**Unit 7: Atomic Theory**

Unit 7C: Photoelectron Spectroscopy (PES)

### Knowledge/Understanding:

* Photoelectric effect
* How photoelectron spectroscopy works

### Skills:

* Determining electron configuration from photoelectron spectra

**Notes:**

**The Nature of Light**

All light (\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_) is electromagnetic radiation. These \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ of energy consist of two perpendicular fields: an \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ field wave and a \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ field wave.

### http://secure.lcogt.net/files/styles/fourcol-image/public/spacebook/Electromagnetic%20waves_0.png?itok=FJgH1k1_

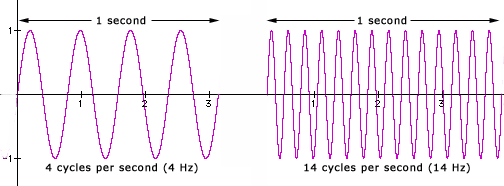
### These electromagnetic waves collectively make up the \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_.

**Light Wave Properties**

Each electromagnetic wave has a unique set of \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_, \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_, and \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ values that describe it.

*Wavelength*:



*Frequency:*

*Speed of light:*

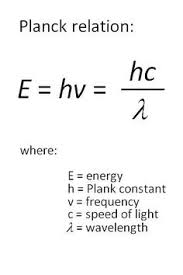
**Speed of Light Equation**

Wavelength and frequency are \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ related in proportion to the speed of light as described by the equation:

\*Note: make sure your units match! Units for c are \_\_\_\_\_\_\_, so wavelength must be in \_\_\_\_\_\_\_\_\_\_\_\_\_\_ before using the equation.

**Energy of a Photon Equation**

The energy of a light wave is directly proportional to its \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ and therefore indirectly related to its \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ per the equations below:



Planck’s Constant (h) = 6.63x10-34 Js

The ability to quantify the energy of a light wave based upon its wavelength was used as evidence to support the presence of \_\_\_\_\_\_\_\_\_\_\_\_\_\_ energy levels via \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ spectra.



3s

3s

Same \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

Emitted/Absorbed

=

Same \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

Required to Move

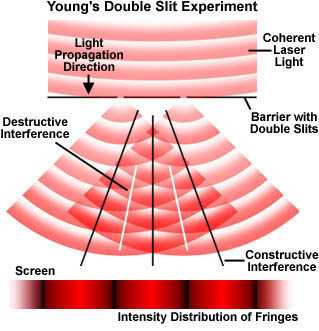
Between Energy Levels

1s

1s

**Duality of Light**

Light energy exhibits evidence of behaving both as a \_\_\_\_\_\_\_\_\_\_\_ and as a \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_. This duality is typically shown with the following experiments.

**Light as a wave**

Dual Slit Clip: <https://www.youtube.com/watch?v=Iuv6hY6zsd0>

## Light as a particle

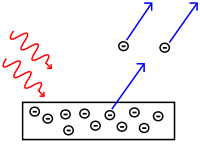
Most commonly observed phenomena with light can be explained by waves.

