ,

$$2\pi(x + \lambda)/\lambda - 2\pi x/\lambda = 2\pi.$$

We see that the phase changes by  $2\pi$  when the position changes by the amount  $\lambda$ . For this reason, then length  $\lambda$  is called the *wavelength* (represented by the Greek letter  $\lambda$ , "lambda"). In a graph of the wave, the wavelength is the distance between two adjacent similar features of the wave, such as two successive crests.

Make a sketch, on the same set of axes, of the wave  $\psi_1 = \sin(2\pi x/3)$  and  $\psi_2 = \sin(2\pi x/6)$ . What is the wavelength of each wave? Does your sketch make sense in terms of the relative wavelength of the two waves?

Now that we know how to identify the length of a wave, let's see the effect of changing time. The way to understand the effect of time is to see how the wave changes at a fixed point in space. We can do this by setting the position  $x$  equal to zero. The expression for the wave when  $x = 0$  is

$$\psi(0, t) = a \sin(-2\pi t/\tau).$$

Now, at  $x = 0$ , let's see how much the phase changes when time changes by the amount  $\tau$ , that is, from  $t$  to  $t + \tau$ ,

$$-2\pi(t + \tau)/\tau - (-2\pi t/\tau) = -2\pi t/\tau - 2\pi + 2\pi t/\tau = -2\pi.$$

This expression shows that when time changes by  $\tau$ , the phase changes by  $-2\pi$ . That is, one wave cycle moves past a fixed point in time  $\tau$ , the *period* of the wave. (We'll see below that the significance of the phase changing by a negative amount is that crests of the wave move toward positive  $x$ .) The number of cycles (of spatial length  $\lambda$ ) which pass by a fixed point per second is the reciprocal of the time required for one cycle to pass by. This is called the *frequency*,

$$\nu = 1/\tau,$$

of the wave (represented by the Greek letter  $\nu$ , "nu"—not to be confused with the Latin letter  $v$ , "vee"). The frequency is commonly measured in *Hertz* (abbreviated Hz), which are inverse seconds,  $s^{-1}$ .

### The speed of a wave: phase velocity

Now that we understand the separate effects of changing location and time, we can see the combined effect of changing both  $x$  and  $t$ . In this way we can study the movement of the wave.

The way we follow the motion of a wave is to identify a unique point on the wave, say a particular crest, and then to see how far it moves in a certain time. Mathematically, choosing a point on the wave means choosing a particular numerical value for the phase,

$$2\pi(x/\lambda - \nu t).$$

This is so because the value of the phase determines the value of the amplitude of the wave at a particular place  $x$  and time  $t$ .

Then, the key idea is that we can analyze the motion of a wave by realizing that the phase of our chosen point on the wave *must remain constant*, for otherwise amplitude of the wave would change. This means that if a point on the wave at position  $x_1$  at time  $t_1$  moves to the position  $x_2$  at time  $t_2$ , then the corresponding phases are equal

$$2\pi(x_1/\lambda - \nu t_1) = 2\pi(x_2/\lambda - \nu t_2).$$

This important equality is called the *stationary phase condition*. We can rearrange the stationary phase condition into the relation

$$(x_2 - x_1)/(t_2 - t_1) = v\lambda.$$

The left hand side of this equality is the ratio of the distance moved,

$$\Delta x = x_2 - x_1,$$

divided by the time elapsed,

$$\Delta t = t_2 - t_1.$$

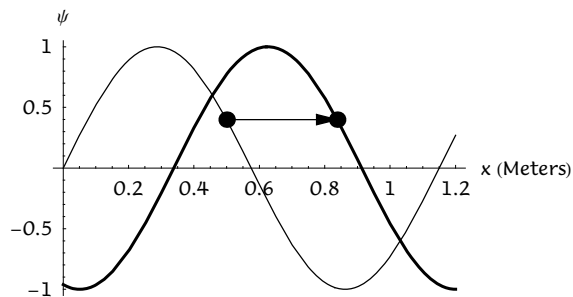
This is the *speed that the wave moves*. This speed,

$$u_{\text{phase}} = \Delta x / \Delta t = v\lambda,$$

is called the *phase velocity* of the wave.

Write down an expression for a wave that travels to the left, towards smaller values of  $x$ , as time increases.

Here is an illustration of these ideas. The figure shows the movement of a sine wave that takes place in 0.025 s.



Movement of a wave. The thin curve is the wave at an initial time,  $t_1$ . The thick curve is at a later time,  $t_2$ . The length of the arrow is the distance,  $\Delta x = x_2 - x_1$ , the wave has moved in the elapsed time,  $\Delta t = t_2 - t_1 = 0.025$  s. The point chosen to track the movement of the wave is arbitrary. The value of the phase,  $2\pi(x_1/\lambda - \nu t_1)$ , at the starting point is equal to the value of the phase,  $2\pi(x_2/\lambda - \nu t_2)$ , at the ending point. The equality of these phases—the stationary phase condition—determines the phase velocity of the wave,  $\Delta x / \Delta t = (x_2 - x_1) / (t_2 - t_1) = v\lambda$ .

Determine from the information in the figure the values of the distance traveled, wavelength, phase velocity, and frequency of this wave. You may want to start by using a ruler to measure the distance traveled. The answers are 0.34 m, 1.2 m, 12 m/s, and 10 Hz.

### Calculations with waves

Here is an example using sound waves, Oxtoby and Nachtrieb, 2e, problem 13.7:

The speed of sound in dry air at 20°C is 340 m/s and the frequency of the sound from the middle C note on a piano is 262 Hz. Calculate the wavelength of the sound and the time it will take to travel 30 m across a concert hall. Answer:  $\lambda = 1.3$  m,  $\Delta t = 0.088$  s.

Phase velocity is a characteristic of each kind of wave. We are going to be concerned especially with light waves. The velocity of light is a *universal constant* of Nature and is given the special symbol  $c$ . For light traveling in a vacuum, its speed (phase velocity) by international agreement is exactly 299792458 m/s. (Note that assigning a value to the speed of light, together with a defined value for the meter, amounts to a choice of values for the second as the unit of time.)

This means that for *electromagnetic radiation of any frequency* the product of its frequency and wavelength is always equal to  $v_{\text{light}}$ . So, the next time someone asks you what's "nu", tell them "c over lambda!"

A nice example of this relation is to calculate the wavelength,  $\lambda$ , of the radio waves from the Boston University FM radio station WBUR, which transmits on a frequency of 90.9 MHz (1 Megahertz =  $10^6$  Hz). Answer: 3.33 m = 10.9 ft.

Compare this value to red light, which has a wavelength of 700 nm =  $7 \times 10^{-7}$  m—ten million times smaller. This means that the frequency of red light is about ten million times higher,  $\nu = 4 \times 10^{14}$  Hz.

Estimate the frequency of electromagnetic radiation with wavelength about the size of an atom. Answer:  $3 \times 10^{18}$  Hz.

This corresponds to X-ray region of the electromagnetic spectrum, and in fact X-rays necessary to "see" the locations of individual atoms.

### Visible wavelengths and the size of atoms

Our eyes are sensitive to the visible range of light, corresponding to wavelengths from 380 nm (deep violet) to 740 nm (dark red), but even the shortest of these wavelengths is much, much larger than atoms, which are about  $1 \text{ \AA} = 10^{-8}$  cm = 0.1 nm across.

This means that at a given moment in time, an atom bathed in light experiences an essentially *constant* electric field. The strength and direction of the electric field—and so the strength and direction of the tugs it exerts on the electron cloud of the atom—fluctuates as time passes, but always such that at a given moment every part of the charge cloud experiences the *same* tug.

For this reason, while it is common to focus on the wave representation of light, from the atomic vantage point, light is experienced as a tugging that changes with time. The experience of an atom in light is analogous to that of a small cork floating on the surface of a very long ocean wave. If we focus on the cork, it just goes up and down, just as the electron cloud in an atom is tugged first one way and then the other, in a rhythmic oscillation.

### Angular frequency and angular wavenumber

We have seen that the motion of a wave is determined by seeing how position and time need to change so that the phase

$$\text{phase} = 2\pi(x/\lambda - \nu t)$$

remains constant—the stationary phase condition, and that the result is that a wave with this phase expression moves with phase velocity  $u_{\text{phase}} = \nu \lambda$ . Another way to characterize the frequency and

wavelength of a wave is in terms of *angular frequency*  $\omega = 2\pi\nu$  and angular wavenumber  $k = 2\pi/\lambda$ . The reason these definitions are made is thereby the expression for the phase becomes

$$\text{phase} = kx - \omega t.$$

Angular wavenumber has the units radian/meter, the increase in phase as a result of a change in position by one meter; angular frequency has units radian/second, the increase in phase as a result of a change in time by one second.

*Recall that a radian is the angle whose arc length on circular path is equal to the radius of the circle. A complete circle corresponds to an angle of  $2\pi$  radians (a little less than 8) and so the circumference of a circle of radius  $r$  is  $2\pi r$ . By comparison, the "circumference" of the square that just encloses a circle of radius  $r$  is  $8r$ , since the "radius" of the square is half its "diameter", the length of one side.*

The phase velocity in terms of these new quantities is  $u_{\text{phase}} = \omega/k$ .

## ■ Interaction of light with matter: resonant "tugs"

As we have described, the way light interacts with atoms is by exerting tugs on the positively charged nuclei and the negatively charged electrons. The tugs follow the rhythm of the oscillations in the electric field of the light. High frequency light tugs rapidly, low frequency light tugs slowly. Now, from the point of view of the charges in the atom, not all tugs are the same. In fact, most tugs have little effect on the electrons and nuclei. Rather, only if the tugs are at just the right frequency will the charges be able to follow them.

Here are what frequencies and wavelengths correspond to the different regions of the spectrum.

Light Region	Typical $\nu$ (Hz)	Typical $\lambda$ (m)	Typical $\lambda$ (nm)
$\gamma$ -rays	$1. \times 10^{19}$	$3. \times 10^{-11}$	0.03
X-rays	$1. \times 10^{17}$	$3. \times 10^{-9}$	3.
UV	$1. \times 10^{15}$	$3. \times 10^{-7}$	300.
Violet	$7.5 \times 10^{14}$	$4. \times 10^{-7}$	400.
Blue	$6.7 \times 10^{14}$	$4.5 \times 10^{-7}$	450.
Green	$6. \times 10^{14}$	$5. \times 10^{-7}$	500.
Yellow	$5. \times 10^{14}$	$6. \times 10^{-7}$	600.
Red	$4.3 \times 10^{14}$	$7. \times 10^{-7}$	700.
IR	$1. \times 10^{14}$	$3. \times 10^{-6}$	3000.
Microwave	$1. \times 10^{10}$	0.03	$3. \times 10^7$
FM Radio	$1. \times 10^8$	3.	$3. \times 10^9$
Short Wave	$1. \times 10^7$	30.	$3. \times 10^{10}$
AM Radio	500000.	600.	$6. \times 10^{11}$
Long radio waves	10000.	30000.	$3. \times 10^{13}$

Frequencies and wavelengths correspond to the different regions of the electromagnetic spectrum.

Roughly speaking, the charges can follow tugs only if their frequency is near a *resonant frequency*,

$$\nu \sim \frac{1}{2\pi} \sqrt{\frac{k}{m}},$$

where  $m$  is the mass of the charged particle experiencing the tug and the *force constant*  $k$  is a measure of how tightly the charged particle is held in the atom. This relation is called the *resonance condition*. Essentially, heavy particles (nuclei) oscillate at lower frequencies than light particles



(electrons), and loosely held particles (electrons far from nuclei) oscillate at lower frequencies than tightly held particles (electrons close to nuclei).

One immediate insight we can draw from the harmonic frequency relation is that while electrons and nuclei experience comparable electrical forces, and so have similar force constants, because nuclei are so much heavier, their resonant frequencies are much lower than those of electrons.

A proton is about 2000 times heavier than an electron. How much would this mass difference alter resonant frequencies? Answer: Frequencies due to motion of protons would be about 40 times lower than those of electrons.

We'll learn that nuclei are what is being tugged in microwave ovens, at frequencies on the order of  $10^{12}$  Hz, whereas electrons are what are being tugged in the photoreceptor molecules of our eyes, at frequencies on the order of  $10^{14}$  Hz.

## ■ Energy conservation in interaction between light and matter

A key concept in the interaction of electromagnetic radiation and matter is *energy conservation*: Energy is exchanged between the radiation and matter in such a way that the net change of energy is zero.

$$\Delta E_{\text{light}} + \Delta E_{\text{matter}} = 0 \text{ or, equivalently, } \Delta E_{\text{matter}} = -\Delta E_{\text{light}}.$$

Electrons and nuclei have mass, and so if light is tugging on them, the tugging takes energy. This means energy in the light is reduced by the amount transferred to the matter. We call this reduction of energy of the light *absorption*. When light (energy) is absorbed by matter, the energy conservation expression gives

$$\Delta E_{\text{light}} < 0, \Delta E_{\text{matter}} = -\Delta E_{\text{light}} > 0 \text{ (light absorption).}$$

The reverse process is also possible: motion of charged particles in matter can give up their energy by creating oscillating electric fields. (This is analogous to the energy required to light a bulb by turning the crank of a hand generator.) We call this reduction (expenditure) of energy in matter light emission. When light (energy) is emitted by matter, the energy conservation expression gives

$$\Delta E_{\text{light}} > 0, \Delta E_{\text{matter}} = -\Delta E_{\text{light}} < 0 \text{ (light emission).}$$

In either case—light absorption or emission—the total energy change is zero,

## ■ Amount of energy exchanged between light and matter

So, a key feature of light-matter interaction is the *exchange of energy*. A remarkable simplifying feature of this interaction is that, assuming the resonance condition between the frequency of light and matter is met, then:

The amount of energy that can be exchanged is *determined solely by the frequency of the light*. That is, it turns out that if we know the frequency of the light—of the oscillations in its electric (and magnetic) field—then we can determine the amount of energy that can be exchanged with matter in resonance with the light at that frequency.

