• Characteristics of Electromagnetic (EM) Radiation - Classical Theory

Electromagnetic waves, as you will learn in physics, are responsible for light - “as we know it”. Light is, in fact, electromagnetic radiation. The wave is comprised of a combined “oscillation” of an electric and magnetic field - undulating perpendicular to each other - and traveling in a third perpendicular direction. Any wave that travels in a direction which is perpendicular to its direction of travel - like a ripple of water which undulates “vertically” while propagating along the surface - is termed a transverse wave. The height and depth of the waves undulation is termed the amplitude (A) of the wave. Other parameters, such as wavelength (λ), phase, and nodes are shown on the pictures that follow. The frequency (f) of a wave is defined as the number of wavelengths or “cycles” that pass a fixed point per second. Thus, frequency has units of (cycles) per second - or usually just 1/s which is given the SI unit hertz (Hz). The inverse of frequency - having units of seconds (per cycle) or usually just seconds - is termed the period of the wave - the time it takes for one complete cycle. Some results are summarized below.

A PICTURE OF A “TYPICAL” TRANSVERSE WAVE FOLLOWS - ALONG WITH SOME OF THE IMPORTANT FEATURES.
A SINE WAVE: \( y = A \sin(2\pi f x) = 4 \sin(2\pi f x) \)

• The Electromagnetic Spectrum

In order of decreasing \( f \) (increasing \( f \)):
AM radio (kHz) > FM radio (MHz) > Microwave > IR > Red > Orange > Yellow > Green > Blue > Indigo > Violet > UV > X-Rays.

Below is a depiction of the electromagnetic spectrum - extending from the short wavelength region of gamma rays to ultraviolet, to the visible region (400 nm - 700 nm), to infrared, to microwaves, and radio waves (FM & AM).
• Energy of the EM wave is proportional to the square of the amplitude \( (A^2) \) which is also termed the Intensity (or brightness) of the EM wave \( (I_{EM}) \).
  In other words, the total energy delivery, i.e., the brightness \( (I_{EM}) \), not the details - such as color \((\square)\ or \(\square\) - characterizes the energy of the EM radiation.
• One measure of total energy delivered = Power \( \cdot \) \( t \).

The SI unit of power = watt \((W) = \text{joule} \over \text{s} \) \( J = W \cdot s \).

• For low frequency (or long wavelength), a charge oscillating with frequency “f” (# of oscillations per second) should radiate EM radiation with the same frequency \((\square), \) i.e.,
  \[ f_{\text{oscillating charged particle}} = \square \text{EM radiation emitted} \]

• Wave-like behavior of EM radiation is demonstrated by elastic scattering experiments (no loss in kinetic energy) such as diffraction. Diffraction is characterized by constructive and destructive interference, i.e., a characteristic pattern of “bright” and “dark” spots, respectively. A simple depiction of constructive & destructive interference of two transverse waves of different amplitudes is shown below. Note that if the two waves had the same amplitude, then full constructive interference would give a wave 2x the original and full destructive interference would cancel both waves completely - “flatline”.

CONSTRUCTIVE INTERFERENCE (in-phase)

\[ y_1 = 4 \sin(2 \pi x) \]
\[ y_2 = 3 \sin(2 \pi x) \]

DESTRUCTIVE INTERFERENCE (out-of-phase)

\[ y_1 = 4 \sin(2 \pi x) \]
\[ y_2 = 3 \sin(2 \pi x) \]
One more item that we will encounter in our discussion of experiments important to quantum theory is the mapping out of the pattern of emission or absorption or EM radiation as a function of the radiation’s wavelength ($\lambda$) or frequency ($\nu$), is termed spectroscopy. The resultant “map”, i.e., the characteristic pattern of colors ($\lambda$ or $\nu$) and corresponding intensities ($I_{\text{EM}}$) - of the atom or molecule -is termed its spectrum (plural = spectra).

In 1800, the English astronomer Sir William Herschel observed that while using a prism to spread sunlight into a color swath, he detected changes in temperature when he moved a blackened thermometer across the spectrum of colors. Herschel found that the heating effect increased toward the red and continued to increase as he moved the thermometer into the dark portion beyond the red end of the visible light spectrum, He found the maximum heating occurred considerably beyond the red, in the region we now call “infrared”. All objects radiate infrared energy (unless the object has a temperature of absolute zero).

- **First Experiment - Blackbody Radiation**

As your text explains, at the beginning of the 1900’s there were attempts to understand the profile (Intensity ($I_{\text{EM}}$) versus wavelength ($\lambda$)) of a body heated to incandescence (glowing) as a function of its kelvin temperature ($T$). **Figure 12.4 of your text** gives such a set of profiles - please refer to it. A version of this is below:
In the above diagram - notice the following:

- The shape of the curves are sort of “Maxwell-Boltzmannish”.
- The peak of the curve shifts to higher frequency as temperature increases.
- The area under the curves increases as temperature increases.

