Spectroscopy & Quantum Dots

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Introduction

Today you will explore some of the physics that underlies spectroscopy and the intriguing modern materials called quantum dots—a sort of synthetic atom! Along the way, you will learn about how we perceive color, explore the quantum mechanical interpretation of light as photons, and learn about some of the common ways in which light is absorbed by and emitted by matter. The spectroscopic techniques we will explore today are used for characterizing systems as diverse as distant stars or newly discovered exoplanets, or for understanding the structure and function of proteins, DNA and novel electronic materials being explored for the next generation of solar cells and computers.

Quantum dots and the photoelectric effect: quantum physics meets light

Our first goal is to understand the physics of how light is absorbed by matter. All of our detectors for light (be it visible, infrared, ultraviolet, x-ray or gamma ray) fundamentally make use of a phenomenon called the ***photoelectric effect*** to measure light. The photoelectric effect involves light being absorbed by an atom (or collection of atoms) and ejecting a free electron. Even our light-sensing cone and rod cells in our eyes work via this mechanism. The photoelectric effect was also the experiment that conclusively established that light is absorbed by matter in discrete packets called ***photons***. Unlike in our wave picture of light, where any amount of energy could be exchanged between a wave and another system, light can only be absorbed or emitted as particles with discrete chunks of energy called ***quanta*** (*quanta* is the plural, while the singular is ***quantum***).

We can understand some very basic quantum mechanics using the emission spectrum of ***quantum dots***, very tiny clusters of atoms of a semiconductor (ours are indium phosphide) only nanometers in radius. (Fig. 1(a)) Because of their tiny sizes and simple structures, these systems have been compared to artificial atoms. Quantum dots absorb and emit light at wavelengths determined by their radius, allowing them to be manufactured to have interesting optical and electronic properties. Researchers like Prof. Josh Schrier (Haverford Chemistry) are exploring quantum dots as possible systems for harvesting light for solar energy, or for novel computing devices. They are also widely used in biology as bright labels for various cellular and molecular processes. (Fig. 1(b)) We will see how simple ideas you've learned about waves can allow us to predict how the light emitted by quantum dots relates to their size.
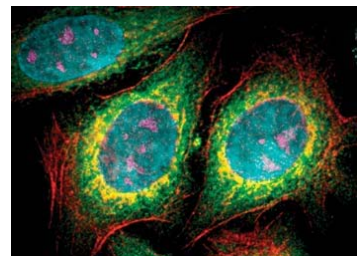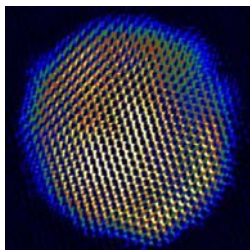
(a)   (b)   (c)

Figure 1. (a) Quantum dot are nanometer-sized clusters of semiconductor. (b) Vials of quantum dots emit light with wavelengths determined by their size. (c) Quantum dots (brightly glowing points of light) are used to label structure in biology. Unlike fluorescent chemicals, they can be manufactured to emit any wavelength of light, they are extremely bright, chemically inert and never bleach out under light exposure. Here, they are being used to label the nucleus blue, mitochondria yellow, microtubules green and actin filaments red. (http://nanoe.ece.drexel.edu/wiki/images/7/7a/Quantum_dots_glowing.jpg; http://www.sciencedaily.com/releases/2009/02/090218141959.htm; Quantum Dot Corp.., Hayward, CA)

Just as light behaves as both waves and particles in different settings, it's possible to show that electrons also have a wave-like character that we can observe in various settings. For example, if electrons are bound into a quantum dot, they have a lower energy within the quantum dot than outside it. This is plotted below. We can describe the wave-like behavior of the electron by using a quantity called the electron's wavefunction. Just as the wavefunction of a wave on a string describes the displacement of the string as a function of time and space, f(x,t), the electron's wavefunction, ψ(x,t), can be used to compute properties of the electron as function of space and time. (Fig. 2) (Here ψ is the Green letter psi.) In particular, the magnitude squared of the wavefunction, $|\psi(x,t)|^2$, can be used to compute the *probability* of finding the electron at time t in the neighborhood of position x. Just as we can have a wave on a string that is confined to a guitar string, we can have a wavefunction of an electron that is confined to the quantum dot. Within the quantum dot, the electron is free to move; its energy is only due to kinetic energy. Outside of the quantum dot, its potential energy is so high there is zero probability of finding the electron there. As a result, ψ(x,t) = 0 outside. For the wave on the string, we had nodes (points of zero amplitude) at the ends of the string. In the quantum dot, there are nodes in $|\psi(x,t)|^2$ at the edges of the quantum dot. The guitar string with length *L* has many possible modes of vibration, described by $n\lambda_n/2= L$, where *n* = 1, 2, 3, etc. , and the electron's wavefunction must obey the same constraint. However, for the electron we have one additional relationship.