Here is one way to determine this energy. Light emitting diodes (LED's) are electronic devices that emit light of a particular color when a precise voltage, known as the *threshold voltage*, is applied. Now, voltage is energy per unit charge, and 1 Volt = 1 Joule/Coulomb. Since the colors are due to electrons oscillating in the electric field of the light, it makes sense to use the electron charge to convert threshold voltage to an energy. We can do this by multiplying the voltage by the electron charge,  $e = 1.60218 \times 10^{-19}$  Coulomb. The resulting energy is known as an electron volt, eV.

Show that an electron volt is  $1.60218 \times 10^{-19}$  Joule.

In this way we can interpret the threshold voltage as an energy.

Here are the colors of five common LED's, displayed as an emission spectrum.



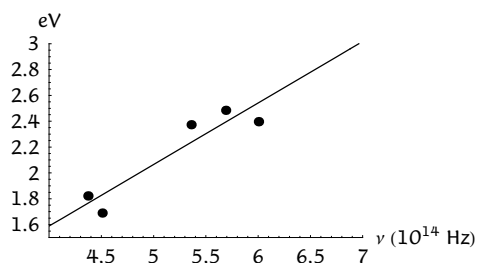
Colors of five different light emitting diodes (LED's). The horizontal axis is wavelength, increasing to the right.

Slight variations in manufacturing result in the color of a particular LED differing slightly from that of another. Typical manufacturing tolerances are  $\pm 15$  nm. Error is also introduced in the measurement of the wavelengths. Finally, manufacturing differences and measurement error also affect the value of the threshold voltage. Let's assume a total error of 10% in the voltage determination.

Here is a table of representative wavelengths,  $\lambda$ , and corresponding frequencies,  $\nu = c/\lambda$ , for the five LED's, together with the minimum energy (in eV) determined to cause them to emit their color, taking into account a 10% error in wavelength determination and a 10% error in threshold voltage determination.

$\lambda$ (nm)	$\nu$ (Hz)	voltage (eV)
665	$4.51 \times 10^{14}$	1.69
635	$4.37 \times 10^{14}$	1.82
590	$5.36 \times 10^{14}$	2.37
560	$5.69 \times 10^{14}$	2.48
480	$6. \times 10^{14}$	2.4

Here is a plot of the threshold voltage versus frequency, together with a straight line fit to the data points.



Threshold energy, in eV, versus frequency, in  $10^{14}$  Hz, required to cause different LED's to emit light. Separate 10% errors are assumed in the determination of LED wavelength and in the determination of the threshold energy.

The plot shows that threshold energy is proportional to frequency, energy  $\propto \nu$ . The constant of proportionality is the slope of the line fitted to the measured points. It has the units energy/frequency, or J s. This proportionality constant is known as Planck's constant and written as  $h$ . Its value for the fit to the data shown is  $7.81203 \times 10^{-34}$  J s.

Confirm this value as follows. First, use a ruler to measure the slope of the line in the figure, in units eV/[ $\nu/(10^{14}$  Hz)]. Then, convert eV to Joule and use the fact that Hz = s<sup>-1</sup>.

The currently accepted value is  $h = 6.62606876 \times 10^{-34}$  J s. We could confirm this value, for example, by averaging results of repeated, more careful measurement using LED's manufactured to higher tolerance.

Calculate the percentage difference in the measured value from the actual value of Planck's constant. That is, evaluate  $[(h_{\text{measured}} - h)/h] \times 100\%$ . Typical percentage differences are 10%.

What we have succeeded in doing is to establish the *equivalence between the frequency and energy change of light*, namely

$$\Delta E_{\text{light}} = h \nu = h c / \lambda.$$

This relation is known as the *Einstein energy-frequency relation*, because Einstein was the first to propose the equivalence between the frequency of light and the amount of energy that light of that frequency can exchange with matter. The relation allows us to track energy flow between light and matter.

The energy unit  $h \nu = h c / \lambda$  is called a *quantum of light energy*, or, more briefly, a *photon*. In terms of the energy of the photon, we can write the light-matter energy balance expressions as

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

These expressions show that when light is absorbed by matter, a photon of light energy is removed from the light, reducing the energy of light by the amount  $\Delta E_{\text{light}} = -E_{\text{photon}} = -h \nu$ , and that when light is emitted by matter, a photon of light energy is added to the light, increasing the light energy by the amount  $\Delta E_{\text{light}} = E_{\text{photon}} = h \nu$ .

A fluorescent bulb emits light of several different wavelengths from each major region of the visible spectrum so that to our eyes its light appears white. Assume that a 45 watt fluorescent bulb emits equal amounts of red, green and blue light. Assume that the blue wavelength is 450 nm. How many energy units (photons) of blue light are emitted each second by the matter composing the fluorescent bulb. Recall that 1 watt = 1 J/s, and assume the bulb operates at 70% efficiency. Answer:  $2 \times 10^{19}$ /s.

The reason the number of quanta (photons) is so large is because a quantum of light energy—one photon—is a very small unit of energy.

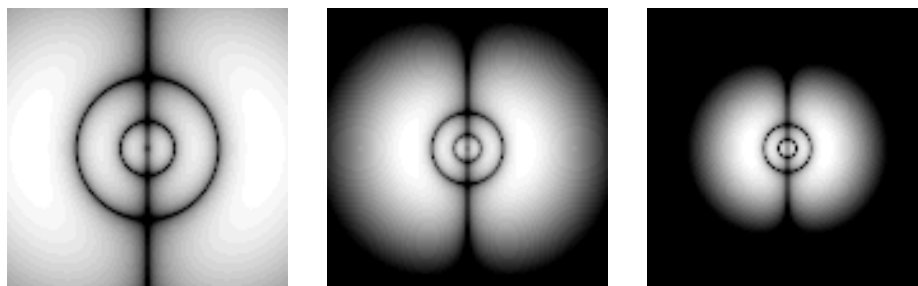
## ■ Quantum picture atoms: like a voice box

The quantum picture of electrons in atoms is a little like how we make musical tones from our voice box. The voice box consists of vocal chords. Each musical tone is the result of vocal chords vibrating in a particular way. Each person's vocal system is different from another, as we may realize listening to ourselves in the shower attempt, for example, to mimic the sound of an operatic tenor such as Luciano Pavarotti.

## Electron clouds are made from electron waves

The atom is like a voice box. The role of vocal chords is played by what we call *quantum waves*. Just as a vocal chord by itself does not make a musical tone, a quantum wave *is not an electron*. Rather, an electron is the result of *combining quantum waves in a special way*, just as the sounds we make are the result of our vocal chords moving in a particular way.

The electron that results from the quantum waves has the form of a *cloud of charge*, centered at the nucleus and distributed in space according to the details of the quantum waves that produce the cloud. This charge cloud is called the *probability density*. Where the cloud is dense, there is a concentration of electron charge, and where the cloud is sparse, there is little electron charge. Here is a cross section of such a charge cloud of hydrogen atom.



Cross section through the nucleus of a hydrogen atom electron cloud (the  $4p_x$  probability density), in the  $xy$  plane. The nucleus is at the center. From left to right, the width and height are 3, 6, and 9 nm. The brightness of the display is proportional to how dense the electron cloud is. The more dense the cloud, the greater the fraction of the that is electron there.

Just as each person's vocal chords are unique to them, each kind of atom (hydrogen, sodium, xenon, etc.) has its own set of quantum waves. As a result, just as each person is able to make their own characteristic sounds, electron clouds in each different kind of atom have shapes unique to the particular type of atom.

Remember, electron waves are *not physical objects*. In particular, *they are not the electrons*. Electron waves are the *components from which electron clouds are built*.

## Where do electron waves comes from?

A *very* good question is “Where do the electron waves of a given atom come from?”

Electron waves are analogous to the  $x$ ,  $y$ , and  $z$  axes that we use to position an object in three dimensions. Just as the coordinate axes are a property of three-dimensional space, the electron waves of an atom (in terms of which electrons clouds can be expressed) play the role of the coordinate axes in terms of which objects in three dimensions can be expressed. Since each atom has many different electron waves, we say that these waves describe a space (called a *Hilbert space*) with many dimensions—many more dimensions than the three dimensions of physical space.

Keeping in mind the difference in number of dimensions, there is a close analogy between the coordinate axes of physical space and the electron waves of the space of electron clouds of atoms.

So, if you are asked, “Where do the electron waves of a given atom come from?”, you can reply “The same place that coordinate axes come from,” in the sense that they play analogous roles. Just as Nature confers properties on physical space, Nature confers analogous properties on the space in which electron waves live.

## Electron clouds sometimes move, sometimes do not

Electron clouds are built from electron waves. Depending on the composition of the waves, the electron cloud may move or not.

If the electron cloud is made from just a single electron wave, the electron cloud *does not move at all*. That is, if the electron cloud is made of only a single quantum wave, then it is like a vocal chord that does not vibrate and so that makes no sound at all.

If instead the electron cloud is made from two (or more) different electron waves, the electron cloud *jiggles* rhythmically. The frequency of the jiggling is equal to the *difference* of the frequencies of the waves that make up the cloud.

## All electron waves change with time

The reason that electron waves can produce moving electron clouds is that the electron waves change with time, but at different rates. Because each wave changes at a different rate, when different waves combine into an electron cloud, they reinforce each other in different places at different times. The result is an electron cloud that is large at different places at different times. The electron cloud changes its shape in a regular way, another way of saying it jiggles.

Please keep in mind that because electron waves are not physical objects, their motion is in a mathematical sense rather than a physical sense. Motion in each electron wave is characterized by the electron wave frequency: An electron wave with frequency  $10^{14}$  Hz returns to the same form every  $10^{-14}$  s.

To distinguish this mathematical frequency from the physical frequency of electron clouds, we will use the Greek letter  $\phi$  (phi) for the *mathematical frequency* of the electron wave, and the Greek letter  $\nu$  (nu) for the *physical frequency* of the electron cloud.

For an electron cloud constructed from only two electron waves,  $\phi_1$  and  $\phi_2$ , the physical frequency,  $\nu_{\text{cloud}}$ , of the cloud is given by

$$\nu_{\text{cloud}} = |\phi_2 - \phi_1|.$$

The magnitude signs are necessary because mathematical frequencies,  $\phi$ , can be negative or positive, but physical frequencies are always positive. For example, the frequencies,  $\phi$ , of the first few (lowest energy) electron waves of hydrogen atom are

wave	$\phi_{\text{wave}}$ (Hz)
6	$-9.133 \times 10^{13}$
5	$-1.315 \times 10^{14}$
4	$-2.055 \times 10^{14}$
3	$-3.653 \times 10^{14}$
2	$-8.22 \times 10^{14}$
1	$-3.288 \times 10^{15}$

Frequency,  $\phi$ , of the first few (lowest energy) electron waves of hydrogen atom.

Note that these frequencies are negative, and that they become less so as energy increases. Here are frequencies of electron clouds made by combining pairs of these electron waves.

combined waves	$\nu_{\text{cloud}}$ (Hz)
2, 1	$2.466 \times 10^{15}$
3, 1	$2.923 \times 10^{15}$
4, 3	$1.598 \times 10^{14}$
6, 2	$7.307 \times 10^{14}$

Frequency,  $\nu_{\text{cloud}}$ , of electron clouds made by combining pairs of hydrogen atom electron waves

Calculate the frequency of motion of the electron clouds made by combining the second electron wave with the third, fourth and fifth electron wave. Answer:  $4.567 \times 10^{14}$  Hz,  $6.165 \times 10^{14}$  Hz,  $6.905 \times 10^{14}$  Hz.

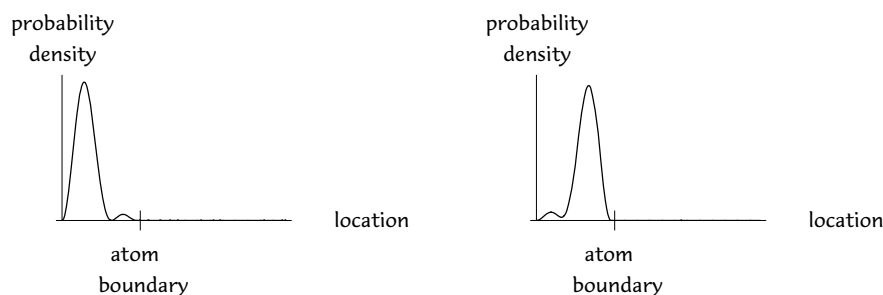
Electron cloud frequencies are always positive, as they must be since they correspond to the physical motion of the electron cloud. Note that none of these frequencies is the same as any of the electron wave frequencies. This is because the physical frequencies are always *differences* of electron wave frequencies.

### Attached and detached electron waves

Electron waves, the components of electron clouds, come in two flavors. *Attached* electron waves extend only a small distance from the nucleus; the size of electron clouds made from these waves determines the size of the atom.

The frequencies of *attached* waves have *discrete values*, say  $\phi_1, \phi_2, \phi_3$ , etc.; that is, only particular frequencies occur and intermediate frequencies, say  $\phi_1 + .1(\phi_2 - \phi_1)$ , cannot occur. This occurrence of only certain frequencies is called *quantization*.

Here are snapshots at two different times of the electron cloud that results from mixing together two attached electron waves that have frequencies  $\phi_1$  and  $\phi_2$ . The electron cloud oscillates back and forth (that is, the electron cloud remains attached to the atom), with frequency  $\nu_{\text{cloud}} = \phi_2 - \phi_1$ ;



Snapshots of an electron cloud formed by mixing attached electron waves of different frequencies,  $\phi_1$  and  $\phi_2$ . The left frame is at the start of the oscillation; the right frame is one-half cycle of oscillation later. The vertical axis is the probability per unit volume that the electron is at the location shown on the horizontal axis. The atom extends from the origin to the location marked "atom boundary".

