# Light & Matter Interactions

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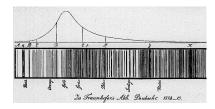
# I. Spectral Lines



William Hyde Wollaston [1766 - 1828] generated a solar spectrum using a prism, and noticed black lines in some sections. "The line A that bounds the red side of the spectrum is somewhat confused, which seems in part owing to want of power in the eye to converge red light. The line B, between red and green, in a certain position of the prism, is perfectly distinct; so also are D and E, the two limits of violet. But C, the limit of green and blue, is not so clearly marked as the rest; and there are also, on each side of this limit, other distinct dark lines, / and g, either of which, in an\_imperfect experiment, might be mistaken for the boundary of these colours."

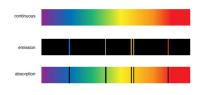
Reproduced from Philosophical Transactions of the Royal Society of London, vol. 92 (1802), p. 380 (Plate XIV).

This was the burgeoning field of **spectroscopy**.



Joseph con Fraunhofer [1787-1826] rediscovered the lines 15 years after Wollaston. If the physical origins of the lines were understood, then we could learn more about the sun and what makes it work.

Denkschriften der K. Acad. der Wissenschaften zu München 1814-15, pp. 193-226.



Different types of spectra: continuous, emission, and adsorption.

- 1) Continuous emission spectra show all the frequencies of light, which no breaks in the spectrum
- 2) An emission spectra shows only the frequencies emitted by the object in question
- 3) An absorption spectrum shows all the frequencies that are not absorbed by the material in the lights path. Black lines are present where certain frequencies have been absorbed.

### I.I Kirchoff's Laws

- 1. A hot, dense gas or hot solid object produces a continuous spectrum with no dark spectral lines
- 2. A hot, diffuse gas produces bright spectral lines (emission lines)
- 3. A cool, diffuse gas in front of a source of a continuous spectrum produces dark spectral lines (**absorption lines**) in the continuous spectrum.

#### Kirchoff



Gustov Kirchoff [1824-1887]

Kirchoff and Bunsen noted that a portion of the dark lines visible in the solar spectrum were the same as 70 bright lines found in the emission spectrum of iron vapor.



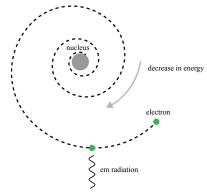
If we let m=2 in the above equation, then setting  $n=3,4,\ldots,6$  yields the following wavelengths for the expected emissions.

n	$\lambda$ [nm]
3	656.3
4	486.1
5	434.0
6	410.2
7	397.0

The equation shown was found by trial and error by Johann Balmer [1825-1898] and could predict the position of emission lines from hydrogen.

However, even though the equation could predict the lines, there was no physical basis for the equation. It wasn't derived from any principles or theory.

## 1.3 Classical Atoms



expect it to undergo centripetal acceleration, which in turn would cause it to loose energy, and eventually spiral into the nucleus. Something must be wrong!

If an electron in an atom were modeled as a planet-like orbiter, then we would

According to Maxwell's laws of EM, a charge moving in a circle should radiate energy because of the centripetal acceleration.

### 1.4 The Bohr Model

If the energy (or angular momentum) of the electrons where quantized however, then that would suggest the orbits could be stable.

#### The Bohr Radius

Starting with Coulomb's Law and F = ma:

$$-\frac{(Ze)e}{4\pi\epsilon_0 r^2} = -\frac{m_e v^2}{r} \tag{2}$$

Then taking the kinetic energy of the orbiting particle:

$$K = \frac{1}{2}m_e v^2 = \frac{Ze^2}{8\pi\epsilon_0 r} \tag{3}$$

The potential energy is

$$U = -\frac{Ze^2}{4\pi\epsilon_0 r} \tag{4}$$

Summing the kinetic and potential to get the total energy:

$$E = K + U = \frac{Ze^2}{8\pi\epsilon_0 r} - \frac{Ze^2}{4\pi\epsilon_0 r} = -\frac{Ze^2}{8\pi\epsilon_0 r}$$
 (5)