Lowest mode: $\lambda / 2 = L$ $\lambda = 2L$

2nd harmonic: $\lambda = L$

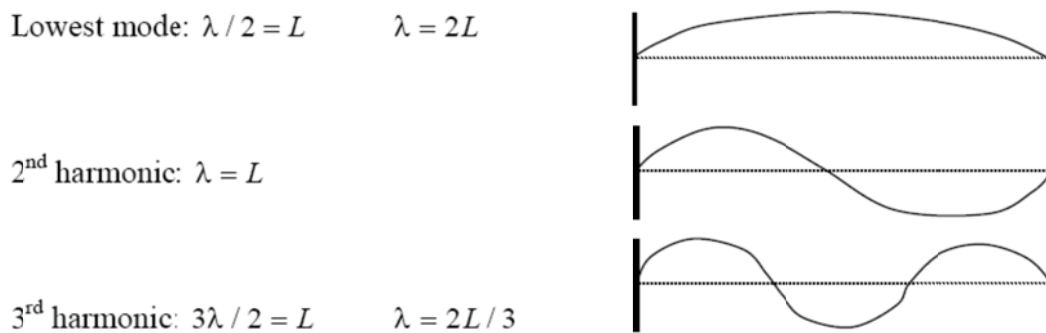3rd harmonic: $3\lambda / 2 = L$ $\lambda = 2L / 3$

Figure 2: Timothy McKay Physics for the Life Sciences. The standing waves on a string are indexed by the harmonic number n = 1, 2, and 3 (top to bottom), which corresponds to the quantum number, n, for electrons in a quantum dot. The plot of the electron wavefunction ψ(x) has the same functional form as

the shape of a standing wave on a taut string. (right). (Tim McKay, Introductory Physics for the Life Sciences, 2010).

We also know from experiment that electrons have momentum, *p*, that is related to their wavefunction's wavelength, λ_n, by $p = h/\lambda_n$, where $h = 6.626 \times 10^{-34}$ Joule sec, a quantity called Planck's constant. Since the electron's energy is only kinetic energy, we have:

$$E_n = \tfrac{1}{2} mv^2 = p^2/2m \qquad\qquad\qquad\qquad\qquad \text{Eq. 1}$$

$$= (h/\lambda_n)^2/2m$$

$$= (h/(2L/n))^2/2m$$

$$= n^2 h^2/(8\, m\, L^2)$$

Where *m* = electron mass and *L* is the width of the quantum dot. We see that the allowable electron energies also are defined by *n*, the number of half-wavelengths fitting into each quantum dot. We say that the energies and states of the electron are **quantized**—discrete and countable using a **quantum number**, *n*.

There is one more phenomenon to account for: electrons in the quantum dot initially start out tightly bound to atomic nuclei, in what is called the **valence band**, so they are not free to move about. The above physics only applies after we have first given an electron a fixed amount of energy, called the **gap energy**, E_{gap} sufficient to put it into a state where it is free to move about; these electrons then are in what is called the **conduction band**. (We'll assume our valence band electron has zero energy to start.) This gap energy gets added to the kinetic energy to describe the total energy of the free electrons:

$$E_{\text{total } n} = E_{gap} + E_n = E_{gap} + n^2 h^2/(8\, m\, L^2) \qquad\qquad\qquad \text{Eq. 2}$$

Note two important facts about this result: 1) there is a minimum energy (for n = 1) to create a free electron in the conduction band and 2) this energy E_n depends upon quantum dot size L as L^{-2}. Similar arguments can be used to derive the allowable energies for atoms such as hydrogen and others, but this gives you a good feeling for how all of these calculations go.