An animation of the oscillation of the electron cloud is at

<http://quantum.bu.edu/notes/GeneralChemistry/LightMatterInteraction/eAttached.gif>

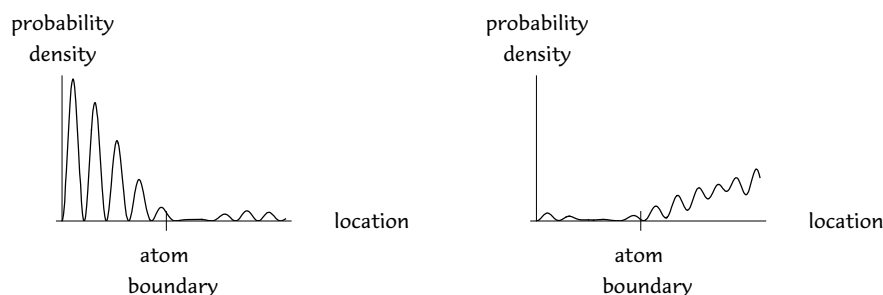
*Detached* electron waves are not confined near the nucleus, but extend far beyond the region of the attached electron waves; electron clouds made from these waves extend far beyond the atom (in principle to infinity, but such waves encounter waves on other atoms long before infinity).

The lowest possible frequency of a detached electron wave is known as the *threshold frequency*,  $\phi_{\text{threshold}}$ . Below the threshold frequency there can only be attached electron waves (with quantized

frequencies). At and above  $\phi_{\text{threshold}}$ , there is a detached electron wave at all frequencies; we say that detached electron waves are *not quantized*.

For example, the threshold frequency of the hydrogen atom is  $\phi_{\text{threshold}} = 0$  Hz. Attached electron waves of hydrogen atom have negative frequencies,  $\phi_{\text{attached}} < \phi_{\text{threshold}} = 0$ , as we have seen above, and detached electron waves of hydrogen atom have positive frequencies,  $\phi_{\text{detached}} \geq \phi_{\text{threshold}} = 0$ .

Here are snapshots at two different times of the electron cloud that results from mixing together an attached electron wave and a detached electron wave. The electron cloud moves away from its initial position; that is, the electron cloud becomes detached from the atom.



Snapshots of an electron cloud formed by an attached electron wave with a detached electron wave. The left frame is at the start of the motion; the right frame is at a later time. The vertical axis is the probability per unit volume that the electron is at the location shown on the horizontal axis. The atom extends from the origin to the location marked "atom boundary". The electron cloud moves off to the right, corresponding to the atom being ionized.

An animation of the oscillation of the electron cloud is at

<http://quantum.bu.edu/notes/GeneralChemistry/LightMatterInteraction/eDetached.gif>

What would the snapshot look like at a still later time than that of the right-hand snapshot above? Does your answer make sense?

Calculate the frequency of motion of the electron clouds made by combing the second, third, and fourth attached electron wave of hydrogen with the detached electron wave of frequency  $\phi_{\text{detached}} = 2.418 \times 10^{14}$  Hz. Answer:  $6.071 \times 10^{14}$  Hz,  $4.473 \times 10^{14}$  Hz,  $3.733 \times 10^{14}$  Hz.

## ■ Light causes electrons to jiggle; jiggling electrons produce light

Light can be absorbed by atoms in a process called *absorption*, and light can be produced by atoms in a process called *emission*.

- Light interacts with an atom by its electric field causing the electron cloud to oscillate from one side of the nucleus to the other. This means that for there to be an interaction, the electron cloud must move. Light (energy) is *absorbed* when some of the energy stored in its electric field transferred to kinetic and potential energy of the electron cloud.
- Light is emitted when an oscillating electron cloud has been created by some other means, and then its changing position exerts fluctuating forces on electrons in other atoms, causing them to oscillate. Thereby energy is transferred from the first electron cloud to the second.

Here are some details.

## Isolated atoms

Since electron clouds made from just a single electron wave do not move, the electron charge is exactly cancelled by the nuclear charge; the atom has no fluctuating dipole moment and so nothing for the electric field of the light to grab hold of. This means when an electron cloud is composed of a single electron wave, there is no way for the electron cloud to cause another electron cloud to jiggle. It is for this reason that electron clouds made from single electron waves *do not absorb light energy and do not exert any forces on other electron clouds*.

## Neighboring atoms

But we know that when atoms come close together they do exert forces on one another. The weakest forces are the *dispersion forces* that account for gaseous atoms coalescing into liquids. The fluctuating dipole moments responsible for dispersion forces arise because each atom causes electron waves in the other atom to combine together, and so causes a fluctuating electron cloud in the other atom. If atoms come very close together, electron clouds can be made from combinations of electrons waves *from both atoms*, and the resulting electron cloud can hold the atom together in a *covalent bond*.

## Light absorption

Of course, atoms also interact with light. When the oscillating electric field of light encounters an atom, *its causes electron waves in the atom to mix together*, and so it causes the *formation of electron clouds that can jiggle*. When the electric field of the light is pointing up (say), the negatively charged electron cloud is tugged up. A half cycle later the electric field of the light is pointing down, and so the negatively charged electron cloud is tugged down.

Usually, the frequency of oscillation of the light will not match well with the possible jiggle frequencies (possible electron wave frequency differences). It is as if the light is a dance partner that wants to dance to one kind of music while the electron cloud is a dance partner that prefers a different kind. The light moves on, and the atom settles back down into a stationary electron cloud. We say the atom is *transparent* to light of that frequency.

When, however, the frequency of the light electric field oscillation exactly matches the frequency of the electron cloud jiggling, the tugging on the electron cloud will be exactly synchronized with the oscillation of the light's electric field. This synchronization is called *resonance*. When there is resonance, some of the energy stored in the electric field of the light is converted into kinetic and potential energy of the moving electron cloud. We call this transfer of energy *absorption of light*.

A typical electron cloud jiggle frequency is  $\nu_{\text{cloud}} = 6 \times 10^{14}/\text{s}$ . What color light does this correspond to? Hint: Calculate the wavelength of light of this frequency.

A typical light intensity is  $10 \text{ W} = 10 \text{ J/s}$ . Calculate the energy loss of the light of frequency  $\nu_{\text{light}} = 6 \times 10^{14}/\text{s}$ , if it causes electron clouds on a trillion ( $10^{12}$ ) atoms to jiggle. The energy in each atom's electron cloud is  $h \nu_{\text{cloud}}$ . Answer:  $4 \times 10^{-7} \text{ J}$ .

Compared to the energy in the light, the amount of energy transferred to the electron clouds of the trillion atoms is tiny. This means that the light intensity, proportional to its energy, will be reduced negligibly when the atoms absorb the light energy.



## Light emission by a gas discharge tube

Moving electron clouds can be made in other ways. A neat example is a gas discharge tube, in which a beam of fast moving electrons passes through a gas of atoms. When an electron from the beam passes near an atom, its electrical repulsion causes the atom electron cloud to be changed into one with a mixture of electron waves. In this way the electron clouds of the atoms of the gas begin jiggling. This jiggling, by electrical repulsion, causes the *emission* of light which in turn causes other electron clouds other electron clouds, such as the ones in the pigment molecules of our eyes, to jiggle in resonance. We call this transfer of energy *emission of light* (from the jiggling electron clouds of the gas atoms to other electron clouds, says, in our eyes). That is, the atoms in the gas give of light.

### ■ Frequency matching (resonance) and energy balance

As we have described, just as different people have different sounding vocal chords, each type of atom has its own set of electron waves, consisting of attached waves with quantized frequencies,  $\phi_1$ ,  $\phi_2$ , etc., and detached waves with continuous frequencies starting at the threshold frequency,  $\phi_{\text{threshold}}$ .

We have described that light interacts with matter by mixing electron waves together, the resulting electron cloud (probability density) oscillates with frequency  $\nu_{\text{cloud}} = |\phi_j - \phi_k|$ , and this frequency matches the oscillation frequency of the electric field of the light,  $\nu_{\text{light}} = \nu_{\text{cloud}}$ .

Light can match the frequency of electron clouds composed of two attached electron waves. The set of these matching frequencies, for example,

$$\nu_{\text{light},a} = \nu_{\text{cloud}} = \phi_2 - \phi_1, \nu_{\text{light},b} = \nu_{\text{cloud}} = \phi_3 - \phi_1, \nu_{\text{light},c} = \nu_{\text{cloud}} = \phi_4 - \phi_1, \text{ etc.}$$

are the frequencies of the lines seen in the absorption spectrum of the atom.

Light can also match the frequency of electron clouds composed of an attached electron wave and a detached electron wave. The difference between the lowest frequency,  $\phi_1$ , attached electron wave and the electron wave threshold frequency,  $\phi_{\text{threshold}}$ , above which there are only detached electron waves, is known as the ionization frequency,

$$\nu_{\text{ionization}} = |\phi_{\text{threshold}} - \phi_1|, \text{ photoionization.}$$

For the hydrogen atom, the threshold frequency is  $\phi_{\text{threshold}} = 0$  Hz and the frequency of the lowest energy attached electron wave is  $-3.288 \times 10^{15}$  Hz. Calculate the ionization frequency of hydrogen atoms. Answer:  $+3.288 \times 10^{15}$  Hz.

The reason for this name is that when an attached electron wave and a detached electron wave combine, the resulting electron cloud escapes from the atom—the atom is ionized. The corresponding ionization energy is

$$\text{IE} = h |\phi_{\text{threshold}} - \phi_1|, \text{ photoionization}$$

The ionization frequency of hydrogen atoms is  $3.288 \times 10^{15}$  Hz. Calculate the ionization energy, in Joules. Answer:  $2.179 \times 10^{-18}$  J.

The atom will interact with light of all frequencies higher than  $\nu_{\text{ionization}}$ . This is because there is a detached electron wave for every electron wave frequency,  $\phi_{\text{detached}}$ , above  $\phi_{\text{threshold}}$ . Since

$$\nu_{\text{light}} = |\phi_{\text{detached}} - \phi_1| = |\phi_{\text{detached}} - \phi_{\text{threshold}}| + |\phi_{\text{threshold}} - \phi_1| = \text{KE}/h + \text{IE}/h,$$

we can express the kinetic energy of the ejected electron cloud as

$$\text{KE} = h \nu_{\text{light}} - \text{IE}.$$

When light ejects an electron from an atom, the process is called *photoionization*.

The ionization frequency of hydrogen atoms is  $\nu_{\text{ionization}} = 3.288 \times 10^{15}$  Hz. Calculate the kinetic energy of an electron ionized from hydrogen atom by light of frequency  $\nu_{\text{light}} = 3.500 \times 10^{15}$  Hz. Answer:  $1.405 \times 10^{-19}$  J.

The kinetic energy of the electron,  $mu^2/2$ , is proportional to the square of the speed,  $u$ , of the electron. Calculate the speed of an electron ejected with kinetic energy  $1.405 \times 10^{-19}$  J. Answer: 555.4 km/s.

Repeat the calculation of the last problem for a proton of the same kinetic energy. Answer: 12.96 km/s. Does it make sense that the proton moves so much more slowly than the electron?

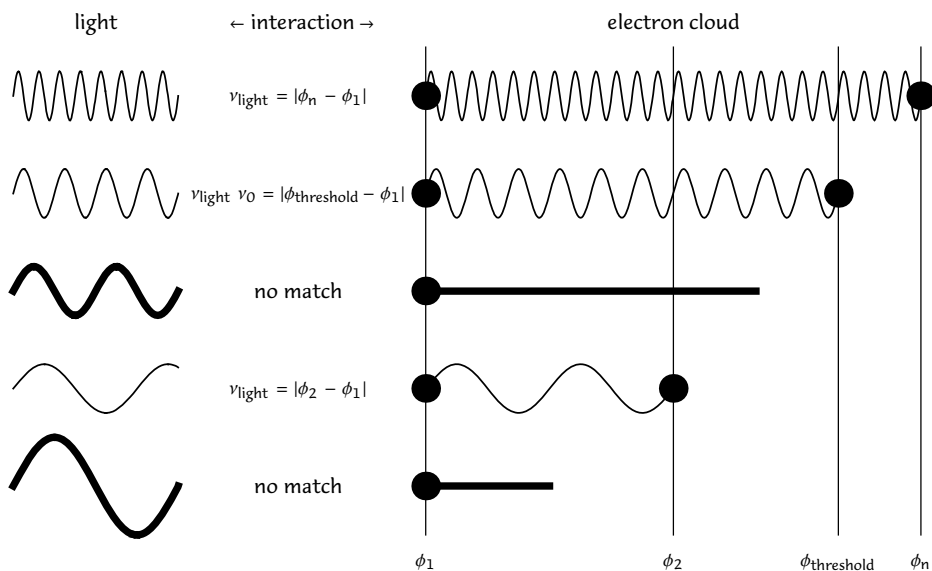
When light ejects an electron from a metal surface, the process is called the *photoelectric effect*. Because electrons are shared between atoms in a metal, the ionization frequency of a metal is different (and lower) than that of an isolated single atom of the metal. The ionization frequency is called the *characteristic frequency*,

$$\nu_0 = |\phi_{\text{threshold}} - \phi_1|, \text{ photoelectric effect}$$

and the corresponding *ionization energy*,  $h\nu_0$ , is called the *work function*.

$$\Phi = h\nu_0 = h|\phi_{\text{threshold}} - \phi_1|, \text{ photoelectric effect}$$

Here is diagram that illustrates interaction of light with matter through matching (resonance) of the light frequency with the frequency the electron cloud oscillation (the difference of the frequencies of its component electron waves).



Light (left side) interacts with matter (right side) when the light frequency matches a matter quantum wave frequency *difference*.

The left side of the figure represents light; five different light waves are shown, increasing in frequency,  $\nu_{\text{light}}$ , going from bottom to top.

The right side of the figure represents matter. The vertical lines mark the increasing frequency (and so the increasing energy) of the electron wave. From the threshold frequency,  $\phi_{\text{threshold}}$ , upwards every electron wave frequency is possible (since the electron is no longer attached); for clarity, in addition to  $\phi_{\text{threshold}}$ , only once such frequency, marked  $\phi_n$ , is shown.

Light can interact with matter only when the *difference* of the electron wave frequencies matches a light frequency. The combining electron wave frequencies are marked with black dots.

Mixing two attached quantum waves happens whenever the light frequency is the same as the difference of the frequencies of the attached electron waves. Here are snapshots at two different times of the electron cloud that results from mixing together attached electron waves with difference frequencies. The electron cloud oscillates back and forth, in resonance with the light frequency; that is, the electron cloud remains attached to the atom. The energy required to make the electron cloud move is supplied by the light, and so this motion corresponds to *absorption* lines seen in the spectra of atoms.

