Atoms, light, and their interaction

Notes on General Chemistry

http://quantum.bu.edu/notes/GeneralChemistry/AtomsLightAndTheirInteraction.pdf
Last updated Tuesday, January 22, 2008 15:51:38-05:00

Copyright © 2007 Dan Dill (dan@bu.edu)
Department of Chemistry, Boston University, Boston MA 02215

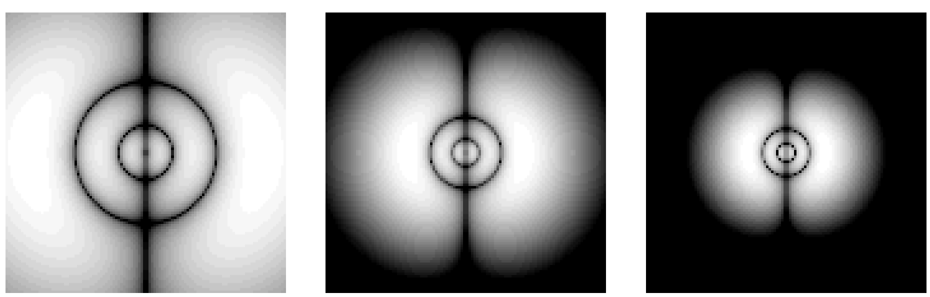
■ The quantum picture atoms: like a voice box

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 form?

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 of 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 changes 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 ϕ (phi) for the *mathematical frequency* of the electron wave, and the Greek letter ν (nu) for the *physical frequency* of the electron cloud.

The general rule relating physical frequency, ν_{cloud}, to the frequencies of its electron waves, ϕ_1 and ϕ_2, is

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

Copyright © 2007 Dan Dill (dan@bu.edu). All rights reserved

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

wave	ϕ_{wave} (Hz)
6	-9.133×10^{13}
5	-1.315×10^{14}
4	-2.055×10^{14}
3	-3.653×10^{14}
2	-8.22×10^{14}
1	-3.288×10^{15}

Frequency, ϕ, 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	ν_{cloud} (Hz)
2, 1	2.466×10^{15}
3, 1	2.923×10^{15}
4, 3	1.598×10^{14}
6, 2	7.307×10^{14}

Frequency, ν_{cloud}, of electron clouds made by combining pairs of hydrogen atom electron waves

> Calculate the frequency of motion of the electron clouds made by combing the second electron wave with the third, fourth and fifth electron wave. Answer: 4.567×10^{14} Hz, 6.165 "×\!\(10\^\"14\"\)Hz, 6.905×10^{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.

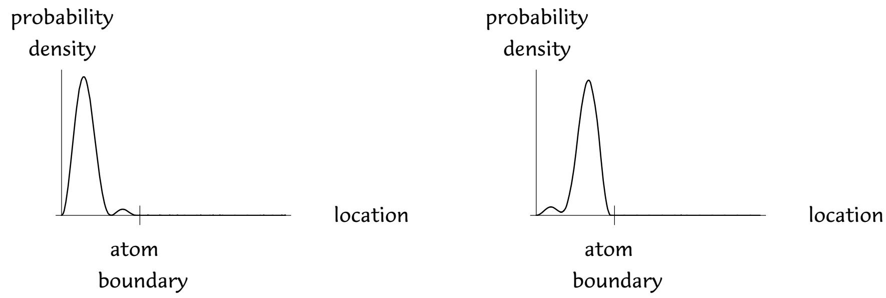
Attached and detached electron waves and the motion of their electron clouds

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 ϕ_1, ϕ_2, ϕ_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 ϕ_1 and ϕ_2. The electron cloud oscillates back and forth (that is, the electron cloud remains attached to the atom), with frequency $\nu_{\text{cloud}} = \phi_2 - \phi_1$;

Copyright © 2007 Dan Dill (dan@bu.edu). All rights reserved



Snapshots of an electron cloud formed by mixing attached electron waves of different frequencies, ϕ_1 and ϕ_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

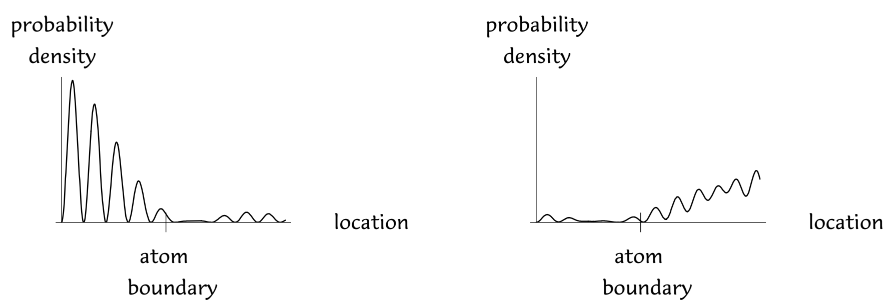
http://quantum.bu.edu/notes/GeneralChemistry/LightMatterInteraction/eAttached.gif

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 detached electron wave at all frequencies; we say that detached electron waves are *not quantized*.

For example, the threshold frequency of 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?