The Bohr model suggests that instead of the total energy being capable of taking on any value, instead it can only take on quantized integer multiples of a constant value. Or, in terms of the angular momentum:

$$L = m_e v r = \frac{nh}{2\pi} = n\hbar \tag{6}$$

Solving for v and combining this with the kinetic energy from equation (3) we'll obtain for the radius, r:

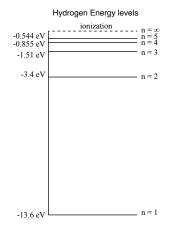
$$r_n = \frac{4\pi\epsilon_0\hbar^2}{Ze^2m_e}n^2 = \frac{5.29 \times 10^{-11} \text{ m}}{Z}n^2$$
 (7)

Here, n is called a quantum number and can take integer values starting with 1. Z is the number of protons in the nucleus. If n = 1 and Z = 1, which corresponds to the lowest energy level of the hydrogen atom,

$$r_{\text{Bohr}} = 5.292 \times 10^{-11} \text{ m} = 0.529 \text{Å}$$
 (8)

 $(1\text{\AA} = \text{one tenth of a nanometer or } 1 \times 10^{-10} \text{ m})$ 

## 1.5 Lowest energy



 $\emph{\textbf{E}}_{1}$  is the lowest energy of the hydrogen atom: -13.6 eV.

The kinetic energy was:

$$K = \frac{Ze^2}{8\pi\epsilon_0 r} \tag{9}$$

Using the Bohr radius, we can obtain:

$$E_n = -\frac{m_e e^4}{32\pi^2 \epsilon_0^2 \hbar^2} \frac{1}{n^2} = -13.6 \text{ eV} \frac{1}{n^2}$$
 (10)

The energy levels of the hydrogen atom.

Now, if we are interested in the difference between two energies levels of an electron:

$$\Delta E = E_{\text{high}} - E_{\text{low}} = E_{\text{photon}} \tag{11}$$

Since  $E = \frac{hc}{\lambda}$  for a photon, we can see that the wavelength of a photon either absorbed or radiated by this transition will be:

$$\frac{1}{\lambda} = \frac{m_e e^4}{64\pi^3 \epsilon_0^2 \hbar^3 c} \left( \frac{1}{n_{\text{low}}^2} - \frac{1}{n_{\text{high}}^2} \right) \tag{12}$$

## Spectrum Lines

Now we have a physical model that predicts the observed phenomena. Great!

Example Problem #1.

Find the wavelength of a photon emitted during a transition from n=3 to n=2 for an electron in a hydrogen atom.

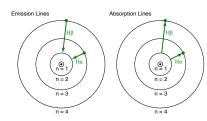
$$E_{\rm photon} = E_{\rm high} - E_{\rm low} \tag{13}$$

$$rac{hc}{\lambda} = -13.6 \; \mathrm{eV} rac{1}{n_{\mathrm{high}}^2} - \left(-13.6 \; \mathrm{eV} rac{1}{n_{\mathrm{low}}^2}
ight) \eqno(14)$$

$$= -13.6 \text{ eV} \left( \frac{1}{3^2} - \frac{1}{2^2} \right) \tag{15}$$

Solving for  $\lambda$  yields:  $\lambda = 656.469 \text{ nm}$ 

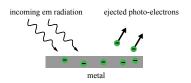
## I.6 Kirchoff's laws, again



- 1. A hot gas, or hot solid produces blackbody radiation. This is a continuous spectrum that follows Planck's Law for  $B_{\lambda}(T)$ .
- 2. A hot diffuse gas produces emission lines caused by energy lost by electrons as they go from a higher level to a lower level and emit photons at the corresponding frequencies.
- 3. A cool diffuse gas in front of a source of continuous spectrum will have dark lines when an electron gets excited by incoming energy.