(a)   (b)
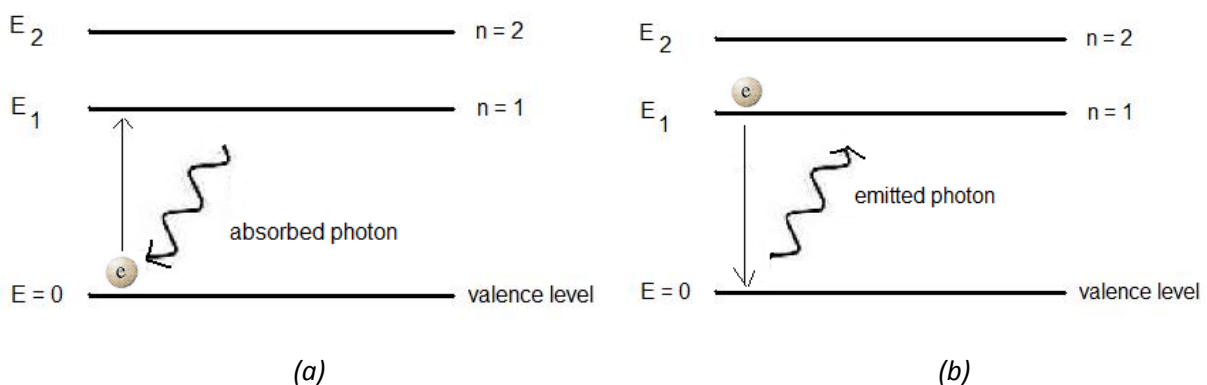
Figure 3. Illustration of the relative energy levels of the valence and conducting states of a quantum dot, showing the energy gap. (a) Absorption of light leads to an electron being excited and making a transition into a higher energy state. (b) Emission of light results from de-excitation, where an electron makes the transition into a lower energy state.

How does all this relate to the light absorbed and emitted by quantum dots? Light interacts with the electrons in materials (including quantum dots) by causing them to make transitions between these quantized energy states. Light is absorbed by matter in packets called photons. We say (amusingly) that the photons **excite** the electrons to higher energies. (Fig. 3(a)) Each photon has an energy determined by its wavelength (but not its intensity) as:

$$E_{photon} = hc/\lambda \qquad\qquad \text{Eq. 3}$$

(Note that now the wavelength, λ, is that of the photon, not the electron's wave!) When electrons absorb light their energy increases by exactly the energy of the photon; when they emit light, their energy decrease by the photon's energy. This means that for photons to be absorbed by the quantum dot, their energy has a *minimum* value of:

$$E_{photon} = hc/\lambda_{max} = E_{\text{total 1}} = E_{gap} + E_1 = E_{gap} + n^2\, h^2/(8\, m\, L^2)\,, \qquad\qquad \text{Eq. 4}$$

since the lowest energy to create a photon in the quantum dot is that for n = 1. This means that the photons will have a maximum wavelength, λ_{max}, since their energy can be no lower than this value. However, higher energy photons can also be absorbed, corresponding to n = 2 and higher; they will have wavelengths shorter than λ_{max}.

The overall phenomenon of light absorption by matter in this fashion is called the photoelectric effect. It makes specific predictions: 1) The intensity of the incident light doesn't influence whether or not absorption takes place, only the wavelength. 2) There is a maximum wavelength at which absorption can take place. Light with longer wavelengths cannot be absorbed, no matter how intense. Light with shorter wavelengths can also be absorbed, though (for example, it could result in electrons making the transition into higher *n* states; there are also more tightly bound valence states that could be excited.)

Now we will consider the emission of light by matter, again using quantum dots as an example. When electrons in quantum dots make the transition from one energy state to another with a lower energy, this can result in the emission of a photon with energy equal to the electron's change in energy ΔE. (We now say the electron is **de-excited**.) (Fig. 3(b)) In that case, we have:

$$E_{photon} = hc/\lambda = \Delta E \qquad\qquad \text{Eq. 5}$$

We again see there is a direct relationship between wavelength of the emitted light and the change in electron energy. In one particularly useful example, when you have quantum dot, you can have an electron in the energy state with n = 1 make the transition to the valence band where E = 0, so then we have:

$$E_{photon} = hc/\lambda = E_{gap} + n^2\, h^2/(8\, m\, L^2) \qquad\qquad \text{or equivalently:}$$

$$1/\lambda = E_{gap}/(hc) + n^2\, h/(8\, m\, c)\, \times (1/L^2)$$ Eq. 6

This electronic transition describes how light is emitted in quantum dots, but also in LED's (light emitting diodes) widely used in lighting, in diode lasers used in supermarket scanners, CD players and laser light shows. This theory makes the prediction that the reciprocal of the wavelength of emitted light, $1/\lambda$, should vary with quantum dot size L as $1/L^2$ and that we also can measure the gap energy by fitting $1/\lambda$ vs. L using Eq. 6. (While our theory has considered only one spatial dimension, a full three-dimensional theory of quantum dots contains little new physics and results in a very similar formula with the same dependence on the gap energy and quantum dot diameter, L.)

To quantify these behaviors, we use **spectrometers**, devices that measure the absorption (or the emission) of light by a sample. The operation of one type of spectrometer is shown in Fig. 4 below. (Other spectrometers operate using the same Fourier transform ideas you encountered in our Sound Lab. If you measure instead the time-varying intensity of light, you can use a Fourier transform to determine the frequency spectrum of the light; this is currently feasible only for lower frequencies.) The fraction of light absorbed (or the intensity of light emitted) is then plotted vs. wavelength to make up what is called an **absorption** (or **emission**) **spectrum** (plural **spectra**).
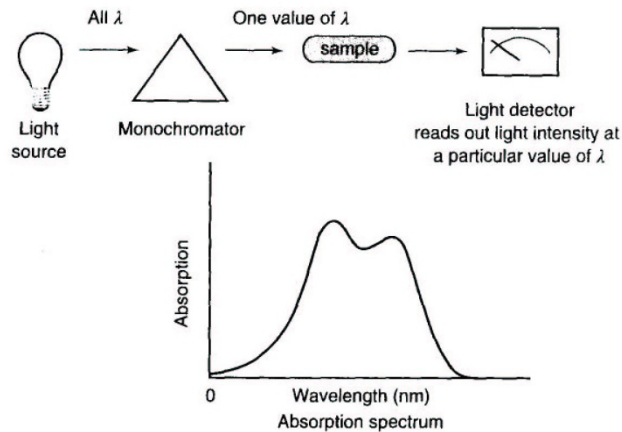

Figure 4. Schematic drawing of the operation of a spectrometer

The physics of energy levels for electrons bound to atoms and molecules is determined by similar arguments. For these systems, we must consider both the electrons' kinetic energy and electrostatic potential energy since they interact with the central nucleus and each other. However, the same quantized energy levels result, indexed by quantum numbers playing a role similar to n. As a result, when gases are heated to high temperatures, their constituent atoms also undergo the same electron excitation processes, with thermal energy from collisions boosting electrons to higher energy levels. When the electrons de-excite and return to their lower energy levels, they emit photons with wavelengths determined by the energy difference between energy levels. The result is emission spectra with discrete wavelengths that are peculiar to each chemical element or molecule making up the gas.

You'll see examples of this in our lab; indeed this form of spectroscopy is widely used in astronomy to identify the constituents of hot gases in stars or other astrophysical objects.

Pre-lab exercise 1: Compute an estimate for the emitted wavelength for cadmium selenide quantum dots with L = 3 nm and E_{gap} = 1.73 eV. (You will have to look up some other values.) What part of the spectrum does this correspond to and what color would you perceive the emitted light to have?

Absorption of light & Beer's law:

Now that we have the quantum basis of absorption down, it's important to appreciate one more complication of how *collections* of molecules or atoms absorb light. This relationship underlies all spectroscopy and is called **Beer's Law** (also called the Beer Lambert Law; it's a scientist's name, not the beverage!)

Let's assume we have a dilute solution of our absorbing molecules upon which we shine an initial intensity I. Light is partly absorbed and partly transmitted by the solution. For a very dilute solution that is very weakly absorbing, the amount of light absorbed depends upon the number of molecules in solution. This is proportional to concentration, c, and the length of the light's path in the solution, Δx. The intensity of light is diminished by:

$$\Delta I = - c\ \Delta x\ \varepsilon\ I \qquad\qquad\qquad\text{Eq. 7}$$

Where ε (called the extinction coefficient) is some constant of proportionality that describes how absorbing our individual molecules are at this wavelength of light.