We have seen that an atomic hydrogen gas discharge consists of three different colored lines. Create a diagram like the one here to account for these lines, and to account for there being only these lines. Your diagram should *not* include any detached matter frequencies.

The heavy horizontal lines that do not terminate in a black dot, signify that there is no corresponding electron wave frequency there. The corresponding light waves are drawn in a heavy line; since these light waves have no matching electron wave frequency difference, matter does not interact with light at those frequencies. We say that matter is *transparent* to light of this frequency.

Air is mostly molecular nitrogen and molecular oxygen. Use these ideas to propose why air is clear.

Mixing an attached quantum wave with a detached quantum wave happens whenever the light frequency is at the characteristic frequency or higher. Here are snapshots at two different times of the electron cloud that results from mixing together an attached electron wave and a detached electron wave. The electron cloud moves away from its initial position; that is, the electron cloud becomes detached from the atom. This accounts for an electron being ejected in the photoelectric effect.

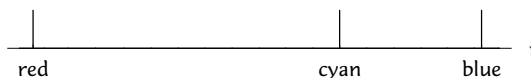
### Worked examples: H atom

The frequency range of visible spectrum is  $4.0 \times 10^{14}$  Hz (the IR-visible boundary) to  $7.5 \times 10^{14}$  Hz (the visible-UV boundary). The frequencies of the five lowest-frequency electron waves in H atom are  $\phi_1 = -3.29 \times 10^{15}$  Hz,  $\phi_2 = -8.2 \times 10^{14}$  Hz,  $\phi_3 = -3.7 \times 10^{14}$  Hz,  $\phi_4 = -2.1 \times 10^{14}$ , and  $\phi_5 = -1.3 \times 10^{14}$  Hz.

Calculate the ionization frequency of (the minimum frequency light that can ionize) H atom, and state what region of the spectrum this corresponds to.

Answer: The ionization frequency is  $|\phi_1 - \phi_{\text{threshold}}| = |\phi_1 - 0| = 3.29 \times 10^{15}$  Hz. This is in the UV region of the spectrum.

The figure represents the three lowest frequency lines seen in the gas discharge spectrum of H atoms.



What two electron waves must be mixed together to account for the red line seen in the spectrum of the hydrogen gas discharge tube?

Answer: Waves 2 and 3 are mixed, since then

$$\lambda_{\text{light}} = c / \nu_{\text{light}} = \frac{c}{|\phi_3 - \phi_2|} = \frac{3.0 \times 10^8 \text{ m/s}}{(8.2 - 3.7) \times 10^{14} / \text{s}} \frac{10^9 \text{ nm}}{\text{m}} = 670 \text{ nm} = \text{red}$$

What is the frequency of light of the cyan line seen in the spectrum of hydrogen gas discharge tube?

Answer: Waves 2 and 4 mix to give the cyan line, since

$$\lambda_{\text{light}} = c / \nu_{\text{light}} = \frac{c}{|\phi_4 - \phi_2|} = \frac{3.0 \times 10^8 \text{ m/s}}{(8.2 - 2.1) \times 10^{14} / \text{s}} \frac{10^9 \text{ nm}}{\text{m}} = 490 \text{ nm} = \text{cyan},$$

and so  $\lambda_{\text{light}} = |\phi_4 - \phi_2| = (8.2 - 2.1) \times 10^{14} \text{ Hz} = 6.1 \times 10^{14} \text{ Hz}$ .

The frequency of the lowest-energy electron wave in  $\text{He}^+$  ion is  $\phi_1 = -13.16 \times 10^{15} \text{ Hz}$ . Can light of frequency equal to that needed to ionize  $\text{He}^+$  ion be absorbed by H atom? Assume the H atom is in its lowest energy state. answer.

Answer: The ionization frequency of  $\text{He}^+$  is  $|\phi_1 - \phi_{\text{threshold}}| = |\phi_1 - 0| = 13.16 \times 10^{15} \text{ Hz}$ . This larger than the ionization frequency of H,  $3.29 \times 10^{15} \text{ Hz}$ . This means H atom *can* absorb the light, with the result that the H atom will be ionized, and that the detached electron will have kinetic energy  $h(13.16 - 3.29) \times 10^{15} \text{ Hz} = h 9.87 \times 10^{15} \text{ Hz}$ .

The electron beam in the hydrogen gas discharge tube mixes the two lowest-frequency waves in an H atom, and the atoms emits light as a result. Can the light given off by the H atom be absorbed by an  $\text{He}^+$  ion? Assume  $\text{He}^+$  is in its lowest energy state.

Answer: The light given off by H atom has frequency  $|\phi_2 - \phi_1| = (-0.82 + 3.29) \times 10^{15} \text{ Hz} = 2.47 \times 10^{15} \text{ Hz}$ . This smaller than the minimum frequency that  $\text{He}^+$  can respond to,  $|\phi_2 - \phi_1| = (-13.16/4 + 13.16) \times 10^{15} \text{ Hz} = 9.87 \times 10^{15} \text{ Hz}$ , since the  $\phi_2 = \phi_1 / 2^2$  for  $\text{He}^+$ . That is, ground state  $\text{He}^+$  *cannot* absorb the light given off by H.

Air is 70%  $\text{N}_2$ . Based on the fact that air is clear and colorless, what is the smallest possible value of  $|\phi_2 - \phi_1|$  for an  $\text{N}_2$  molecule? Assume that  $\text{N}_2$  does not interact with light at frequencies lower than  $4.0 \times 10^{14} \text{ Hz}$  (the IR-visible boundary).

Answer:  $|\phi_2 - \phi_1| \geq 7.5 \times 10^{14} \text{ Hz}$ .

An H atom is ionized by light of frequency  $\nu_{\text{light}} = 4.0 \times 10^{15} \text{ Hz}$ . Calculate the kinetic energy of the ionized (detached) electron. Assume H is in its lowest energy state.

Answer: The kinetic energy

$$\text{KE} = h \nu_{\text{light}} - h |\phi_1| = h(4.0 \times 10^{15} - 3.29) \times 10^{15} \text{ Hz} = h 0.7 \times 10^{15} \text{ Hz}$$

evaluates to

$$h 0.7 \times 10^{15} \text{ Hz} = 6.6 \times 10^{-34} \text{ kg m}^2 / \text{s} \times 0.7 \times 10^{15} / \text{s} = 5 \times 10^{-19} \text{ J}.$$

### Worked examples: Ionization

The ionization energy of  $\text{Li}^{2+}$  ion  $2 \times 10^{-17} \text{ J}$ . When the ion is irradiated with X-ray light, an electron is ejected with kinetic energy  $2 \times 10^{-17} \text{ J}$ . What is the wavelength, in  $\text{nm} = 10^{-9} \text{ m}$ , of the X-ray light.

Answer: The energy of the light quanta (photons) must be the sum of the ionization energy of the  $\text{Li}^{2+}$  and the kinetic energy of the electron.

$$\lambda_{\text{light}} = c / \nu_{\text{light}} = \frac{h c}{h \nu_{\text{light}}} = \frac{6.6 \times 10^{-34} \text{ J s} \times 3.0 \times 10^8 \text{ m/s}}{(2 + 2) \times 10^{-17} \text{ J}} \times \frac{10^9 \text{ nm}}{\text{m}} = 5 \text{ nm.}$$

What is the speed of an ejected electron, in m/s, that has kinetic energy  $2 \times 10^{-17} \text{ J}$ ?

Answer: Since  $\text{KE} = m u^2 / 2$ ,

$$u = \sqrt{2 \text{ KE} / m} = \sqrt{\frac{2 \times 2 \times 10^{-17} \text{ kg m}^2 / \text{s}^2}{9.1 \times 10^{-31} \text{ kg}}} = 7 \times 10^6 \text{ m/s.}$$

What will be the effect on the speed of an ejected electron if the intensity of the light is increased?

Answer: There will be no change in speed. What will change is the number of electrons ejected.

## Questions

What is true about light of frequency less than  $|\phi_2 - \phi_1|$ ? (a) It can only be absorbed but not emitted; (b) it can only be emitted but not absorbed; (c) it can be both absorbed and emitted; (d) matter will be transparent to light of this frequency.

What is true about light of frequency equal to  $|\phi_2 - \phi_1|$ ? (a) It can only be absorbed but not emitted; (b) it can only be emitted but not absorbed; (c) it can be both absorbed and emitted; (d) matter will be transparent to light of this frequency.

When light of frequency  $|\phi_2 - \phi_1|$  is absorbed, what happens to the amplitude of the light wave? (a) It is not affected, since all that matters is that  $\nu_{\text{light}} = |\phi_2 - \phi_1|$ ; (b) it goes down; (c) it goes up.

What is true about light of frequency greater than  $|\phi_2 - \phi_1|$  but less than  $|\phi_{\text{threshold}} - \phi_1|$ ? (a) It can only be absorbed but not emitted; (b) it can only be emitted but not absorbed; (c) it can be both absorbed and emitted; (d) matter will be transparent to light of this frequency.

What is true about light of frequency greater than  $|\phi_{\text{threshold}} - \phi_1|$ ? (a) It can only be absorbed but not emitted; (b) it can only be emitted but not absorbed; (c) it can be both absorbed and emitted; (d) matter will be transparent to light of this frequency.

What is true about light of frequency equal to  $|\phi_n - \phi_1|$ ? (a) It can only be absorbed but not emitted; (b) it can only be emitted but not absorbed; (c) it can be both absorbed and emitted; (d) matter will be transparent to light of this frequency.

Light of frequency  $|\phi_n - \phi_1|$  is absorbed. Can an atom absorb light of frequency greater than  $|\phi_n - \phi_1|$ ? (a) Yes; (b) no; (c) further information needed.

When light of frequency  $|\phi_n - \phi_1|$  is absorbed, what happens to the amplitude of the light wave? (a) It is not affected, since all that matters is that  $\nu_{\text{light}} = |\phi_n - \phi_1|$ ; (b) it goes down; (c) it goes up; (d) further information needed.

Light of frequency  $|\phi_n - \phi_1|$  is absorbed. If the light is made brighter, then ... (a) more atoms can absorb energy  $h|\phi_n - \phi_1|$ ; (b) there will be no change, since each atom can only absorb energy  $h|\phi_n - \phi_1|$ ; (c) further information needed.

Light of frequency  $|\phi_n - \phi_1|$  is absorbed. If the light is made brighter, then ... (a) more energy is available in the light, since its amplitude is higher; (b) there is no change, since all that matters is that  $\nu_{\text{light}} = |\phi_n - \phi_1|$ ; (c) further information needed.

Light of frequency greater than  $|\phi_{\text{threshold}} - \phi_1|$  is absorbed. If the light is made brighter, then ... (a) more electrons will be ejected and each electron will have more kinetic energy; (b) more electrons will be ejected and each electron will have the same kinetic energy; (c) further information needed.

## ■ Photoelectric effect

In 1905 Einstein proposed the idea that light exchanges energy with matter in indivisible "chunks" of size  $h\nu$ , to explain peculiar aspects of the *photoelectric effect* and *photoionization*. We now know, as discussed above, that the photoelectric effect can be understood instead as a consequence of the wave picture of matter, and in particular it does not depend on the particle aspects of light.

If the frequency of light is high enough, its electric field can tug on an electron in an atom so strongly that the electron is torn loose. This phenomena when applied to the atoms of a metal surface is known as the *photoelectric effect*, and when it is applied to an isolated atom is known as *photoionization*.

To appreciate what is peculiar about the photoelectric effect and photoionization, let's consider, based on the wave properties of light, what we might expect to be the dependence of the ejection on the intensity and frequency of the light.

- First, we might expect that no matter how low the frequency of the light, if it is intense (bright) enough, electrons will be ejected. What is observed is that if the frequency of the light is below a characteristic value  $\nu_0$ , then *no electrons are ejected*, no matter how bright—no matter how intense—the light.
- Second, no matter how high the frequency of the light, we might expect that if the light is not intense enough, then no electrons will be ejected. What is observed is that if the frequency of the light is above the characteristic value, then *electrons are always ejected*, no matter how faint the light. Making the light weaker decreases the number of electrons ejected each second, but there are always some electrons being ejected, no matter how weak the light.
- Finally, we might expect that, at a given frequency, the more intense the light, the faster the ejected electrons will be moving after they leave the metal.

It turns out that all three of these expectations are wrong. What is observed is that the kinetic energy of the ejected electrons,  $mu^2/2$ , is proportional to the amount

$$\nu_{\text{light}} - \nu_0 = \nu_{\text{light}} - |\phi_{\text{threshold}} - \phi_1|$$

by which the frequency of the light,  $\nu_{\text{light}}$ , exceeds the characteristic frequency,  $\nu - |\phi_{\text{threshold}} - \phi_1|$ .

It is commonly taught that to understand the photoelectric effect we need to invoke the particle aspect of light. In fact, the particle aspect of light effectively *plays no role* in the photoelectric effect. Rather, the key to understanding the photoelectric effect is how light interacts with electron clouds in matter, by causing them to jiggle at the same frequency as the light.

Einstein won the Nobel prize for his analysis of the photoelectric effect in which he assumed that what was essential was a particle picture of light, composed of photons of energy  $h\nu_{\text{light}}$ ,

<http://www.nobel.se/physics/laureates/1921/einstein-bio.html>

However, what was not yet known by Einstein (or anyone else at the time) was that the role of  $h\nu_{\text{light}}$  is a consequence of the wave nature of matter rather than the particle nature of light. It would not be for several more years after Einstein received the Nobel prize that quantum nature of matter would finally be elucidated by Heisenberg, etc.

The shift of view, made possible by our evolving understanding of the quantum world, from the particle aspect of light to the wave aspect of matter is part of the unease reflected in Einstein's comment late in his life that, "All the fifty years of conscious brooding have brought me no closer to the answer to the question: What are light quanta? Of course today every rascal thinks he knows the answer, but he is deluding himself." To quote Arthur Zajonc, "Light Reconsidered," *Optics & Photonic News*, October 2003, "We are today in the same state of "learned ignorance" with respect to light as was Einstein."