Wien determined the following empirical relationship between the brightest color emitted (the observed color) - $\lambda_{\text{brightest}}$ - and the kelvin temperature of the material. This result was known as Wien’s Law and shows that there is an inverse relationship between $\lambda_{\text{brightest}}$ and $T$:

$$\lambda_{\text{brightest}} = \frac{2.898 \, \text{nm} \cdot K}{T} \quad \text{Wien’s Law}$$

You can see that at temperatures below about 600°C (873 K) the object would glow ($\lambda_{\text{brightest}}$) in the IR region. This is true for human beings ($T = 37^\circ C = 310 \, K$). Once again, from the remarks above, we have:

- As the $T$ of the sample ↑, there is an ↑ in the total amount of radiant energy emitted.
  (From the profiles area under the curve gets larger and larger).
- The concentration of energy moves to shorter wavelengths as the temperature ↑.
  (From the profiles $\lambda_{\text{brightest}}$ as $T ↑$, i.e., the peak shifts to shorter wavelengths.)

All attempts to explain the profiles using classical physics - assuming the radiation emitted behaved purely as a wave - failed. A plot of the theoretically predicted classical profile - due to Rayleigh and Jeans - in comparison with the actual profile, becomes markedly different as $\lambda$ (as $n ↑$). The classical theory predicts that there is no maximum and also that the profile increases to infinity ($\lambda$) as the wavelength [ ]. This extremely disturbing result was termed the ultraviolet catastrophe by the bewildered scientists.

- An Attempt at a rationalize - Max Planck & the Quantum of EM Radiation

The theoretical model of this phenomenon was termed a blackbody for the following reason. Since a model is an idealized construct, it often is simplified from the real situation so that only the relevant features are included. In this case, scientists wanted to considered a body (piece of material) that was a perfect absorber (i.e., could absorb all colors - thus it would appear black). This was desired so that any radiation emitted would be solely due to the heating and does not include any radiation reflected from the object and does not depend on the specific details of the material itself.

In 1900, Max Planck came up with an empirical function that fit the experimental profile. However, in order to reconcile this result with a theoretical “explanation” he had to invoke (as a calculation aid) the partitioning (discretizing) of the total energy (or $I_{\text{EM}}$) emitted into discrete packets (or lumps) which he termed quanta (singular = quantum). These discrete packets - were color [ ] dependent. The number of discrete packets emitted for each color depended on the total intensity contributed to the profile by that color and on the color itself. Planck invoked the idea that each color’s contribution to the intensity was in the form of packets - the size of which was directly proportional to the frequency of the particular color. The proportionality constant was symbolized as $h$ (later named Planck’s constant).

In mathematical form:

$$E_{\text{total}} (I_{\text{total,EM}}) = E_{\text{color 1}} + E_{\text{color 2}} + E_{\text{color 3}} + ...$$

$$= N_{\text{quanta-color 1}} \cdot (h \frac{c_{\text{color 1}}}{}) + N_{\text{quanta-color 2}} \cdot (h \frac{c_{\text{color 2}}}{}) + N_{\text{quanta-color 3}} \cdot (h \frac{c_{\text{color 3}}}{})$$

Thus, the total energy contributed by each color (and hence the total intensity contributed by each color) emitted was proportional to the number of packets of that color - the size of which varied
directly with the frequency \( (\nu) \). So, it would require less violet packets (quanta) then red packets (quanta) to achieve a given total energy (or intensity) since violet quanta have larger individual energy (larger \( \nu \)) than do red quanta. These quanta or packets of EM energy were later termed **photons**. The value of Planck’s constant (which was firmly established by Robert Millikan - of oil drop fame) when he carried out experiments to verify Einstein’s explanation of the photoelectric effect is approximately:

\[
    h = \text{Planck’s constant} = 6.626 \times 10^{-34} \text{ joule-seconds (J s)}
\]

Hence, Planck hypothesized - as a calculation aid to arrive at the experimental profile - that EM radiation exchanged energy with the walls of the blackbody in lumps or packets or quanta or photons the size of which were color dependent and directly proportional to the frequency \( (\nu) \) of the color and thus inversely proportional to \( \frac{1}{\nu} (= \frac{c}{\nu}) \) of the color. In mathematical form:

\[
    E_{\text{photon or quantum of a particular color}} = h \nu = \frac{hc}{\nu}.
\]

Hence, the total energy delivered by a particular color (proportional to the \( I_{EM} \) delivered by that color) is given by:

\[
    E_{\text{total of particular color}} = N_{\text{photons or quanta of the color}} \cdot \frac{hc}{\nu}.
\]

For future reference, light of one \( \nu \) (equally - one \( \frac{c}{\nu} \)) is termed **monochromatic**.

- **2nd Experiment - The Photoelectric Effect**

  The photoelectric effect was discovered by Hertz in 1887 and was studied by Lenard in 1900. The effect is basically as follows. When light of high enough frequency \( (\nu) \) is incident on the clean metal surface of the (photo) cathode (C), electrons \( (e^-) \) are emitted (ejected). When the anode is positively charged, the electrons are attracted to the anode. If some of these electrons strike the anode (A), there is a current in the external circuit. However, independent of intensity \( (I_{EM}) \), no electrons are ejected - and hence no current flows - if the light frequency is too low. Only at a minimum or threshold frequency \( (\nu_0) \) will there be current production. The following results are also observed - as the plots that follow show.
Summarizing the results from the previous graphs, we note the following.