|  |  |  |
| --- | --- | --- |
| Phenomenon | Can be explained in terms of waves. | Can be explained in terms of particles. |
| [Reflection](http://hyperphysics.phy-astr.gsu.edu/hbase/phyopt/reflectcon.html#c1) | http://hyperphysics.phy-astr.gsu.edu/hbase/imgmod2/wavp.gif | http://hyperphysics.phy-astr.gsu.edu/hbase/imgmod2/parp.gif |
| [Refraction](http://hyperphysics.phy-astr.gsu.edu/hbase/geoopt/refr.html#c1) | http://hyperphysics.phy-astr.gsu.edu/hbase/imgmod2/wavp.gif | http://hyperphysics.phy-astr.gsu.edu/hbase/imgmod2/parp.gif |
| [Interference](http://hyperphysics.phy-astr.gsu.edu/hbase/phyopt/interfcon.html#c1) | http://hyperphysics.phy-astr.gsu.edu/hbase/imgmod2/wavp.gif | http://hyperphysics.phy-astr.gsu.edu/hbase/imgmod2/parn.gif |
| [Diffraction](http://hyperphysics.phy-astr.gsu.edu/hbase/phyopt/diffracon.html#c1) | http://hyperphysics.phy-astr.gsu.edu/hbase/imgmod2/wavp.gif | http://hyperphysics.phy-astr.gsu.edu/hbase/imgmod2/parn.gif |
| [Polarization](http://hyperphysics.phy-astr.gsu.edu/hbase/phyopt/polarcon.html#c1) | http://hyperphysics.phy-astr.gsu.edu/hbase/imgmod2/wavp.gif | http://hyperphysics.phy-astr.gsu.edu/hbase/imgmod2/parn.gif |
| [Photoelectric effect](http://hyperphysics.phy-astr.gsu.edu/hbase/mod1.html#c2) | http://hyperphysics.phy-astr.gsu.edu/hbase/imgmod2/wavn.gif | http://hyperphysics.phy-astr.gsu.edu/hbase/imgmod2/parp.gif |

But the \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ suggested a particle nature for light.

photoelectric effect:

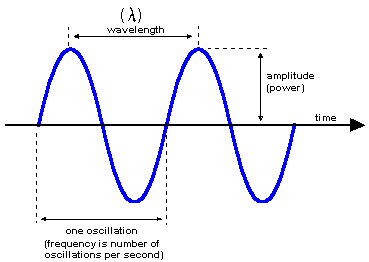
When visible or ultraviolet light is shone on a substance, the energy from the photons of light \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ electrons in the substance. If the energy exceeds the \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ of an atom in the substance, the electron is \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_.

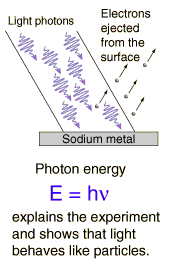


The emitted electrons are called \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_.

The effect is produced strongly by \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ light and more weakly by lower \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_. Light whose frequency was lower than a certain critical value did not \_\_\_\_\_\_\_\_\_\_\_\_\_ any electrons at all. This dependence on frequency didn't make any sense in terms of the classical wave theory of light.

If light is only behaving as a wave, it would consist of \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ and \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ fields. The stronger the fields, i.e., the greater the wave's \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_, the greater the forces that would be exerted on electrons that found themselves bathed in the light. Therefore, it should have been amplitude (\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_) that was relevant, not frequency.

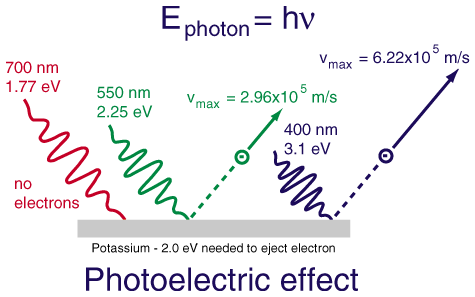


However, the only effect amplitude (brightness) had on electron emission was the \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ of electrons emitted. It had no effect on their \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ (speed they are eject with)!

This provides evidence that light was behaving as “\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_” of energy. The more we increase the intensity, the more packets of energy we are sending at the metal to come into contact with the \_\_\_\_\_\_\_\_\_\_\_.

Photoelectric Effect Simulation:

http://phet.colorado.edu/en/simulation/photoelectric

The dependence on \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ not only proves that the wave model of light needs modifying, but with the proper interpretation it allows us to determine how much energy is in one \_\_\_\_\_\_\_\_\_\_\_\_\_, and it also leads to a connection between the wave and particle models that we need in order to reconcile them.

## 1 eV = 1.602x10-19 J

A low-frequency red or infrared photon has less energy than the \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ of the electron to its nucleus (EB), so a beam of them will not \_\_\_\_\_\_\_\_\_\_ any electrons.