## Understanding the photoelectric effect.

Let's use these results to understand the three aspects of the photoelectric effect.

- If the light has a frequency lower than the characteristic frequency,  $\nu_{\text{light}} < \nu_0$ , there are two possibilities. Either there will not be two attached electron waves whose frequency difference matches the frequency of the light,  $\nu_{\text{light}} \neq |\phi_{\text{attached},2} - \phi_{\text{attached},1}|$ , in which case the light will not interact with the matter; or, if the frequency difference of two attached electron waves does match the frequency of the light,  $\nu_{\text{light}} = |\phi_{\text{attached},2} - \phi_{\text{attached},1}|$ , then light will interact with matter, but since both electron waves are attached, no *detached* electron will be present.
- If the light has a frequency lower than the characteristic frequency,  $\nu_{\text{light}} < \nu_0$ , since either the light does not interact with the matter, or it interacts only with attached electron waves, increasing the intensity of the light cannot detach an electron.
- Finally, If the frequency of the light is at or above the characteristic frequency,  $\nu_{\text{light}} \geq \nu_0$ , then there will always be mixing of an attached electron wave with a detached electron wave, independently how dim the light is. Making the light brighter will just mix attached and detached electron waves from more atoms and so produce more detached electrons. But they will all have the same kinetic energy.

## Calculating the photoelectric effect

Different terminology is used depending in whether the electron is detached from a metal surface (photoelectric effect) or from an isolated atom (photoionization). In the photoelectric effect, the minimum energy,  $h\nu_0$ , required to eject an electron is called the *work function* of the metal and it is written as the Greek letter  $\Phi$  (capital "phi"). In photoionization, the minimum energy,  $h\nu_0$ , required to eject an electron is called the *ionization energy* (or *ionization potential*) of the atom and it is written as IE.

The ionization energy of a hydrogen atom is 13.6 eV. Calculate the characteristic frequency,  $\nu_0$ , and wavelength,  $\lambda_0 = c/\nu_0$ , needed to photoionize a hydrogen atom. Answer:  $3.29 \times 10^{15}$  Hz, 91.2 nm. To what region of the electromagnetic spectrum does this belong? Answer: UV.

Assume a hydrogen atom is photoionized by light of frequency 1.0% greater than the hydrogen atom characteristic frequency,  $IE/h$ . Calculate the speed of the ejected electron, in m/s. Recall that kinetic energy is  $mu^2/2$ , where  $u$  is the speed of the electron. Answer: 219 km/s.

Assess whether your answer to the previous question is physically reasonable. For example, how long would it take an electron moving at that speed to cover the distance from Boston to Chicago? Answer: Using 1000 mi as the distance, the time to travel this distance is 7.35 s.

Electromagnetic radiation is found to eject electrons from isolated hydrogen atoms and the electrons are measure to have a speed of 0.1% of the speed of light. Calculate the wavelength of this radiation. Answer 90 nm.

Make a table of the lowest ionization energy of the hydrogen, lithium, sodium and potassium atoms. Compare the maximum possible speed of electrons ejected from these atoms by light of wavelength 205 nm. Answer: H will not be ionized; Li, 480 km/s; Na, 565 km/s; K, 775 km/s.

The work function of the chromium metal is  $\Phi_{\text{Cr}} = 7.2 \times 10^{-19}$  Joule. What is the value of the work function in eV? Answer: 4.5 eV.

What is the maximum speed an electron could be moving if it is ejected from chromium metal by light of wavelength 250 nm? (Oxtoby and Nachtrieb, 2e, problem 13.13.). Answer: 405 km/s.

Here is a question for you. Can some photoelectrons have velocity less than the maximum velocity? If so, what could cause them to have a correspondingly lowered kinetic energy?

## ■ Waves of matter

It is now known that light interacts with matter by means of exchange of photons in such a way that both *energy and momentum* are transferred in amounts determined only by the frequency of the light,

$$E_{\text{photon}} = h \nu_{\text{light}}$$
$$p_{\text{photon}} = h / \lambda_{\text{light}}$$

Einstein energy-frequency and momentum-wavelength relations.

(Note carefully that the wavelength and frequency are *not* those of the photon, but rather those of the light *wave*!) In 1924 Louis de Broglie had the idea that perhaps these relations could be turned around,

$$\phi_{\text{matter}} = E_{\text{matter}} / h$$
$$\lambda_{\text{matter}} = h / p_{\text{matter}}$$

de Broglie energy-frequency and momentum-wavelength relations.

and so interpreted as applying also to matter! Why on earth would someone have such an idea? The reason de Broglie made his proposal—at the time viewed as a bit crazy—was this: Just as a violin string is able to oscillate at only certain frequencies, electrons in atoms are in some sense like waves, then this might account for why only certain frequencies are seen in their spectrum.

As incredible as de Broglie's hypothesis that matter in some sense has an associated wavelength seems, it was soon confirmed experimentally. Davisson and Thomson showed, in separate experiments in 1927, that electrons passing through a crystal lattice of atoms in fact do diffract like waves, with wavelengths computed from their kinetic energy that agree precisely with those predicted by the de Broglie momentum-wavelength relation.

Details of the Davisson's experiment are at

<http://hyperphysics.phy-astr.gsu.edu/hbase/davger.html#c1>.

Davisson and Thomson shared the Nobel prize in 1936 for their work,

<http://www.nobel.se/physics/laureates/1937/index.html>.

An extraordinary side note is that Thomson's father, JJ Thomson had won the Nobel prize in 1906,

<http://www.nobel.se/physics/laureates/1906/thomson-bio.html>,

for showing that electrons behave like particles!

As a result the experimental verification of his hypothesis, de Broglie was awarded the Noble prize in 1929 for his reinterpretation of the Einstein relations,

<http://www.nobel.se/physics/laureates/1929/broglie-bio.html>.

## ■ Electron in a box

It turns out that de Broglie's hypothesis refers to electron waves. A very important example is to use the hypothesis to account for the resonant frequencies of an electron confined to a one-dimensional region, of length  $L$ . If we assume that the electron is able to move freely in that region, then its energy is just the kinetic energy due to its motion,

$$E_{\text{matter}} = \frac{1}{2} m u_{\text{matter}}^2 = \frac{p_{\text{matter}}^2}{2m}.$$

If we assume further that the electron wave must vanish at each edge of the region, then this means an integer number of half-wavelengths (called *loops*) must span the width of the region,

$$j \frac{\lambda_{\text{matter}}}{2} = L, \quad j = 1, 2, \dots$$

as illustrated in the figure below for electron waves with one, two, three, and four loops.

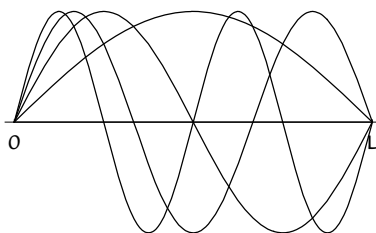


Illustration electron waves with one, two, three and four loops.

These two relations, together with the two de Broglie relations are what we need to find those values of the frequency and energy corresponding to each electron wave. From the de Broglie relation, the momentum of the electron is restricted to those values corresponding to the possible electron wave wavelengths that can exactly fit in the box,

$$p_{\text{matter}} = h / \lambda_{\text{matter}} = \frac{h j}{2 L}.$$

This means that the kinetic energy that a particle can have is proportional to the square of the number of half-wavelengths in the matter wave,

$$E_j = \frac{(p_{\text{matter}})^2}{2m} = \frac{h^2 j^2}{8mL^2}, \quad j = 1, 2, \dots$$

This last expression shows that the electron wave can have only the only certain frequencies.

$$\phi_j = E_j/h = \frac{h j^2}{8mL^2}, \quad j = 1, 2, \dots$$

### Absorption spectrum of an electron in a box

Now, the frequencies corresponding to the possible energies, do *not* agree with those that we would measure for a particle confined in a one dimensional box. Here is an example that shows this. The frequency of lowest energy absorption line of an electron confined to a 1.00 nm region is  $2.73 \times 10^{14}$  Hz. But as the following question shows, this frequency does *not* agree with any of the frequencies of the matter waves of the electron.

Show that the frequencies of the first three matter waves, namely those for  $j = 1, 2,$  and  $3,$  matter wave of such an electron are  $0.909 \times 10^{14}$  Hz,  $3.64 \times 10^{14}$  Hz, and  $8.18 \times 10^{14}$  Hz

You may have anticipated that the previous question is a bit of a trap: Should the frequencies of an electron in a box agree with the absorption frequencies? The answer is No! Here is why. Recall that the guiding principle of our analysis of the interaction of light with matter is that the light frequency must match the frequency,

$$\nu_{\text{cloud}} = |\phi_j - \phi_k| = \frac{h}{8mL^2} |j^2 - k^2|,$$

of oscillation of the electron cloud resulting from the mixture of two different electron waves. It is crucial to understand that while de Broglie's relations allow us to associate a frequency and energy with an electron wave, this de Broglie frequency does *not* correspond to any frequency seen in the spectrum of the matter. The frequencies we *do* see in spectra are *always* determined by *differences of electron wave frequencies*.

Show that the frequency lowest energy absorption line of an electron confined to a 1.00 nm one-dimensional region is indeed equal to  $2.73 \times 10^{14}$  Hz.

Calculate the frequencies of the next two absorption lines of an electron confined to a 1.00 nm one-dimensional region. Answer:  $7.27 \times 10^{14}$  Hz,  $1.36 \times 10^{15}$  Hz.

Calculate the de Broglie frequencies of the electron waves with three and four loops. Answer:  $8.18 \times 10^{14}$  Hz,  $1.45 \times 10^{15}$  Hz.

Use the de Broglie frequencies of the electron waves with three and four loops energies and the de Broglie frequency for the one-loop electron wave to calculate the frequencies of the next two absorption lines. Answer:  $7.27 \times 10^{14}$  Hz,  $1.36 \times 10^{15}$  Hz.

### Estimating the size of a molecule

Here is a worked example showing how to estimate the size of a molecule.

The lowest three electron wave frequencies of a molecule are  $\phi_1 = -5 \times 10^{13}$  Hz,  $\phi_2 = -4 \times 10^{13}$  Hz, and  $\phi_3 = -2 \times 10^{13}$  Hz. The energy of an electron confined to a one-dimensional region of length  $L$  is  $j^2 h^2 / (8 m L^2)$ , where  $j$  is the number of loops in the electron wave. Use this one-dimensional model to estimate the size,  $L$ , of the molecule. Express your answer in  $\text{\AA} = 10^{-10} \text{ m} = 0.1 \text{ nm}$  state circle whether your result is reasonable as a molecular dimension.

The stated frequencies are negative and so cannot be used in the energy formula, since when the square root is taken  $L$  would come out imaginary. More fundamentally, the only thing we can measure using light are electron wave frequency *differences*. So, the idea is to use the model to match the frequency differences. Note that the model is only approximate, because the stated (observed) three electron wave frequencies do not obey those predicted by the model in that the model frequencies are positive and increase quadratically, while observed frequencies are negative and do not obey quadratic variations.

The light frequency that interacts with the model system by mixing the two lowest waves of the model system is

$$|\phi_2 - \phi_1| = (E_2 - E_1)/h = \frac{3h}{8mL^2}.$$

Solving for  $L$  we get

$$L = \sqrt{\frac{3h}{8m|\phi_2 - \phi_1|}} = \sqrt{\frac{3 \times 6.6 \times 10^{-34} \text{ kg m}^2/\text{s}}{8 \times 9.1 \times 10^{-31} \text{ kg} (5 - 4) 10^{13} / \text{s}}} \times \frac{1 \text{ \AA}}{10^{-10} \text{ m}} = 52 \text{ \AA}.$$

This is a reasonable size for a large molecule.

### The orange of carrots

Carrots appear orange because they absorb light in the cyan region of the spectrum. Model this cyan absorption as being due to that of an electron confined in a one-dimensional region of length  $L$ , and so estimate the length of the molecule in carrots that accounts for their color. Assume the cyan absorption is at 450 nm. The energy of an electron confined to a one-dimensional region of length  $L$  is  $j^2 h^2 / (8 m L^2)$ , where  $j$  is the number of loops in the electron wave. Assume that the light mixes the two lowest energy electron waves.

The light mixes the two lowest waves of the model system, and so

$$hc/\lambda_{\text{light}} = |\phi_2 - \phi_1| = (E_2 - E_1)/h = \frac{3h}{8mL^2}.$$

Solving for  $L$  we get

$$L = \sqrt{\frac{3h\lambda_{\text{light}}}{8mc}} = \sqrt{\frac{3 \times 6.6 \times 10^{-34} \text{ kg m}^2/\text{s} \times 450 \times 10^{-9} \text{ m}}{8 \times 9.1 \times 10^{-31} \text{ kg} \times 3.0 \times 10^8 \text{ m/s}}} \times \frac{1 \text{ \AA}}{10^{-10} \text{ m}} = 6.4 \text{ \AA}.$$

## Mathematical details (optional)

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The ideas that we have presented are the essence of how light and matter interact, and your goal should be to become comfortable with what we have done up to this point.

The remainder of this chapter provides the details on which these ideas are based. It is meant to address questions about quantum aspects of light and matter that you may have wondered about. However, this material is *not* required.

### ■ Particles of light

At about the same time that Einstein made his analysis of the photoelectric effect, he also proposed his *special theory of relativity*, based on the extraordinarily puzzling experimental finding in 1887 by Michelson and Morley that (strictly, in a given medium such as air or a vacuum) light always has the same speed, *independently of the speed of the source of the light*.

This does not seem to have much to do with the quantum nature of atoms and light, but a consequence of special relativity is the prediction that quanta of light also have momentum, and so in this sense behave like particles of matter. This was the first hint of what is now known as the *wave-particle duality*.

Michelson's paper, with Edward W. Morley, "On the Relative Motion of the Earth and the Luminiferous Ether," American Journal of Science (vol. 35, 1887, p. 333-45), is available at

<http://www.aip.org/history/gap/PDF/michelson.pdf>,

and a biography and further resources are available at

<http://www.aip.org/history/gap/Michelson/Michelson.html>.