- **Graph 1:** Photocurrent (# e⁻'s per second vs Incident Light frequency (n))
  - Above the threshold frequency ($n_0$), increasing $I_{EM}$ at constant increases the # of e⁻'s ejected per second.
  - Above the threshold frequency ($n_0$), increasing at constant $I_{EM}$ does not change the # of e⁻'s ejected per second.

- **Graph 2:** Photoelectron KE (KE per e⁻) vs Incident Light frequency (n)
  - Above the threshold frequency ($n_0$), increasing $I_{EM}$ at constant does not change the KE per ejected e⁻ - only the # of e⁻'s ejected increase proportionately.
  - Above the threshold frequency ($n_0$), increasing at constant $I_{EM}$ linearly increases the KE per ejected e⁻.
  - Also, the value of $n_0$ is characteristic of the metal surface.
In other words, at constant brightness ($I_{\text{EM}}$) an increase in the frequency ($\nu$) of the incident light (or a decrease in the $l$) increases the velocity (speed) of an ejected electron but does not change the # of electrons ejected per second. Alternately, at constant frequency ($\nu$) - or at constant $l$ - as $I_{\text{EM}}$ increases (increase brightness) there is an increase in the # of electrons ejected per second but the velocity (speed) of an ejected electron does not change. More electrons are ejected but not with greater individual kinetic energy $KE_e = \frac{1}{2} m_{\text{electron}} (v_{\text{electron}})^2 = \frac{1}{2} m_e v_e^2$.

Classically, the increased light energy incident on the metal surface (total energy delivered) should increase the energy absorbed by a given electron on the metal surface and hence increase the kinetic energy of the subsequently ejected electron. As the above results demonstrate, this is clearly not the case.

There must be something about how the total delivered energy (i.e., the total delivered intensity ($I_{\text{EM}}$)) is received by matter. There seems to be a discretization of the $I_{\text{EM}}$ when delivered to the metal surface. In other words, there seems to be a discretization of the total energy delivered to the metal surface. It appears to be color-dependent (i.e., dependent upon $\nu$ or $l$). Hence, the information from the two graphs can be boiled down to the following.

- **Summary of Results from the Photoelectric Effect:**
  - # of photoelectrons ejected from surface does not change as $\nu$ ↑ at constant $I_{\text{EM}}$.
  - # of photoelectrons ejected from surface ↑ as $I_{\text{EM}}$ ↑ at constant $\nu$.
  - Individual photoelectron $KE_e$ ↑ linearly as $\nu$ ↑ at constant $I_{\text{EM}}$.
  - Individual photoelectron $KE_e$ does not change as $I_{\text{EM}}$ ↑ at constant $\nu$.
- **Einstein considers Planck’s quantum idea as a fundamental property of EM radiation (energy exchange) - and explains the Photoelectric Effect.**

Albert Einstein, in 1905, suggested that the discretization (quantization) of the total EM energy exchange with matter into packets (quanta or photons) of size $\hbar$ or $\hbar \nu$ was a fundamental property of EM radiation. He thus explained the photoelectric effect in terms of a Principle of Photochemical Equivalence in which each photon is completely absorbed by one and only one electron on the metal surface. In other words, the irradiation of the metal surface could be considered a series one-photon-one-electron events.

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Each incident photon is absorbed only by one electron on surface

So, there was merely an energy balance condition between the incident photon and a single electron on the metal surface. A photon delivers all of its energy to one and only one electron. The photon cannot share its energy with several electrons. When the electron takes up (absorbs) this energy, two things can happen. First, the electron is “unglued” from the metal surface - the amount of energy required to completely “unglue” one electron from the metal surface is termed the **work function or binding energy or threshold energy of the metal**. Second, if there is energy “left over”, then the rest of the energy is converted to the **kinetic energy of the ejected electron**. (Some texts will refer to this as the **maximum** kinetic energy of the electron, since it is the largest amount of kinetic energy that the electron can have.
In general, the electrons are not all equally bound (“glued”) to the metal surface. The work function \( F \) represents the binding energy of the least tightly bound electrons - thus, for the more tightly bound electrons the resultant kinetic energy will be less.) Thus, we can write the energy balance condition:

\[
E_{\text{photon}} = F + KE_e
\]

where \( E_{\text{photon}} \) is defined above and \( F = \) work function or binding energy or threshold energy of the metal - its value depends on the particular metal surface used. Following, is a schematic diagram (cartoon) of the process.

\[
KE_e = \text{(maximum) kinetic energy of the electron} = \frac{1}{2} m_e v_e^2
\]

where \( v_e = \) speed of the electron and \( m_e = \) mass of the electron = \( 9.11 \times 10^{-31} \) kg.

Solving for \( KE_e \) and rewriting \( E_{\text{photon}} \) in terms of frequency (\( h \)) we have:

\[
KE_e = h F
\]

Comparing this to the previous graph of \( KE_e \) vs \( F \) - note the following.