## 2. Quantum Theory

## 2.7 The Photoelectric Effect



Shining light on a metal can knock electrons out of their atomic orbitals and enable them to become free electrons, and thus produce a current. If you think about this phenomenon based on classical physics, it would seem likely that the amount of energy in each of these electrons would be dependent on the brightness of the light. However, experiments showed that it didn't depend on the brightness of the light. Increasing the intensity of the light does increase the number of electrons produced, but not their kinetic energy. It turned out that the frequency of the light, or its color, was instead correlated with the energy of the electrons produced.

Each of the metals will have a *cut-off frequency* that determines how much energy is needed to knock an electron out of the orbit. Thus, the light hitting the metal will only be able to eject electrons if its frequency is above a certain amount. This is the photoelectric effect in a nutshell.

This was a mystery because the classical Maxwell equations didn't imply that different colors have different energies. Einstein solved this problem by suggesting that light traveled as photons, each with a definite energy given by:

$$E_{
m photon} = h 
u = rac{h c}{\lambda}$$

Modern terminology call this the work function,  $\phi$  of the metal:

$$\phi = hf_0$$

where h is the Planck Constant, and  $f_0$  is the threshold frequency of the material.

#### 2.8 Photons

The energy of a single, reddish, photon:

$$E_{
m photon} = h 
u = rac{hc}{\lambda} \simeq rac{1240 ext{ eV nm}}{700 ext{ nm}} = 1.77 ext{ eV}$$
 (16)

is about half that of a blue photon:

$$E_{
m photon} = h 
u = rac{hc}{\lambda} \simeq rac{1240 ext{ eV nm}}{400 ext{ nm}} = 3.10 ext{ eV}$$
 (17)

While the spectroscopy experiments were made possible by the wave nature of light, a full explanation of what caused the dark (or bright) lines would require using the particle description of light: the **photon**.

\*Note on the electron-volt: remember the definition of a volt: the potential difference that will give a 1 Coulomb charge 1 Joule of energy if it passes through that difference. The units are:

$$V = rac{ ext{Potential Energy}}{ ext{Charge}}$$

So if we multiply the Volt times a Coulomb, we'll obtain a unit of energy, and that's exactly what an electron volt is:

$$an electronvolt = Volt \times Charge = energy$$

It's the energy gained or lost by an electron as it moves across 1 volt or potential difference.

$$1 \text{ eV} = 1 \text{ V} \times 1.6021766208(98) \times 10^{-19} \text{ C}$$

It's a very small amount of energy, but useful when dealing with photons. Some of the other physical constants can be expressed in units of eV rather than Joules:

Constant	symbol	SI	eV
Planck's Constant	h	$6.626 \times 10^{-34} \mathrm{J s}$	$4.1357 \times 10^{-15} \text{ eV s}$
Reduced	ħ	$1.055 \times 10^{-34}  \text{J s / rad}$	$6.582 \times 10^{-16} \text{ eV s / rad}$
	hc	1.99 × 10 <sup>-25</sup> J m	1240 eV nm

## 2.9 de Broglie wavelength

$$\lambda = \frac{h}{p} \tag{18}$$

Louis de Broglie [1892-1987] proposed that all matter should have be able to be considered a wave. Anything with a p (momentum) will have a **de Broglie wavelength**. If that wavelength is too small (i.e. if momentum is large) then we don't see the effects. If however, that wavelength is big, then we might se wavelike effects.

#### 2.10 Uncertainty Principle

$$\Delta x \Delta p \ge \frac{1}{2}\hbar \tag{19}$$

Start with a pure sine wave. Since the frequency is the same everywhere, it is known with infinite precision. However, since the amplitude is also the same everywhere, the position is not known at all.

Adding more waves of slightly different frequencies will cause interference amongst all the waves. This ends up creating the wave packet shape visible when you select n = 50 from the radio buttons. Now, the position is well known (or better known) but the frequency is harder to determine since it's made up of all the different summed waves, each with a different frequency!

Other forms of the uncertainty Principle

 $\Delta E \Delta t \approx \hbar$  (20)

# 2.11 Tunneling

Tunneling through a barrier.