Michelson was the first American scientist to win a Nobel Prize (1907),

<http://www.nobel.se/physics/laureates/1907/michelson-lecture.html>

Einstein developed his theory of special relativity in order to account for how it could be that light always has the same speed, whether the light source is moving or not. To see how strange this behavior of light is, let's imagine instead that we fire a bullet from a gun just as Superman flies by at the speed of the bullet (being Superman, he could go faster, of course!). Since Superman has matched his speed to that of the bullet, to him the speeding bullet appears to be standing still. Now, if instead of firing a bullet, we set off a flash bulb just as Superman flies by, Superman being Superman, he'll naturally speed up to catch the light. The most amazing thing, however, is that no matter how fast Superman goes, the light recedes from him at exactly the same speed as it recedes from us. From Superman's point of view of the light from the flash bulb, it as if he is standing still, no matter how fast he is going! For some reason, light seems to disobey the rules about the speed of a projectile being relative to its source!

An exceptionally introduction to these ideas is Edwin F. Taylor and John Archibald Wheeler, *Spacetime Physics: Introduction to Special Relativity*, 2nd edition (1992) W H Freeman & Co.; ISBN: 0716723271,

<http://www.amazon.com/exec/obidos/ASIN/0716723271/dandillcom>.

The extension by Einstein to reference frames accelerating with respect to one another is

called general relativity, and a very accessible treatment of the key consequences of general relativity is Edwin F. Taylor and John Archibald Wheeler, *Exploring Black Holes: Introduction to General Relativity*, 1st edition (2000), Benjamin/Cummings; ISBN: 020138423X,

<http://www.amazon.com/exec/obidos/ASIN/020138423X/dandillcom>.

The essence of Einstein's theory to account for this very strange behavior of light is the following remarkable prediction: *time proceeds at different rates* in a stationary frame of reference (us) and a moving frame of reference (Superman) in just the right amount so that light is always measured to travel the same distance in a given time. There is much more to the story (a very nice exposition is *Space and time in the modern universe*, by P. C. W. Davies), and the incredible end result is Einstein's famous relation,

$$E = m c^2,$$

expressing the equivalences between mass and energy.

The first thing to appreciate about the mass-energy relation is that the mass,  $m$ , is not the ordinary mass of an object, which we denote as  $m_0$ , but instead it is related to it as

$$m = m_0 / \sqrt{1 - \left(\frac{u}{c}\right)^2}.$$

where  $u$  is the speed of the particle. Speeds encountered in everyday experience result in a negligible increase in mass.

Calculate the ratio,  $m/m_0$ , as a result of a 3 gram bullet moving at 600 mph. It may be helpful to use logarithms to evaluate the ratio. Answer: 1.0000000004.

For particle speeds close to the speed of light, the increase in mass becomes very significant.

Calculate the ratio,  $m/m_0$ , as a result of a 5 gram bullet moving at 95% of the speed of light. Answer: 3.2.

A crucial feature of the relation is that *the mass  $m$  becomes infinite as its speed  $v$  approaches the speed of light*.

Calculate the ratio,  $m/m_0$ , as a result of a 2 gram bullet moving at the speed of light. Answer:  $\infty$ !

A consequence of this mass relation is that it would require an infinite amount of energy to accelerate a mass to the speed of light. This is why anything with mass may only move *slower* than the speed of light.

On the other hand, since light itself *does* move at speed  $c$ , we must conclude that *the rest mass of light is 0!*

In the limit that the speed of a mass is very much smaller than the speed of light, then we can approximate the mass as

$$m = m_0 \left\{ 1 + \frac{1}{2} \left(\frac{u}{c}\right)^2 - \dots \right\}$$

and so approximate the energy of matter as

$$E_{\text{matter}} = m_0 c^2 + \frac{1}{2} m_0 u^2 - \dots$$

That is, the energy is just the ordinary kinetic energy,  $m_0 u^2 / 2$ , plus an additional so-called *rest mass energy*,  $m_0 c^2$ . All matter has such rest mass energy. (It is rest mass energy that is released in *nuclear fusion*, in which two masses combine to form a new mass smaller than their sum, with the difference released as energy.)

You may be surprised at how large your own rest mass energy is!

I weigh about 170 lb = 77 kg. Show that my rest mass energy is  $6.9 \times 10^{18}$  J!

This is a huge amount of energy, by everyday measures.

I am a rower and on a good day am able to achieve speeds in a one-person shell (called a single scull) of 5 m/s. Show that then my kinetic energy is 1000 J. Actually, the value is a little more when the mass of the shell (about 27 pounds) and oars are taken into account.

Typically, kinetic energy is a negligible fraction of a particle's rest mass energy.

It turns out that light also has a mass, and so energy, even though light has no rest mass. To see this, we need to rewrite the Einstein mass-energy equation in a form that makes clear the distinction between particles with a rest mass, and light, which has no rest mass. We do this by using the relation between  $m$  and  $m_0$ , squaring both sides of Einstein's equation and then rearranging to get

$$E^2 \left\{ 1 - \left( \frac{u}{c} \right)^2 \right\} = m_0^2 c^4,$$

or

$$E^2 = m^2 c^2 u^2 + m_0^2 c^4.$$

We can simplify this expression a little by using the symbol  $p$  for the (relativistic) momentum  $m u$  (not  $m_0 u$ ), and then taking the square root. The result is

$$E = \sqrt{p^2 c^2 + m_0^2 c^4}.$$

Carry out the steps described to obtain this expression for the energy.

Now, since light has no rest mass, this expression when applied to light becomes

$$E = p c.$$

But what is this the energy of? Einstein's proposal was that *this is not the total energy of light but the energy of just one photon of light energy*. That is, Einstein said that

$$E_{\text{photon}} = p c.$$

Now the extraordinary thing about this proposal by Einstein is that it amounts to saying that a photon of light energy also has a momentum  $p = E_{\text{photon}} / c$ ! Since we have already determined that the energy of a photon is  $h \nu$ , this means that the momentum of a photon is

$$p_{\text{photon}} = h \nu / c = h / \lambda.$$



The two relations,  $E_{\text{photon}} = h\nu$  and  $p_{\text{photon}} = h/\lambda$ , taken together imply a profound expansion of our conception of how light interacts with matter. While many properties of light—the way it moves through space, how it is dispersed into colors in a prism, how it is focus by lenses, etc.—are well described terms of waves of electric and magnetic fields, Einstein proposed that the *interaction* of light with matter has distinctly particle-like character of exchanging fixed amounts of energy and momentum with matter. That is, while exchanging fixed amounts of energy can be taken as just the way the oscillating fields that compose light tug on matter, proposing that a photon also has momentum suggests that in some sense light must interact with matter as one billiard ball does with another. And that is quite peculiar.

A fluorescent bulb emits light of several different wavelengths from each major region of the visible spectrum so that to our eyes its light appears white. Assume that a 45 watt fluorescent bulb emits equal amounts of red, green and blue light. Assume that there are  $2 \times 10^{19}$  photons of energy given of each second at the blue wavelength 450 nm. Calculate the total momentum in the blue light emitted each second, Answer:  $3 \times 10^{-8}$  kg m/s

This momentum is equivalent to  $3 \times 10^{-6}$  kg cm/s = 0.003 g cm/s,. If the light were focused in a single direction, we could think of this being the same momentum as a stream on 3 mg objects travelling at 1 cm/s.

Since the momentum of light is  $p_{\text{photon}} = mc$ , we can interpret the mass of a quantum to be  $m_{\text{photon}} = h/(c\lambda)$ . Calculate the "mass" of a quantum of red light ( $\lambda = 700$  nm) and of x-ray light ( $\lambda = 0.1$  nm). Answer:  $3 \times 10^{-36}$ kg,  $2 \times 10^{-32}$ kg.

What wavelength light would has a photon mass equal to the electron mass? Answer: 0.002 nm

It is important to understand that the relation  $E = pc$  is true *only* for light, that is, only when the rest mass,  $m_0$ , is zero. That is, it is *not* true for matter, for which the rest mass is *not* equal to zero, and the velocity is always less than  $c$ .

### Measuring the momentum of light: Compton scattering

So peculiar was Einstein's proposal that quanta of light carry a fixed amount of momentum, it was not accepted as so until it was verified by direct measurement. The experiment was carried out in 1923 by A. H. Compton. Compton's idea was that if light had momentum, then when it's energy is transferred to an electron, its momentum should also be transferred.

What Compton measured was the momentum imparted to an electron initially at rest by the absorption of one photon. He found that increase in the momentum was not equal to the momentum of the photon, but only a fraction of the momentum. However, he also measured that following the absorption of the light by the electron, light of longer wavelength was emitted by the electron (due to its motion).

The emission of a light of longer wavelength suggested to Compton that the amount of momentum transferred to the electron may be a measure of the momentum difference between a photon of the incident and emitted light. It turns out that if he assumed, according to Einstein's proposal, that the momentum of the photons of the absorbed light was  $h/\lambda_{\text{absorbed}}$  and that of the photons of the emitted light was  $h/\lambda_{\text{emitted}}$ , then the n the increase in wavelength,  $\lambda_{\text{emitted}} - \lambda_{\text{absorbed}}$ , that he observed accounted precisely for the momentum gained by the electron.

The gist of Compton's analysis is (1) that momentum of the absorbed photon is partitioned between the emitted photon and the electron (momentum conservation)

$$\vec{p}_{\text{photon,absorbed}} = \vec{p}_{\text{photon,emitted}} + \vec{p}_{\text{electron,scattered}}$$

(since the electron is initially assumed to be at rest, its momentum is zero and so not included on the left hand side of this equation), and (2) that the combined energy of the absorbed photon and the electron before the absorption (energy conservation).

$$m_{0,e} c^2 + h c / \lambda_{\text{absorbed}} = \sqrt{m_{0,e}^2 c^4 + p_{e,\text{scattered}}^2 c^2} + h c / \lambda_{\text{emitted}}$$

He then used these two relations to show that

$$\lambda_{\text{emitted}} - \lambda_{\text{absorbed}} = \frac{2h}{m_{0,e} c} \sin^2(\theta/2)$$

where  $\theta$  is the angle at which the emitted photon is detected relative to the direction of the absorbed photon's light beam. The greater the angle, the greater the transfer of momentum to the electron and so the greater the increase of the wavelength of the light as a result of the interaction.

The quantity  $h / (m_{0,e} c)$  is known as the Compton wavelength. Show that its value is 0.0024263 nm.

Calculate the wavelength difference between an absorbed photon and one emitted along direction  $10^\circ$  and along direction  $90^\circ$ . Answer: 0.0000368611 nm, 0.00242631 nm.

Do the relative values of these wavelength shifts make sense physically?

Details of Compton's calculation are at

<http://scienceworld.wolfram.com/physics/ComptonEffect.html>,

and you can explore the calculations interactively at

<http://hyperphysics.phy-astr.gsu.edu/hbase/quantum/compmat.html#c1>.

Compton's paper is "A quantum theory of the scattering of X-rays by light elements," Phys. Rev. 21, 483–502 (1923),

<http://www.aip.org/history/gap/PDF/compton.pdf>.

In the paper Compton concludes that the "experimental support of the theory indicates very convincingly that a radiation quantum carries with it directed momentum as well as energy." A biography of Compton is available at

<http://www.aip.org/history/gap/Compton/Compton.html>.

In this way, the momentum of photon came to be accepted. And in this way Compton won his Nobel prize in 1927, <http://www.nobel.se/physics/laureates/1927/compton-bio.html>.

## ■ What's waving in a matter wave?

The first step in answering this question is to see what the mathematical expression is for the matter wave. The first thing to try is to rewrite the general expression for a wave that we have discussed,

$$\psi(x, t) = a \sin[2\pi(x/\lambda - \nu t)].$$

using the de Broglie relations. The result is

$$\psi(x, t) = a \sin[2\pi(x/\lambda_{\text{matter}} - \phi_{\text{matter}} t)] = a \sin[(p_{\text{matter}} x - E_{\text{matter}} t) / \hbar],$$

where  $\hbar$ , pronounced "h bar," is the standard abbreviation for  $h / (2\pi)$ . We can interpret this expression as meaning that the matter wave is moving, with phase velocity

$$u_\phi = \phi_{\text{matter}} \lambda_{\text{matter}}.$$

For example, for a particle confined to a one-dimensional region of width  $L$ , in which it moves freely, the phase velocity is

$$u_\phi = \frac{h j}{4 m L}.$$

Use the expressions we have found for the energy and wavelength of such a particle to show that this expression for the phase velocity is true.

Calculate the phase velocity of an electron confined to a one-dimensional 1.00 nm region when it has the lowest possible energy. Answer:  $1.82 \times 10^5$  m/s. This illustrates that the phase velocity of such an electron is much less than that of light.

It turns out that this form of the matter wave is not quite right. One of the requirements of the quantum description of matter that has a definite energy is that the time variation of its matter wave be

$$e^{-i E_{\text{matter}} t / \hbar} \text{ (time variation of matter wave with energy } E_{\text{matter}} \text{)}.$$

In this expression,  $e$  is the base of the natural logarithm and  $i = \sqrt{-1}$  (and so  $i^2 = -1$ ). The factor  $e^{-i E_{\text{matter}} t / \hbar}$  is an example of what is known as a *complex exponential*. A general complex exponential  $e^{i x}$  is a special combination of sine and cosine known as the *Euler relation*,

$$e^{-i x} = \cos(x) - i \sin(x),$$

and so  $e^{-i E_{\text{matter}} t / \hbar} = \cos(E_{\text{matter}} t / \hbar) - i \sin(E_{\text{matter}} t / \hbar)$ .

Show that  $e^{i \pi/2} = i$ ,  $e^{i \pi} = -1$ ,  $e^{i 3 \pi/2} = -i$ , and  $e^{i 2 \pi} = e^0 = 1$ .