- The slope = \( h \).
- The x-intercept (when \( KE_e = 0 \)) = \( F_0 = \frac{F}{h} \) & the y-intercept is \( h \).
• **3rd Experiment:**

**Emission spectra of gases in discharge tube (demo)**

Near the turn of the century, experiments were performed in which samples of gas at low pressure - sealed in a glass tube - were excited by an electrical discharge and the pattern of emitted EM radiation was studied. The emitted light from these “discharge tubes” was passed through a spectroscope (like a prism) with a narrow slit (aperture). The resultant spectrum of emitted light was then either viewed directly or exposed to photographic film so that more quantitative studies could be carried out. It turned out that each unique gaseous sample had its own characteristic pattern of colors and corresponding intensities. The emission spectrum of atomic hydrogen (H(g)) was studied carefully due to its apparent simplicity. The most remarkable feature was that the resultant spectrum was **discrete not continuous.** In other words, there were sparse regions of color (which appeared as **lines**) but there was also a lot of “empty space”, i.e., regions where no light or color appeared on the photographic film. Such spectra where termed **line spectra.** Classical physics predicted that there should be a gradual or continuous shading of colors form red to orange to yellow to violet - as when you separate sunlight streaming through an open window into its rainbow of colors with a prism. There were other issues also. These are summarized below.

**Results of H-atom Emission Spectrum:**

- **Line spectrum** [only certain colors emitted] - not continuous.
- Lines unequally spaced - lines get closer together as $\ell_\ell$.
- Intensities vary in non-obvious manner.

What came next was a search for some kind regularity or pattern in the H atom emission spectrum, i.e., an attempt to quantify the troublesome data.

• **Visible emission spectrum of atomic hydrogen - Balmer Series**

The visible line spectrum of atomic hydrogen (H(g)) was found to contain only four (4) lines. The wavelengths were (approximately): **410 nm, 434 nm, 486 nm, and 656 nm.** It was also noted (and quantified) that the spacing between the lines were unequal. In fact, it was observed, that as the wavelength ($\ell\ell$) became shorter (toward violet), the spacing between the lines decreased, i.e., the lines got closer together. See your text (Fig. 12.8) for a picture of this.

In 1884, a Swiss schoolteacher, Johann Balmer, found that these lines could be represented by the empirical relationship:

\[
\frac{1}{\ell_{\text{vis}}} = (1.097 \times 10^7 \text{ m}^{-1}) \cdot \frac{1}{n^2} ; \quad n = 3, 4, 5, 6, \ldots
\]

This pattern of lines was termed the **Balmer Series** in his honor.

In fact, other such empirical relationships or patterns were found. Such a series was found in the UV region of the emission spectrum of atomic hydrogen by Lyman and another series was found in the IR region of the emission spectrum of atomic hydrogen by Paschen. These were termed the **Lyman and Paschen Series,** respectively. Actually, Balmer suggested that his empirical relationship might be the special case of a more general pattern. This was in fact the case.

In 1908, Johannes R. Rydberg and Walter Ritz found such a relationship. The resultant formula - known as the Rydberg-Ritz formula (or sometimes just the Rydberg formula) - relates the reciprocal of the wavelength ($1/\ell\ell$) to the difference of of the inverse-square of **two whole positive numbers** $n_1$ and $n_2$. For the hydrogen atom spectrum, it took the form:
\[
\frac{1}{\ell} = 1.097373 \times 10^7 \text{ m}^{-1} \cdot \frac{1}{n_2^2} - \frac{1}{n_1^2} \quad \text{where } n_1 > n_2
\]

Correspondence with the Balmer series above gives the following. Prove this for yourself.

- **Balmer Series** (vis): \( n_2 = 2 \); \( n_1 = “n” = 3, 4, 5, ... \)
  
  [Also, Lyman Series (UV): \( n_2 = 1 \); \( n_1 = “n” = 2, 3, 4, ... \)
  
  Paschen Series (IR): \( n_2 = 3 \); \( n_1 = “n” = 4, 5, 6, ... \)]

In fact, Rydberg and Ritz found that the above formula was valid not only for hydrogen but could be adjusted for any **hydrogenic atom of atomic number** \( Z \). Other than hydrogen itself (with \( Z = 1 \), of course), a **hydrogenic** atom is actually a **one-electron cation** with **atomic number** \( Z \) (i.e., nuclear charge +Ze).

So: \( _2\text{He}^+ \), \( _3\text{Li}^+ \), and \( _4\text{Be}^+ \) are **hydrogenic atoms** (cations).

They found that the right-hand side of the equation should be multiplied by \( Z^2 \) in order to agree with experiment.

- **Empirical relationship of observed \( \ell \)'s (lines) for hydrogenic species**:

\[
\frac{1}{\ell} = Z^2 \cdot (1.097373 \times 10^7 \text{ m}^{-1}) \cdot \frac{1}{n_2^2} - \frac{1}{n_1^2} \quad \text{where } n_1 > n_2
\]

and \( n_1 \) and \( n_2 \) are whole positive numbers = 1, 2, 3, ... and \( Z \) is the atomic number (nuclear charge) of the hydrogenic (one-electron) atom or cation. **For H, Z = 1**.