Copyright © 2007 Dan Dill (dan@bu.edu). All rights reserved

> 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: 6.071×10^{14} Hz, 4.473×10^{14} Hz, 3.733×10^{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 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 as if the light is a dance partner that wants to dance to one kind of music while the electron cloud is 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.

Copyright © 2007 Dan Dill (dan@bu.edu). All rights reserved

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 energy of the moving electron cloud. We call this transfer of energy *absorption of light*.

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

> A typical light intensity is 10 W = 10 J/s. Calculate the energy loss of the light of frequency is $\nu_{\text{light}} = 6 \times 10^{14}$/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: 4×10^{-7} 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 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 in light-matter interaction

As we have described, just as different people have different sounding vocal chords, each type of atom has it own set of electron waves, consisting of attached waves with quantized frequencies, ϕ_1, ϕ_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, ϕ_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,

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

Copyright © 2007 Dan Dill (dan@bu.edu). All rights reserved

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

$$\text{IE}_1 = h\,|\,\phi_{\text{threshold}} - \phi_1\,|, \ \text{photoionization}$$

> The ionization frequency of hydrogen atoms is 3.288 "×\!\(10\^\"15\"\)Hz. Calculate the ionization energy, in Joules. Answer: 2.179×10^{-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, ϕ_{detached}, above $\phi_{\text{threshold}}$. Since

$$\nu_{\text{light}} = \,|\,\phi_{\text{detached}} - \phi_1\,| = \,|\,\phi_{\text{detached}} - \phi_{\text{threshold}}\,| + |\,\phi_{\text{threshold}} - \phi_1\,| = \text{KE}/h + \text{IE}_1/h,$$

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

$$\text{KE}_1 = h\,\nu_{\text{light}} - \text{IE}_1.$$

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: 1.405×10^{-19}J.

> The kinetic energy of the electron, $m\,u^2/2$, is proportional to the square of the speed, u, of the electron. Calculate the speed of an electron ejected with kinetic energy 1.405×10^{-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 move 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*,

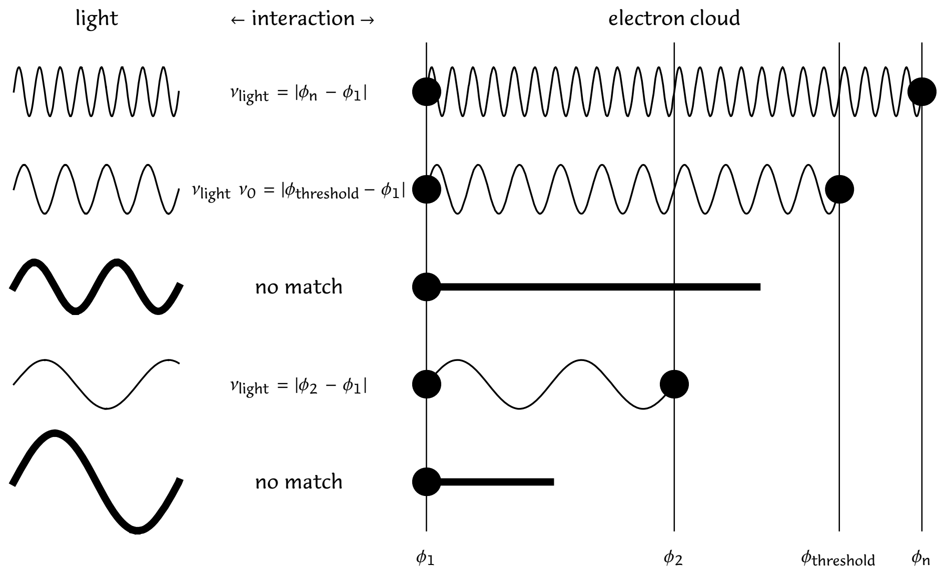
$$\nu_0 = \,|\,\phi_{\text{threshold}} - \phi_1\,|, \ \text{photoelectric effect}$$

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 light frequency with frequency the electron cloud oscillation (the difference of the frequencies of its component electron waves).

Copyright © 2007 Dan Dill (dan@bu.edu). All rights reserved



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, ν_{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, $\phi_{threshold}$, upwards every electron wave frequency is possible (since the electron is no longer attached); for clarity, in addition to $\phi_{threhold}$, only once such frequency, marked ϕ_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 and 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.

Copyright © 2007 Dan Dill (dan@bu.edu). All rights reserved

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 $|\phi_n - \phi_1|$ 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.

■ The 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.

Copyright © 2007 Dan Dill (dan@bu.edu). All rights reserved

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 lose. 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 ν_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, $m\,u^2/2$, 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, ν_{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

Copyright © 2007 Dan Dill (dan@bu.edu). All rights reserved

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 Φ (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, ν_0, and wavelength, $\lambda_0 = c/\nu_0$, needed to photoionize a hydrogen atom. Answer: 3.29×10^{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 that the hydrogen atom characteristic frequency, IE/h. Calculate the speed of the ejected electron, in m/s. Recall that kinetic energy is $m\,u^2/2$, 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 $\Phi_{\text{Cr}} = 7.2\times10^{-19}$ 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.

Copyright © 2007 Dan Dill (dan@bu.edu). All rights reserved

> 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?

Copyright © 2007 Dan Dill (dan@bu.edu). All rights reserved