In terms of the exponential time dependence, the matter wave for a particle in a box with energy  $E_{\text{matter}}$  is

$$\psi(x, t) = a \sin(p_{\text{matter}} x) e^{-i E_{\text{matter}} t / \hbar}.$$

To focus our attention on this particular form of the time dependence in matter waves, let's write a general matter wave (in one dimension) as

$$\psi(x, t) = \psi(x) e^{-i E_{\text{matter}} t / \hbar},$$

with the understanding that  $\psi(x)$ , the spatial part of the matter wave, is different for different kind of systems; for example,  $\psi(x) = a \sin(p_{\text{matter}} x / \hbar)$ . As we will now see, there are two very good reasons why time needs to appear in a matter wave that has a definite energy,  $E_{\text{matter}}$ , in terms of the complex exponential  $e^{-i E_{\text{matter}} t / \hbar}$ .

The first reason is that then matter in its lowest energy state will be stable, in the sense that it cannot drop to a still lower energy state by emission of light energy.

The second reason is that then interaction of light with charged particles makes them oscillate at frequencies determined by *differences* of de Broglie frequencies (and so, particle energies).

Here is a worked example illustrating these ideas.

The lowest three electron wave frequencies of a molecule are  $\phi_1 = -7 \times 10^{13}$  Hz,  $\phi_2 = -6 \times 10^{13}$  Hz, and  $\phi_3 = -1 \times 10^{13}$  Hz. Assume the electron is described by electron wave with frequency  $\phi_2$ . Show that the molecule *cannot* absorb light of frequency  $|\phi_2|$ .

Answer: The electron cloud made from electron wave with frequency  $\phi_2$  does not move, since  $\exp(-i 2 \pi \phi_2 t) \exp(+i 2 \pi \phi_2 t) = \exp(0) = 1$ ; that is, there is no possibility of an electron cloud moving at frequency  $|\phi_2|$ .

### ■ Born interpretation: What's waving is *probability amplitude*

It was Max Born who provided the answer that we use today. Born postulated that matter waves, or *wavefunctions* as they are more commonly known today, are oscillations of *probability amplitudes*. Probability amplitudes have physical meaning according to the following *recipe* (or rule):

The product of a wavefunction corresponding to time increasing (flowing forward) and the same wavefunction corresponding to time decreasing (flowing backward) is the *probability density* of the particle.

The formulation of Born's recipe in terms of a time-symmetric prescription is due to John Cramer, *Transactional interpretation of quantum mechanics*, Reviews of Modern Physics, Volume 58, 1986, pages 647–687. A very nice, qualitative discussion of this interpretation is given in John Gribbin, *Schrodinger's Kittens and the Search for Reality* (Little Brown & Company, 1995, ISBN 0316328383), pages 223–247.

This is a real mouthful, so let's digest it a bit at a time.

First, about probability density: The terminology probability density is used because in three dimensions, the product has the dimensions probability *per unit volume*. To know the *probability* of a particle being within a small volume  $dV$  centered at a particular point in space, we need to multiply the probability density there by the small volume.

If we are working in just one dimension, the probability density has the dimensions probability *per unit length*. To know the *probability* of a particle being within a small distance  $dx$  centered at a particular point in one dimension, we need to multiply the probability density there by the small length.

How would you use probability density to determine probability working in two dimensions?

It is because of this connection between the wavefunction and probability that wavefunctions are sometime referred to as probability *amplitudes*.

Second, about the direction of time: A neat device to change the direction of time in a wavefunction is to replace everywhere  $i$  by  $-i$ ; this replacement is called *complex conjugation*, and a function  $f(x, t)$  to which complex conjugation has been applied is written  $f(x, t)^*$ . So we can write the probability of a particle represented by a wavefunction  $\psi(x, t)$  being within  $dx$  of a particular place, say  $x'$ , is

$$\psi(x', t)^* \psi(x', t) dx = \psi(x')^* e^{i E_{\text{matter}} t/\hbar} \psi(x') e^{-i E_{\text{matter}} t/\hbar} dx = \psi(x')^* \psi(x') dx = |\psi(x')|^2 dx.$$

Here we have introduced the standard notation  $|f(x)|^2$  for the product of a function and its complex conjugate. The crucial feature of Born's recipe is that whenever the wavefunction has a definite energy, then probabilities computed from it *are independent of time*, since the complex exponentials cancel,

$$e^{i E_{\text{matter}} t/\hbar} e^{-i E_{\text{matter}} t/\hbar} = e^0 = 1.$$

For this reason, we say a particle with a well defined energy is in a *stationary state*, in that its probability density not change over time.

In three dimensions, the probability of the electron being within a volume  $d\mathbf{r}$  centered at a particular place, say  $\mathbf{r}' = (x', x', x')$ , is

$$\psi(\mathbf{r}', t) \psi(\mathbf{r}', -t) d\mathbf{r} = |\psi(\mathbf{r}')|^2 d\mathbf{r}.$$

The probability of finding the particle within a larger region, say (for one dimension) between  $x = a$  and  $x = b$ , is

$$\int_a^b |\psi(x)|^2 dx.$$

Since a particle must be found *somewhere*, the Born recipe requires that the probability of finding it anywhere at all must be one,

$$\int_{-\infty}^{\infty} |\psi(x)|^2 dx = 1.$$

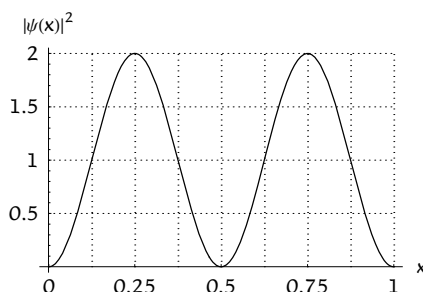
This relation is known as the *normalization condition* and wavefunctions that satisfy this condition are said to be *normalized*.

### Calculating probability densities

To get familiar with calculating probabilities from wavefunctions, let's use as example a wavefunction of a particle confined in the region  $0 \leq x \leq 1$ ,

$$\psi(x) = \sqrt{2} \sin(2\pi x).$$

Here is the corresponding probability density,



Probability density of a particle confined to the region  $0 \leq x \leq 1$ .

The essence of computing probabilities of a particle being within a region  $\Delta x$  of a particular place  $x_0$  is to multiply the probability density at  $x_0$  by the width of region,  $|\psi(x_0)|^2 \Delta x$ .

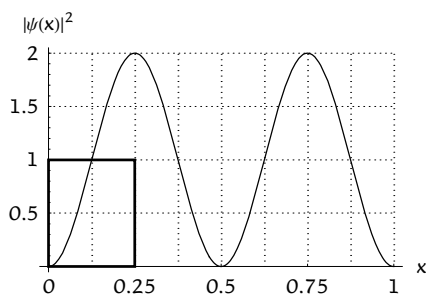
What is the probability of finding the particle within  $\Delta x = 0.01$  of  $x_0 = 0.25$ ? Answer: 0.02.

What is the probability of finding the particle within  $\Delta x = 0.01$  of  $x_0 = 0.125$ ? Answer: 0.01.

What is the probability of finding the particle within  $\Delta x = 0.01$  of  $x_0 = 0.50$ ? Answer: 0.

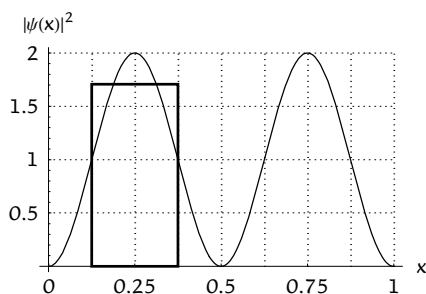
Computing probabilities using  $|\psi(x_0)|^2 \Delta x$  assumes that  $\psi(x)$  changes negligibly over the region  $\Delta x$ . If the region is so large that this is not the case, we can still easily approximate probabilities by using rectangular areas.

For example, we can estimate the probability of the particle being somewhere in the region  $0 \leq x \leq 0.25$  by evaluating the area of the rectangle of width equal to  $\Delta x = 0.25$  and height equal to the value of the probability density,  $|\psi(x = 0.125)|^2 \approx 1$ , evaluated at the midpoint of the region,  $x = 0.125$ . This is illustrated in the following figure.



The result is  $|\psi(x = 0.125)|^2 \Delta x = 1 \times 0.25 = 0.25$ .

Use the rectangle illustrated in the following figure to estimate the probability of finding the particle within  $\Delta x = 0.25$  of  $x_0 = 0.25$ ? Answer: 0.4.



Such estimates can be made as exact as we wish by spanning the region with increasing numbers of adjacent small rectangles. Of course, in the limit of infinitesimally narrow rectangles we have the result from calculus that the calculation reduces to an integral. For the example wavefunction here, the general expression for the probability of finding the particle somewhere in the region  $a \leq x \leq b$  is

$$\int_a^b \psi(x)^2 dx = 2 \int_a^b \sin^2(2\pi x) dx = b - a + \frac{\sin(4\pi a) - \sin(4\pi b)}{4\pi}.$$

Using this expression, we can evaluate the exact value of the previous problem to be 0.41. In practice, however, we can make quite reasonable estimates by careful choice of a single rectangle, or at most just a few.

Use the calculus result given above to show that the probability of finding the particle somewhere between  $x = 0$  and  $x = 1$  is 1. That is, show that the wavefunction is normalized.

Use the result of the previous problem, but without using the calculus result quoted above and without using any rectangles, to show that the probability of the particle being in the region  $0 \leq x \leq 1/2$  is exactly  $1/2$ .

### Are wavefunctions real?

It is crucial to understand that the Born recipe gives only *indirect* physical meaning to the wavefunction, as a means to compute probabilities. In particular, as far as we know today, the wavefunction itself does not appear to be directly accessible. Indeed, so far as I am aware we do not have any experimental evidence of the physical reality of wavefunctions; that is, wavefunctions are abstract quantities rather than physical objects, and so in this sense they may simply be calculational tools.

### ■ How does light make electrons jiggle?

The Born interpretation tells us how matter waves relate to physical reality. With this insight, let's return to the question of how interaction of light with charged particles makes them oscillate at frequencies determined by *differences* of de Broglie frequencies (and so, particle energies).

The key is to recall that light interacts with matter by causing its charged particles to oscillate in synchrony with the oscillation of the electric field of the light. So, we need to understand how light can make an electron jiggle.

Heisenberg's first paper on quantum mechanics addressed this question.

W. Heisenberg, "Quantum-theoretical re-interpretation of kinematic and mechanical relations," *Z. Phys.* 33 (1925) 879-893. A translation of this paper into English, and also of most of the other key works on the creation of quantum mechanics is in B. L. van der Waerden, "Sources of Quantum Mechanics," (Dover, 1968, ISBN 0-486-61881-1).

The challenge (and what Heisenberg set himself to) is to identify something in matter that (1) has the needed frequency of oscillation, proportional to a *difference* of atom energies, but (2) that at the same time does not lead to motion of charges in matter in the absence of light. The reason for requiring no motion of charges in the atom in the absence of light is that such motion would cause atoms to emit light when no light is present (which they do not) and quickly collapse (which they do not) due to the loss of energy to light. That is, the question is how to account for oscillation in the atom in the presence of light, but to have no oscillation—and so no radiative collapse—if no light is present?

Heisenberg won the Nobel prize for his answer. Heisenberg knew he had to associate something with each possible energy value of the electron that, when connected to another energy value, would result in a frequency proportional to the *difference* of the energy values.

The essence of Heisenberg's approach amounts to the following three steps (Heisenberg did not lay them out separately, however). First is the idea we have already introduced, to associate with the spatial matter wave,  $\psi_{\text{atom},j}(x)$ , corresponding to each possible energy value,  $E_j$ , of the electron, the complex exponential  $e^{-i2\pi E_{\text{atom},j}t/h} = e^{-i\omega_{\text{atom},j}t}$ ; that is, to express the matter wave of the  $j$ -th energy level as

$$\Psi_j(x, t) = \psi_j(x) e^{-i\omega_{\text{atom},j}t}.$$

Next, is the idea that the effect of the light on the atom was to produce a *mixture of two matter waves*, say,

$$\psi_j(x) e^{-i\omega_{\text{atom},j}t} + \psi_k(x) e^{-i\omega_{\text{atom},k}t}.$$

Finally, Heisenberg postulated that interaction with light results in a spatial distribution of electron charge given by Born recipe (which he anticipated), the product of the mixture of matter waves and their time reversed mixture, for the two energy levels,

$$\begin{aligned} &|\psi_j(x) e^{-i\omega_{\text{atom},j}t} + \psi_k(x) e^{-i\omega_{\text{atom},k}t}|^2 = \\ &\psi_j(x)^2 + \psi_k(x)^2 + 2\psi_j(x)\psi_k(x)\cos[(\omega_{\text{atom},k} - \omega_{\text{atom},j})t]. \end{aligned}$$

Here, for simplicity, we assume the spatial parts of the wavefunctions are real and so that complex conjugation is moot for them.

Show that this expression is correct, using the consequence of the Euler relation that  $e^{ix} + e^{-ix} = 2\cos(x)$ .

The key feature of this result is that the distribution of the electron probability density, and so the electron charge distribution, oscillates with the required frequency, given by the *difference of the de Broglie frequencies*.

Let's see how Heisenberg's approach works for an electron in a one-dimensional box and an electron in a hydrogen atom.

### Example: Electron in a one-dimensional box

We know that for an electron in bound electron to interact with light, it must oscillate at the frequency of the light. The matter wave of an electron with energy  $E_n$  is

$$\psi_n(x, t) = \sqrt{2/L} \sin(k_n x) e^{-i\omega_n t},$$

where the factor  $\sqrt{2/L}$  insures the wavefunction is normalized.

If you have had calculus, you can confirm that the wavefunction is normalized by verifying that  $\int_0^L [\sqrt{2/L} \sin(k_n x)]^2 dx = 1$ .

Such an electron with fixed energy *cannot oscillate*, since its probability density is independent of time,

$$\psi_n(x, t)^* \psi_n(x, t) = (\sqrt{2/L} \sin(k_n x) e^{-i\omega_n t})^* (\sqrt{2/L} \sin(k_n x) e^{-i\omega_n t}) = \frac{2}{L} \sin^2(k_n x).$$

For there to be oscillation at a particular frequency, the matter wave of the electron must be a mixture of matter waves for different energies. The simplest such mixed matter wave is

$$\Psi(x, t) = \frac{1}{\sqrt{2}} \{\psi_1(x, t) + \psi_2(x, t)\} = \frac{1}{\sqrt{2}} \{\sin(k_1 x) e^{-i\omega_1 t} + \sin(k_2 x) e^{-i\omega_2 t}\},$$

where the factor  $1/\sqrt{2}$  insures the mixture is normalized.