- **Non-Classical Model of the Hydrogenic Atom** - **Niels Bohr**

  The classical planetary model of the atom was no good because of a feature inherent in electrostatic interactions that is not exhibited by gravitational interactions. Unlike a planet revolving around a “sun” under the attractive force of gravity, an electric charge revolving around another (opposite) electric charge - to which it is attracted - is predicted to radiate EM radiation at the frequency that it is revolving (frequency of revolution \( \equiv f = 1/\text{Period} = \ell_{\text{EM}} \)). Since the revolving charged particle is presumed to be in continual circular motion at frequency \( f \), it should continually radiate EM radiation. Thus, this charge should continually lose energy as it radiates and eventually spiral into the nucleus. So, according to classical physics, i.e., classical EM theory, a planetary atom consisting of a charge revolving around a charge to which it is attracted is doomed. Niels Bohr, assuming that the radius of the orbiting electron in the hydrogenic atom was about 1 Ångstrom (Å) \( = 10^{-10} \text{ m} \) - which he estimated from the size of atoms according to data from Rutherford’s scattering of \( \alpha \)-particles by gold foil - calculated a hydrogenic atom lifetime of about \( 10^{10} \text{ seconds} \) (1 ns). Clearly, classical physics was seriously wanting.
Bohr’s Postulates for a Hydrogenic (Z protons and one electron) Atom

1. The electron travels in circular orbits around the nucleus.

2. Only certain circular orbits are allowed - those for which \( m_e v r \) (the angular momentum) is quantized, i.e.,
   \[
   m_e v r = \frac{n h}{2\pi}
   \]
   where \( n \) is termed the principal quantum number = 1, 2, 3, ..., \( m_e \) is the mass of the electron, \( v \) is the velocity of the electron, and \( r \) is the radius of its circular orbit. \( h \) is Planck’s constant = 6.626 x 10\(^{-34}\) J s. [Note that quantized means that only certain values (not just any value) are allowed.]

Such orbits - termed stationary (constant energy) states - have a radius \( r \) given by:
   \[
   r_n = \frac{n^2 a_0}{Z}
   \]
   where \( Z \) is the atomic number of the hydrogenic atom and \( a_0 \) = Bohr radius = 52.9 pm or 0.529 Å. The energy of an orbit of radius \( r_n \) is given by:
   \[
   E_n = Z^2 \cdot 2.18 \times 10^{18} \text{ J/atom}
   \]
   where
   \[
   2.18 \times 10^{18} \text{ J/atom}
   \]
   is the combination of fundamental constants - \( m_e, c, e, ... \) required by Bohr when he mathematically balanced the forces acting on this orbiting electron.

[A common unit of energy in “quantum theory” calculations is the electron volt (eV). It is a convenient unit, when very small energies (on the order of 10\(^{-19}\) J) are involved. The definition is:
   \[
   1 \text{ eV} = 1.60 \times 10^{-19} \text{ J}
   \]
   In eV, \( 2.18 \times 10^{18} \text{ J/atom} \) is equal to 13.61 eV/atom].

[What’s with the minus (\( \square \)) sign in \( E_n \)? The minus sign comes about due to the fact that the electron is bound to the nucleus, i.e., the hydrogenic atom is a bound state due to the (electrostatic) attraction of the negatively charged electron to the positively charged nucleus. This bound energy state is designated as minus (\( \square \)) because a bound state is more stable (i.e., lower in energy) than the unattached electron and nucleus. In other words, the dissociated (i.e., ionized) atom - with the nucleus (of charge +Ze) and electron (e\( ^- \)) infinitely far apart (\( r_e = \)) - is defined as zero (0) energy.]

As long as the electron is in one of these stationary states, it will not radiate, lose energy, and spiral into the nucleus.

3. The only time that electromagnetic radiation (light) is emitted or absorbed by the atom is if the electron undergoes a transition to a lower (emission of radiation) or to a higher (absorption of radiation) stationary energy state (energy level). The resultant energy change of the electron exactly equals the energy of one (1) photon (quantum) of electromagnetic radiation, i.e.,
\[ E_e = E_{\text{final}} - E_{\text{initial}} + E_{\text{photon}} = \frac{hc}{n^2} \]

[If emission is taking place, then \( E_e \) is negative - indicating that energy is released (a photon is emitted). If absorption is taking place, then \( E_e \) is positive - indicating that energy is taken in (a photon is absorbed).] Let’s see where these postulates lead.

As is made clear above, a transition of the electron - from an orbit with principal quantum number \( n_i \) - to another orbit with principal quantum number \( n_f \) - will experience an energy change (\( E_e \)) given by:

\[ E_e = E_f - E_i = \frac{Z^2}{n_f^2} \left(2.18 \times 10^{18} \text{ J/atom}\right) - \frac{Z^2}{n_i^2} \left(2.18 \times 10^{18} \text{ J/atom}\right) \]

\[ = \frac{1}{n_i^2} - \frac{1}{n_f^2} \]

This \( E_e \), in turn (according to one of Bohr’s postulates), equals \( E_{\text{photon}} \):

\[ E_{\text{photon}} = \frac{hc}{n_i^2} - \frac{hc}{n_f^2} \]

Finally, since \( E_{\text{photon}} = \frac{h}{n_i^2} \) or \( \frac{hc}{n_f^2} \), we have:

\[ \frac{h}{n_i^2} - \frac{hc}{n_f^2} = \frac{Z^2}{n_i^2} \left(2.18 \times 10^{18} \text{ J/atom}\right) - \frac{Z^2}{n_f^2} \left(2.18 \times 10^{18} \text{ J/atom}\right) \]