A high-frequency blue or violet photon, on the other hand, packs enough of a punch to allow an electron to get out of the metal electrode. At frequencies \_\_\_\_\_\_\_\_\_\_\_\_\_\_ than the minimum, the photoelectric current continues to increase with the frequency of the light as electrons are ejected with more and more kinetic energy (\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_).

## Photoelectron Spectroscopy

photoelectron spectroscopy or photoemission spectroscopy (PES):

The term “photoelectron spectroscopy” is generally used for the technique when applied to \_\_\_\_\_\_\_\_\_\_\_, and “photoemission spectroscopy” is generally used for electrons emitted from \_\_\_\_\_\_\_\_\_\_\_ surfaces.

In photoelectron (or photoemission) spectroscopy, a substance is bombarded with \_\_\_\_\_\_\_\_\_\_\_\_\_, which have a given amount of \_\_\_\_\_\_\_\_\_\_\_\_\_ based on their frequency:

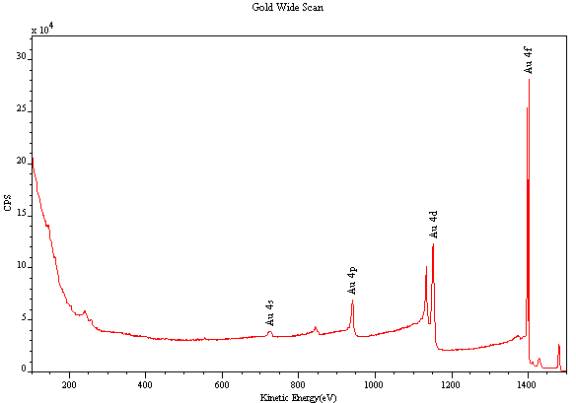
By measuring the \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ of the emitted electron, *Ek*, and predetermining the “\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_”, *Wo*, of the substance (the amount of additional energy it takes to move the delocalized electron to the \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ of the material—zero for gases, but nonzero for solids), we can calculate the \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_, *EB*, of the electron from Einstein’s equation for the photoelectric effect:

The photons used for photoelectron spectroscopy range from ultraviolet light to X-rays.

Ultraviolet photoelectron spectroscopy (UPS) and extreme ultraviolet photoelectron spectroscopy (EUPS) are used to study \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ electrons and the electrons that participate in chemical bonding. X-ray photoelectron spectroscopy (XPS) is most often used to study \_\_\_\_\_\_\_\_\_\_\_ electrons, particularly in solids.

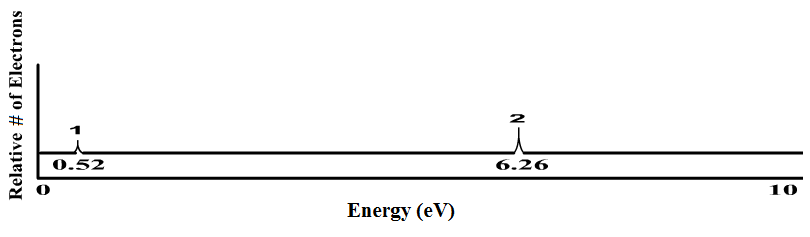
## Interpreting Photoelectron Spectra

The XPS spectrum for gold looks like the following:



Notice that the peaks for 4s, 4p, 4d, and 4f are different \_\_\_\_\_\_\_\_\_\_\_\_\_. The height of the peak is proportional to the \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ of electrons in a given sublevel.

Analysis of UV photoelectron spectra for a single element with a relatively low atomic number is straightforward. For example, the following is an idealized plot of the photoelectron spectrum for lithium:



1s

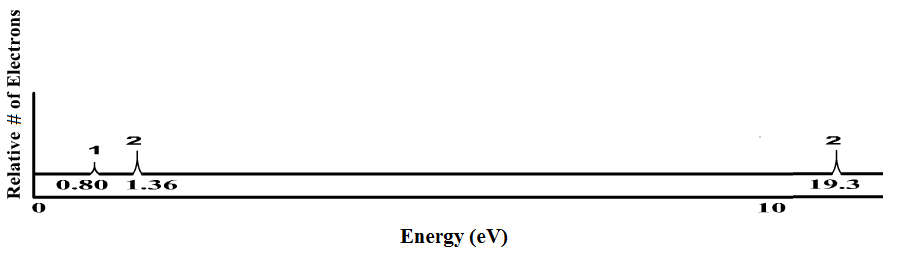
2s

The *x*-axis has units of \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ of the electron, usually electron-volts (\_\_\_\_). Recall that electrons in higher sublevels have \_\_\_\_\_\_\_\_ binding energy, which makes them easier to remove. This means the peak at the left corresponds with the easiest-to-remove electrons (for lithium, this is the \_\_\_\_ electron). The peak at the right corresponds with the electrons that are \_\_\_\_\_\_\_\_\_\_\_\_\_ to remove (for lithium, these are the two \_\_\_\_ electrons).

The *y*-axis indicates the \_\_\_\_\_\_\_\_\_\_\_\_\_ of photons emitted with that energy. This means the height of each peak is proportional to the \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ in the corresponding sub-level. Notice that the peak at 6.26 eV (the 1s electrons) is twice as high as the peak at 0.52 eV (the 2s electron). This means there are twice as many electrons in the 1s sublevel as in the 2s sublevel. The only element that matches this spectrum is lithium (\_\_\_\_\_\_\_\_\_\_\_\_\_).

### Sample Problem:

Q: Identify the element represented by the following photoelectron spectrum:

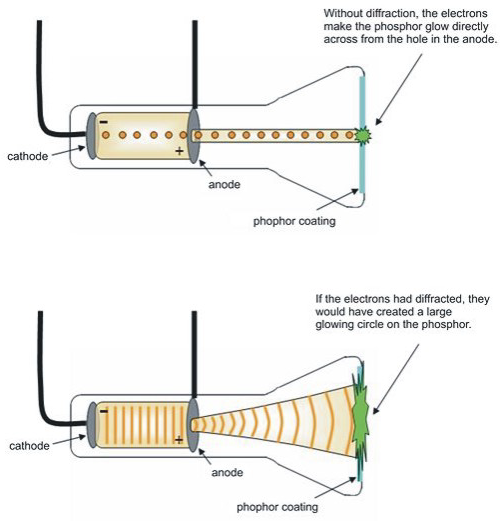


A:

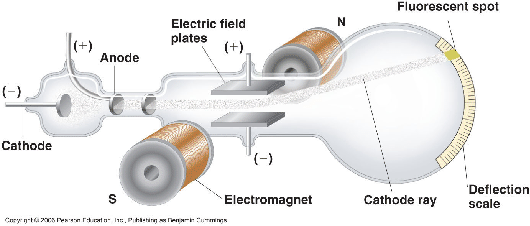
**Duality of Electrons**

It wasn’t long after the duality of light was discovered that similar behavior was theorized and supported for electrons.

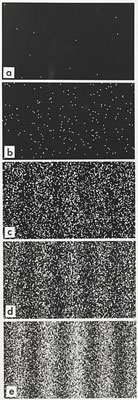
### The \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ behavior of electrons was well accepted and supported by multiple experiments, including the \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_.



### Additionally, the ability to \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ the cathode beam with a given electrostatic charge allowed for a specific \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ ratio to be determined. Evidence for mass characteristics supports particulate behavior.



### Young's duel slit experiment with electrons

A group from the lab of Akira Tonomura performed an analogous experiment with electrons: [Young's experiment, one electron at a time](http://www.tiptop.iop.org/full/pwa-pdf/16/5/phwv16i5a24.pdf), from which we take the following images.

|  |
| --- |
|  |
| Successively longer integration times as electron arrivals (white dots) are recorded. |

The \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ pattern mirrors the results of light \_\_\_\_\_\_\_\_\_\_\_\_\_\_ from the duel-split experiment.

Evidence for electron wave behavior provides further support for the \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ and the application of \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ equation to predict electron positioning in \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_, since it assumes wave behavior.