This relationship holds for so few molecules in solution that the absorption of light is very tiny. What about the case where appreciable absorption takes place? In that case we can rewrite our equation as:

$$\Delta I\ /\ \Delta x\ = - c\ \varepsilon\ I \qquad\qquad\qquad\text{Eq. 8}$$

Which becomes in the limit as $\Delta x \rightarrow$ 0,

$$dI\ /\ dx\ = - c\ \varepsilon\ I \qquad\qquad\qquad\text{Eq. 9}$$

The solution to this equation is an exponential:

$$I(x) = I_o\ exp(-c\ \varepsilon\ x)\ , \qquad\qquad\qquad\text{Eq. 10}$$

where I_o = the incident intensity (the value when x = 0). This relationship describes how intensity, $I(x)$, varies with distance x inside an absorbing solution with concentration c and extinction coefficient ε. The quantum physics (and chemistry!) of the absorbing molecules is described by ε, while c and x define how many molecules the light encounters.

This same exponential fall-off of radiation with distance holds true in x-ray imaging, nuclear medicine and radiation therapy, laser surgery and ultrasound imaging. As a result, it is of widespread importance in medicine as well as physics.

Prelab problem 2: (a) Prove by taking the derivative of Eq. 10 that Eq. 9 is true. (b) Then, solve for the absorbance, A, a quantity used often in spectroscopy, defined as: $A = - \ln (I/I_o)$ in terms of x, c and ε. (Different scientific publications report spectroscopic results in terms of A, ε and $c\varepsilon$, so it is useful to get these definitions straight.)

Experiment 1A: Quantum dots and the photoelectric effect

You have been provided with a series of LED (light emitting diode) light sources and a set of quantum dots. (Fig. 5) The latter are in a set of 4 vials (do not open!) sorted by size. You can turn on the LED sources by sliding a little switch on the side; these can be turned on momentarily or clicked so they stay lit. To excite the quantum dots, hold the LED to the hole under each vial. Try this for the red, green and blue LED sources. Why do the quantum dots only glow when exposed to one of these colors? Which one? Explain using the photoelectric effect.

Figure 5. (left) Quantum dots in vials (each vial holds a different size quantum dot) being excited by a blue LED source. (CENCO Scientific) (center) SpectraVis Plus spectrometer. The hole accommodates cuvettes for absorption spectroscopy. (right) A fiber optic accessory can be inserted with its black box like end into the cuvette hole in the spectrometer (aligning the arrows) for emission spectroscopy. Point the fiber optic end at the light source to measure a spectrum.

The largest quantum dots will glow red-orange when excited, while the smallest glow green. Their sizes are on your report form. (While we will not do it today, you could find out the sizes by using experimental techniques that measure size independently, such as electron microscopy or light scattering.)

Using the LED you found from the first step and the array of quantum dots, stimulate the quantum dots to emit light by placing the LED below each vial at a time. (See Fig. 5) You will measure the emission spectrum two ways. First, you will use diffraction gratings like those we studied in the lab on interference and diffraction to visualize the wavelength distribution of light. Your lab instructors will show you how to see an interference spectrum using these gratings. Then, you will use a SpectraVis Plus spectrometer (Fig. 5) connected to your computer using the USB cable provided. Start LoggerPro once you have the devices connected and choose to setup the spectrometer from the Experiment/Connect