So:

\[ \frac{1}{n_i^2} - \frac{1}{n_f^2} = Z^2 \cdot \frac{2.18 \times 10^{18} \text{ J/atom}}{hc} \cdot \frac{1}{n_i^2} \cdot \frac{1}{n_f^2} \]

and the original Rydberg-Ritz formula again appears if \( \frac{2.18 \times 10^{18} \text{ J/atom}}{hc} \) comes out right. Show for yourself that \( \frac{2.18 \times 10^{18} \text{ J/atom}}{hc} = 1.096 \times 10^7 \text{ m}^2/\text{mol} \). From now on, we will think of \( 2.18 \times 10^{18} \text{ J/atom} \) - or its equivalent in other energy units - as Rydberg’s constant - and symbolize it as \( R_y \).

**Some comments** -

Note that the formula for the possible energy states of the electron is inversely proportional to \( n^2 \). This mathematical relationship gives rise to the behavior that as \( n \) increases, the energy levels get closer together. Prove this for yourself. The figures in your text - show this clearly. Be sure that you thoroughly understand this.

**Why do the spectral lines arising from transitions to (or from) a common level group together and why they “bunch up” as \( n \) gets shorter?** See the diagrams on the following page.

For any of the above formulae depicting a transition, note that as we proceed from higher and higher initial levels (say \( n_i = 2, 3, 4, \ldots \)) to the same final level (say \( n_f = 1 \)) - as in an
emission series, i.e., \( n_i = 2 \rightarrow n_f = 1 \); then \( n_i = 3 \rightarrow n_f = 1 \); then \( n_i = 4 \rightarrow n_f = 1 \); even though the wavelengths get shorter (i.e., larger \( E_e = E_{\text{photon}} \)), the wavelengths get shorter by less and less since the energy levels get closer and closer together. Since the wavelengths get shorter by less and less - spectral lines should get closer as one proceeds to larger \( E_e = E_{\text{photon}} \). This was exactly observed in the Balmer emission spectrum (\( n_f = 2 \)). Remember, the spectral line is due to the emitted light (photons) - which is a result of the transitions depicted below:

![Diagram of energy levels - Hydrogenic Atom: Balmer Emission Series First 4 lines: 1, 2, 3, & 4](image)
Note that we number the lines (photons) in the spectrum beginning with the lowest energy (longest $\lambda$) line. Thus, the red line in the Balmer series ($\lambda = 656$ nm) is the 1st line, the 486 nm line is the second, etc.

- For an emission transition: note that $n_i > n_f$, i.e., a “downward transition”:

$$\Delta E = Z^2 \frac{1}{n_i^2} - \frac{1}{n_f^2}$$

is negative (_negative_) (check it out.).

This means that energy is released - the photon is emitted. Energy is leaving the atom in the form of light. Following is an example of such a process for $n_i = 4$ (3rd excited state) $\rightarrow n_f = 2$ (1st excited state). This transition gives rise to a (the second) line in the Balmer emission series.
Note: This is a Balmer emission transition

\[ n_i = 4, \text{3rd excited state} \]
\[ n = 3, \text{2nd excited state} \]
\[ n_f = 2, \text{1st excited state} \]

\[ n = 1, \text{ground state} \]

• For an absorption transition: note that \( n_i < n_f \), i.e., an “upward transition”:

\[ \mathcal{E}_e = Z^2 R_y \left( \frac{1}{n_i^2} - \frac{1}{n_f^2} \right) \]

is positive (+) (check it out.).

This means that energy is absorbed - the photon is absorbed. Energy is absorbed by the atom in the form of light. Below is an example of such a process for \( n_i = 1 \) (ground state) \( \rightarrow \) \( n_f = 3 \) (2nd excited state). This transition gives rise to a (the second) line in the Lyman absorption series.

Note: This is a Lyman absorption transition

\[ n = 4, \text{3rd excited state} \]
\[ n_f = 3, \text{2nd excited state} \]
\[ n = 2, \text{1st excited state} \]

\[ n_i = 1, \text{ground state} \]

So, a line in an emission (or in an absorption) spectrum arises due to the change in energy of the electron (\( \mathcal{E}_e \)) as it undergoes a transition from one stationary state (parameterized by \( n_i \)) to a different stationary state (parameterized by \( n_f \)). In symbols:

\[ E_{\text{photon}} \text{ (produces spectral line)} = \mathcal{E}_e \text{ (transition of e\( \square \) from } n_i \text{ to } n_f \). \]
• Photoelectric Effect - Examples & Problem Solving Hints:

Concept: Principle of Photochemical Equivalence -

A photon delivers all of its energy to one and only one electron.

Cartoon:

![Cartoon of photon and electron](image)

Energy Balance: \[ E_{\text{photon}} = F + K.E_e \]

Example # 1 - Threshold frequency - # of ejected electrons

A particular metal has a work function of \(3.2 \times 10^{-19} \text{ J}\). Monochromatic light, with a frequency of \(6.0 \times 10^{14} \text{ Hz}\) shines upon the metal surface, causing a photocurrent.