Show that if  $\psi_1$  and  $\psi_2$  are normalized, then this mixture of them is normalized.

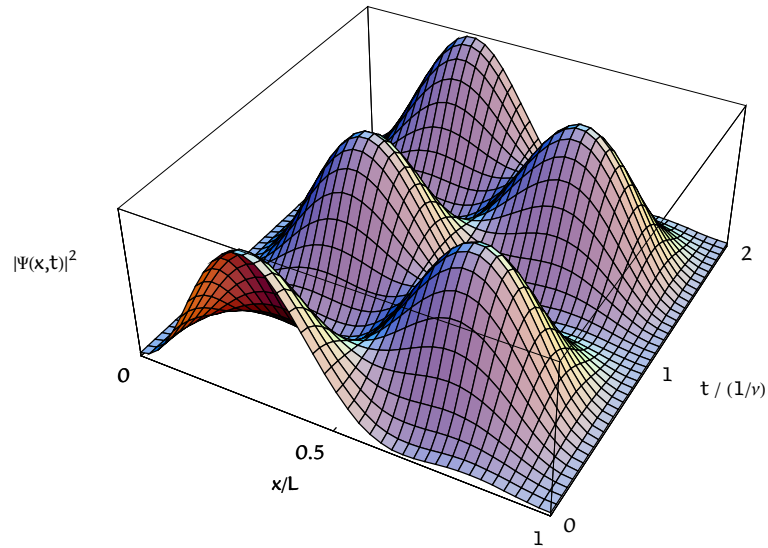
The probability density corresponding to this mixed matter wave,



$$\Psi(x, t)^* \Psi(x, t) = \frac{1}{L} \{ \sin^2(k_1 x) + \sin^2(k_2 x) + 2 \sin(k_1 x) \sin(k_2 x) \cos[(\omega_2 - \omega_1) t] \}$$

does oscillate, at frequency  $\omega = \omega_2 - \omega_1$ , just as required by the Einstein energy-frequency relation.

Here is a visualization of the oscillation of the probability density.

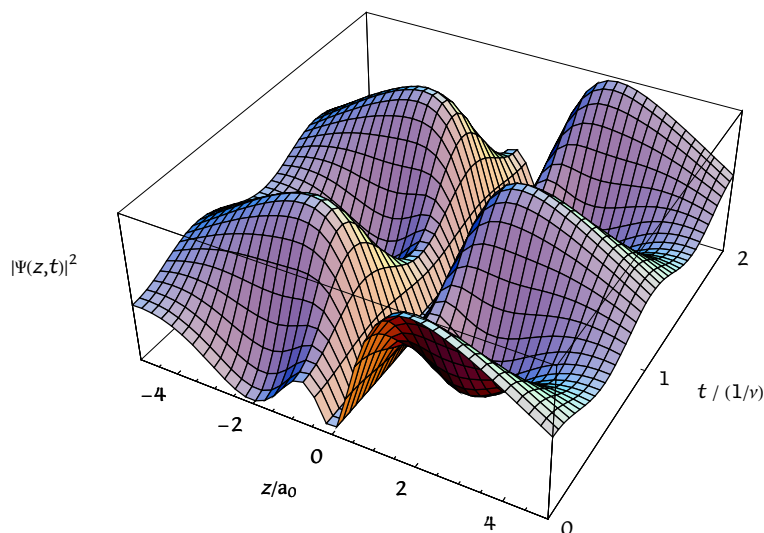


Probability density on an electron in a one-dimensional box of width  $L$  interacting with light of angular frequency  $\omega$  equal to the difference in angular frequency of the lowest and next lowest energy of the electron in the box. This frequency corresponds to the fundamental absorption line of the electron in the box.

The figure shows two frequency cycles of time. In this time the electron probability density is seen to shift back and forth across the box twice, matching the oscillation of the electric field of the light of the same frequency.

### Example: Electron in hydrogen atom

Here is a visualization of the analogous probability density oscillation corresponding to the hydrogen atom Lyman  $\alpha$  ( $n = 1 \rightarrow n = 2$ ) absorption.



Probability density on the electron in hydrogen atom interacting with light of angular frequency  $\omega$  equal to the difference in angular frequency of the lowest ( $n = 1$ ) and next lowest ( $n = 2$ ) energy of the electron. This frequency corresponds to the Lyman  $\alpha$  absorption line of atomic hydrogen. Oscillation is along the axis,  $z$ , of the electric field of the light. The hydrogen atom nucleus is at  $z = 0$ .

As before, the figure shows two frequency cycles of time. The electron probability density is seen to shift back and forth from one side of the nucleus (at  $z = 0$ ) to the other twice, matching the oscillation of the electric field of the light of the same frequency.

## ■ Representing a "particle" with waves: wavepackets

At this point we know a little about what a matter wave—a wavefunction—is and how the combination of matter waves of two different energies account for the frequency of spectral lines being determined by *differences* of matter wave de Broglie frequencies.

What you may be wondering, however, is: How can a particle, which we think of as something being in a particular region of space ("here, and not there"), be represented by a wave, which is by definition spread throughout space (else its length—the distance from peak to peak—has no meaning)? That is, how can we reconcile our image of a particle as a localized object with our image of a wave as oscillating over an extended region?

A caution on the use of language:

We will show now one way to reconcile the wave aspect of electrons with the image of an electron as being a localized object—a "particle." But at a more fundamental level, whether quantum objects appear as waves or particles has meaning **only** in terms of the kinds of measurements we make on them. That is, as far as anyone knows, the so-called wave-particle duality is an inescapable aspect of every quantum object.

This duality can trap us in a thicket of fantasy that can be avoided only by being careful to **not** to ascribe to quantum objects a **preexisting** particle or wave character, but instead to do so only in terms of the **behavior** exhibited in measurements we make upon them. That is, if in a measurement a quantum object appears as a particle, that does **not** mean that the object behaved as a particle **before** we measured it. In particular, quantum mechanics tells us **nothing** about what quantum objects are before we make measurements on them.

For example, if you find yourself visualizing an electron, say, either as a particle or as a

wave, then you are indulging in fantasy as far as quantum mechanics is concerned. Please keep this in mind when we speak of something as behaving as a wave or as a particle.

In particular, we are now going to see how to represent quantum objects as being localized in space. This is quite different than to say (incorrectly) that we are now going to see how to represent localized quantum objects, for quantum objects have no such characteristic except in terms of measurements made on them

We might agree that perhaps an electron does behave as a wave inside an atom. But surely it behaves as a particle as it traces out images on the insides of the cathode rays tubes of our televisions and CRT computer monitors. (Remember, as noted above, such language is unjustified by quantum mechanics, but seems reasonable to us because objects in our everyday world can be talked about as *either* waves or particles.)

In fact it *is* possible to reconcile a wave picture and a localized particle picture, by using the property of waves that they oscillate between *positive and negative values*, for this means waves can cancel each other out (*destructive interference*) or reinforce one another (*constructive interference*), depending on their relative wavelengths and phases. We can use wave interference to construct combinations of wavefunctions—a so-called *wavepacket*—that can have any degree of localization that we choose. Highly localized particles, in particular, are wavepackets composed of wavefunctions with so many different wavelengths that the wavefunctions interfere destructively everywhere except in a small region of space. This small region where the resulting probability amplitude is large is "where the particle is."

### Wavepacket example

The equal mixture of  $\psi_1(x, t)$  and  $\psi_2(x, t)$  that we used to understand how light makes an electron jiggle is a simple example of a *wavepacket*—a combination of waves of different energies and so different wavelengths. That example illustrated two key aspects of all wavepackets. The first, which we have focused on earlier, is that, because they are composed of wavefunctions with different energies, wavepackets *move*. The second, which we investigate now, is that the wavepacket has a different shape than its parts, owing to wavefunction interference. It is this second aspect that allows us to tailor a wavepacket to be localized over a narrow region.

Remember, the key idea is that the more different wavelengths we combine in a wavepacket, the more localized is the resulting wavepacket and so probability density. We have already seen how mixing wavefunctions of different energies results in motion, so here we focus instead on the effect, for a given time, of the number of wavefunctions we add to the mixture.

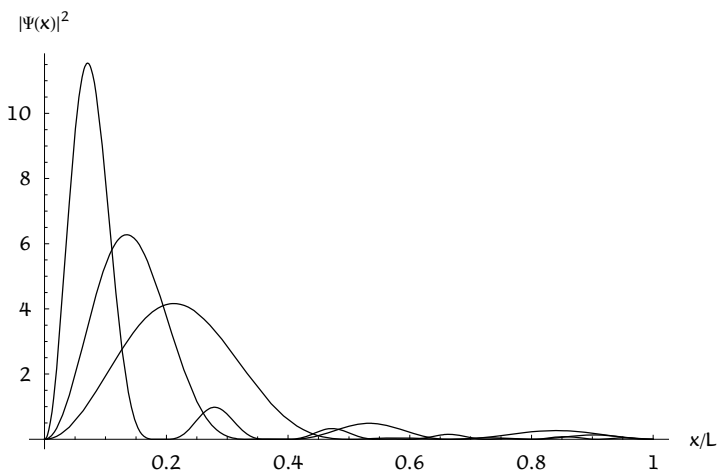
For convenience, let's set the value of time to be  $t = 0$ . Then a simple extension of the two-wavefunction mixture is a mixture

$$\Psi(x) = \frac{1}{\sqrt{N}} \{ \psi_1(x, 0) + \psi_2(x, 0) + \psi_3(x, 0) \dots + \psi_N(x, 0) \}$$

of  $N$  lowest energy wavefunctions  $\psi_j(x, 0) = \sqrt{2/L} \sin(j \pi x / L)$  of a particle confined to the region  $0 \leq x \leq L$  but free to move within that region. (The factor  $1/\sqrt{N}$  makes the total probability computed from the wave packet equal to one.) For example, here is the wavepacket consisting of equal amounts of the three lowest-energy wavefunctions

$$\Psi(x) = \sqrt{\frac{2}{3}} \{ \sin(\pi x / L) + \sin(2 \pi x / L) + \sin(3 \pi x / L) \}.$$

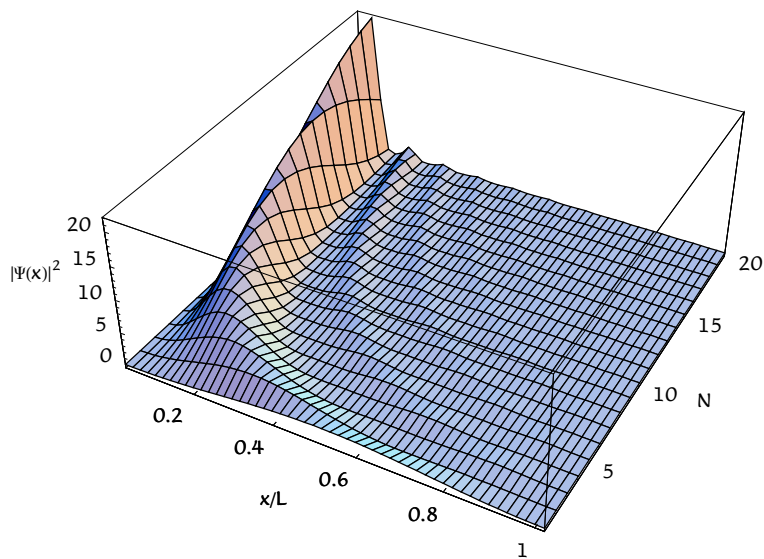
To illustrate the effect of increasing the number of different wavefunctions in the wavepacket, here are the probability densities corresponding to this wavepacket, and to the wavepackets consisting of equal amounts of the five and ten lowest-energy wavefunctions.



Probability density of wavepackets consisting of equal amounts of the three (lowest leftmost peak), five, and ten (highest leftmost peak) lowest-energy wavefunctions of a particle confined to the one dimensional region of  $0 \leq x \leq L$ .

We see that as the number of different wavelengths increases, the wavepacket becomes increasingly peaked and so localized near the left edge of the region.

We can illustrate the effect of the number of different wavefunctions in the wavepacket on its localization more strikingly with a surface plot of probability density versus number of wavefunctions.



Probability density of wavepackets consisting of equal amounts of the  $N$  lowest-energy wavefunctions of a particle confined to the one dimensional region of  $0 \leq x \leq L$ .

## Heisenberg uncertainty principle

The surface shows that the peaks in the probability density becomes sharper and sharper as more and more different wavelength wavefunctions are combined. In the extreme, to represent a highly localized particle, very many different wavelengths need to be combined. But this in turns means, by the de Broglie relation,  $p = h/\lambda$ , that very many different momenta,  $p$ , need to be combined. That is, the price we pay to localize a particle to a within a small region is to lose knowledge of the momentum of the particle. That is, the uncertainty in where the particle is,  $\delta x$ , is inversely proportional to the uncertainty in the momentum,  $\delta p = h/\delta\lambda$ , of the particle.

The precise relation, known the *Heisenberg uncertainty principle*, is

$$\delta x \delta p \geq \frac{h}{2\pi}.$$

It means that there is a fundamental limitation on how precisely we can localize a particle. If we are very precise, then there is a very large uncertainty in the momentum (and so speed and direction) of the particle, so that a short time later we will not know where the particle will be. Conversely, if we specify the momentum of a particle very precisely, then its wavepacket will contain only a few different wavelengths and so be very spread out, so that we will not know where the particle is.

For these reasons, it is not meaningful to ask what is the de Broglie wavelength of a localized particle, for such a particle is composed of many different wavelengths. Similarly, it is not meaningful to ask where a particle is that has a precisely defined energy and so just a single de Broglie wavelength.

It is in this way that we see that wave and particle viewpoints a *mutually incompatible descriptions of reality* at the quantum level. This is the profound consequence of the wave nature of matter (and so also of the particle nature of light).