Interface/Spectrometer menu. After you have chosen the spectrometer, your screen should look like the figure below. Then, choose Experiment/Calibrate and choose "Disable Calibration". On your y-axis, choose "autoscale from zero". To do absorption spectrum, you would insert cuvettes full of solution into the hole on the spectrometer. For now we'll use a fiber optic accessory (see figure) inserted with its black box-like-end into the cuvette hole in the spectrometer (aligning the side using the white arrows) for emission spectroscopy. You then point the fiber optic end at the light source to measure an emission spectrum. Make sure you are working in a darkened room at this point. Click Collect in LoggerPro and try this now for the quantum dots while you excite them with the LED. Click Stop to stop collecting and save your spectrum for your report. Adjust your axes if necessary to get a good display.
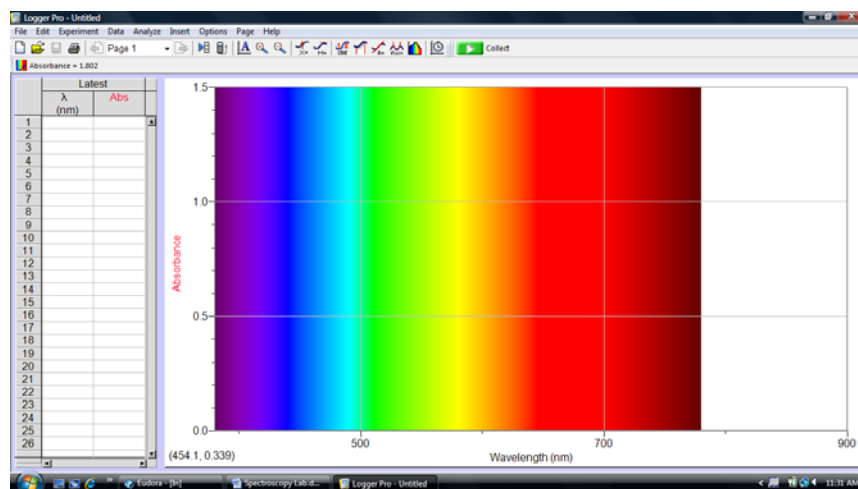

Fig. 7. The display in LoggerPro for your spectroscopy experiments.

Measure the emission spectrum of each quantum dot solution while it is being stimulated. Also measure the emission spectrum of the exciting LED so you can control for the light from it. Explain what you see with your diffraction grating in each case. Using LoggerPro, find the peak emitted wavelength for each size quantum dot. Using Origin, plot 1/wavelength vs. 1/(radius)^2, and using Eq. 6 from the introduction, determine your gap energy. Does your measured data follow the predicted dependence (that is, is this plot linear within error bars?) How does your gap energy agree with quoted values? (Do a web search on indium phosphide to find out.)

Experiment 1B: Emission Spectra for various sources

You will now look at the light emitted by a heat lamp, black light, UV lamp, a mercury vapor lamp, and two sources of "white" light: a regular incandescent lightbulb and a compact fluorescent lightbulb. We also have several atomic vapor sources, including hydrogen, helium, neon and mercury. (The lasers are too intense, so please do not use these!) Some of these emit light with a continuous distribution of wavelengths, while others will have discrete emission lines like the quantum dots.

Now, observe a variety of emission sources using first a diffraction grating, then your spectrometer and its fiber optic probe. For each source, first observe how its light is decomposed into different wavelengths by the diffraction grating; record which sources have continuous distributions of emitted

wavelength and which have discrete emission spectra with distinct lines. Then, record the emission spectra of each source using your spectrometer. How do the atomic vapor sources differ from each other and from the "white" lightbulbs. How do the heat lamp and black light emission spectra differ from those of the "white" lightbulbs? Explain how the last two sources generate what appears to be "white" light to humans. How are their emission spectra are similar and different? Why do your eyes still see them both as "white"?

Physics of Color & Spectroscopy Report Form

Experiment 1: Photoelectric effect & Quantum Dots

Why do the quantum dots only glow when exposed to one of the red, green or blue LED's (which one?) Explain using the photoelectric effect.

Quantum dot radius (nm)	Peak emitted wavelength (nm)
2.37 (glows green)	
2.53	
2.72	
2.92 (glows red)	

Attach the plot indicated in the lab manual and show your fits. What is the energy gap? How does it compare to the accepted values for this material? (You will need to convert units and find the error bars in your measured value.) How big (or small!) would your quantum dots have to be to emit blue

Describe your emission spectra for these sources:

Incandescent lightbulb

Compact fluorescent lightbulb

How do the first 2 light sources generate "white" light? Explain in words, also using their emission spectra, how their emission spectra are similar and different, and why your eyes still see them both as "white".

Heat lamp (how does it differ from the incandescent bulb in particular?)

Black light (how does it differ from the incandescent bulb in particular?)

Atomic vapor sources:

Hydrogen

Helium

Neon

Mercury