(a) Determine the threshold frequency (in Hz) for this metal surface.
(b) Determine the maximum wavelength (in nm) that can cause a photocurrent.
(c) Determine the speed of an ejected electron (in km/s).
(d) If the total energy of the incident light is \(3.98 \times 10^{-18} \text{ J}\), determine the number of electrons ejected and the total energy (in eV) of the photocurrent.

Solution to Example # 1:

(1a) \( F = h \nu_o \) ; where \( F \) = work function and \( \nu_o \) = threshold frequency.

\[ \nu_o = \frac{3.2 \times 10^{-19} \text{ J}}{6.63 \times 10^{-34} \text{ J s}} = \frac{4.83 \times 10^{14} \text{ s}^{-1}}{\text{Hz}} \]

(1b) Because of the inverse relationship between frequency and wavelength; the maximum photon wavelength to cause ejection of electrons will correspond to minimum photon frequency. The minimum photon frequency is the threshold frequency \( \nu_o \) determined in (1a).

\[ \nu_o = \frac{c}{\lambda_{\text{max}}} = \frac{3.00 \times 10^8 \text{ m/s}}{621 \text{ nm} \times 10^{-9} \text{ m}} = \frac{621 \text{ nm}}{10^{-9} \text{ m}} = \lambda_{\text{max}} \]

(1c) We start off with the energy balance equation:

\[ E_{\text{photon}} = F + K.E_e \]

Solving for \( K.E_e \) and substituting \( E_{\text{photon}} = h \nu \), we have:

\[ K.E_e = E_{\text{photon}} \nu = h \nu = \frac{6.63 \times 10^{-34} \text{ J s}}{(6.0 \times 10^{14} \text{ s}^{-1})} \cdot 3.2 \times 10^{-19} \text{ J} \]

\[ 7.78 \times 10^{-120} \text{ J} \]
Since \( K.E_e = \frac{1}{2} m_e v_e^2 \)

\[
v_e = \sqrt{\frac{2 K.E_e}{m_e}}
\]

\[
= \sqrt{\frac{(2)(7.78 \times 10^{20} \text{ J})}{9.11 \times 10^{31} \text{ kg}}}
\]

\[
= 4.13 \times 10^5 \text{ m/s} = 413 \text{ km/s}.
\]

(1d) Remember:

\[
\text{# of “successful” photons in} = \text{# of ejected electrons out}.
\]

\[
\text{# of photons in} = N_{\text{photons}} = \frac{E_{\text{total}}}{E_{\text{photon}}} = \frac{E_{\text{total}}}{h\nu}.
\]

\[
N_{\text{photons}} = \frac{3.98 \times 10^{18} \text{ J}}{6.63 \times 10^{-34} \text{ J s/photon} \times 6.0 \times 10^{14} \text{ s/1}} = 10 \text{ photons in}.
\]

Since the photons are successful in causing a photocurrent (as determined above), then there must be the same number of electrons ejected. Thus, 10 electrons are ejected.

Since each electron should obey the energy balance equation - each electron should then have a kinetic energy of 7.78 x 10^{20} \text{ J} (see (1c)). Then:

\[
K.E_{e,\text{total}} = N_{\text{electrons}} K.E_e = (10 \text{ e}) \frac{1 \text{ eV}}{1.60 \times 10^{19} \text{ J}} = 4.86 \text{ eV}.
\]

Example #2 - Determining if radiation will cause a photocurrent

A certain metal has a binding energy of 1.875 eV. The metal surface is subjected, separately, to three (3) types of electromagnetic radiation: Green light (\( \lambda = 486 \text{ nm} \)), Red light (\( \lambda = 656 \text{ nm} \)), and radiation from radio station “WXPN” - broadcasting at 88.9 MHz.

(a) Which of the above radiation sources will produce a photocurrent? For those cases in which a photocurrent is produced, determine the kinetic energy (in J) of an ejected electron.

(b) For those cases in which a photocurrent is produced, determine the speed (in km/s) of the ejected electrons.

Solution to Example #2:

(2a) Beginning with the energy balance equation:

\[
E_{\text{photon}} = \square + K.E_e.
\]
Solving for K.E.\(_e\):

\[
\text{K.E.} = E_{\text{photon}} - F = \frac{\text{hc}}{\text{eV}} \quad \text{or} \quad h \nu - F
\]

depending on whether wavelength (\(\lambda\)) or frequency (\(\nu\)) is supplied for the photon.

\[
\begin{align*}
\lambda &= (1.875 \text{ eV}) \times 1.60 \times 10^{19} \text{ J/eV} = 3.00 \times 10^{19} \text{ J} \\
\end{align*}
\]

For a green photon: 

\[
E_{\text{green photon}} = \frac{(6.63 \times 10^{-34} \text{ J s}) \times 3.00 \times 10^8 \text{ m/s}}{486 \times 10^{19} \text{ m}} \\
E_{\text{green photon}} = 4.09 \times 10^{19} \text{ J}
\]

For a red photon: 

\[
E_{\text{red photon}} = \frac{(6.63 \times 10^{-34} \text{ J s}) \times 3.00 \times 10^8 \text{ m/s}}{656 \times 10^{19} \text{ m}} \\
E_{\text{red photon}} = 3.03 \times 10^{19} \text{ J}
\]

For a WXPN photon: 

\[
E_{\text{WXPN photon}} = (6.63 \times 10^{-34} \text{ J s})(88.9 \times 10^6 \text{ s/m}) \\
E_{\text{WXPN photon}} = 5.89 \times 10^{26} \text{ J}
\]

Now, if the kinetic energy is negative (an impossibility) - this implies that the incident photon does not have enough energy to overcome the binding energy of the metal surface and hence, to cause ejection of an electron. We tabulate the results. Verify them for yourself.

<table>
<thead>
<tr>
<th>Photon</th>
<th>(E_{\text{photon}})</th>
<th>K.E.(<em>e) = (E</em>{\text{photon}}) - (F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Green</td>
<td>4.09 \times 10^{19} \text{ J}</td>
<td>+ 1.09 \times 10^{19} \text{ J} - Yes.</td>
</tr>
<tr>
<td>Red</td>
<td>3.03 \times 10^{19} \text{ J}</td>
<td>+ 0.03 \times 10^{19} \text{ J} - Yes.</td>
</tr>
<tr>
<td>WXPN</td>
<td>5.89 \times 10^{26} \text{ J}</td>
<td>(\nabla) 3.00 \times 10^{19} \text{ J} - No.</td>
</tr>
</tbody>
</table>

Green light and red light has sufficient energy to cause ejection of electrons; however, WXPN radiation does not - this is why the K.E.\(_e\) comes out negative.

(2b) From (2a), only the green and red photons will cause ejection of electrons. Thus, we can only determine the electron ejection speed in these two cases. So, using:

\[
\text{Since } K.E. = \frac{1}{2} m_e v_e^2 \quad \Rightarrow \quad v_e = \sqrt{\frac{2 K.E.}{m_e}}
\]
For the electron ejected by the green light:

\[ v_e = \sqrt{\frac{(2)(1.09 \times 10^{19} \text{ J})}{9.11 \times 10^{31} \text{ kg}}} \]

\[ v_e = 4.89 \times 10^5 \text{ m/s} = 489 \text{ km/s} \]

For the electron ejected by the red light:

\[ v_e = \sqrt{\frac{(2)(0.03 \times 10^{19} \text{ J})}{9.11 \times 10^{31} \text{ kg}}} \]

\[ v_e = 8.12 \times 10^4 \text{ m/s} = 81.2 \text{ km/s} \]

- **Hydrogenic Atom (Ion) - Bohr Energy Formula**

Examples & Problem Solving Hints:

**Concept:** A spectral “line” is due to the transition of the single electron in atomic hydrogen from one energy state to another. The energy difference \( \Delta E \) between these stationary states is related to the wavelength (or frequency) of the “line” in the spectrum. Specifically, the energy difference for a particular electron transition (“jump”) equals the energy of the corresponding photon (emitted or absorbed):

\[ E_{\text{photon}} = \Delta E_e \]

Where - \( E_{\text{photon}} \) is from Planck:

\[ E_{\text{photon}} = \frac{hc}{\lambda} \]

and

\( \Delta E_e \) is from Bohr:

\[ \Delta E_e = E_{f,e} - E_{i,e} = Z^2 R_y \frac{1}{n_f^2} - \frac{1}{n_i^2} \]

[where, \( Z = 1 \) for H]

**Example - Transitions & Hydrogen-like (Hydrogenic) atoms:**

(a) What exactly is meant by a “line” in the (electronic) spectrum of an atom? What is the exact relationship between a spectral line and the energy levels of the atom that produced it?

(b) Consider the hydrogen-like atom (cation) B\(^+4\) cation. Determine the wavelength (in nm) for the second line in the Lyman emission spectrum for this cation.

(c) Consider again the hydrogen-like atom (cation) B\(^+4\) cation. Determine the wavelength (in nm) for the second line in the Balmer absorption spectrum for this cation.

(d) Determine the energy (in eV) and frequency (in Hz) needed to ionize the ground state B\(^+4\) cation.
(e) The electron in B\(^{+4}\) is originally in an excited state “\(n\)”. It subsequently makes a transition to the first excited state - emitting a photon with a wavelength of 17.38 nm. Determine the quantum number “\(n\)”, of the original excited state.

(f) A certain line in the Balmer emission spectrum of the hydrogenic beryllium cation has a wavelength of 30.4 nm. Determine \(n_{\text{initial}}\) for the electron for this transition.

“Extra Credit”: To which line in the Balmer emission series (i.e., 1st, 2nd, 3rd, ... ) does this correspond? How do you know?

**Solution to Example:**

(a) A line in a spectrum (whether absorption or (more commonly) emission) refers to a particular (monochromatic) photon wavelength (\(\lambda\)) or frequency (\(\nu\)). This wavelength or frequency corresponds to a photon energy \(E_{\text{photon}}\) that equals the difference in energy \(\Delta E\) between two of the allowable energy levels in the atom. Specifically, for an electronic spectrum (the only kind we have looked at so far) the energy levels represent the allowable quantized energies of the electron. When an electron in an atom undergoes a transition from one of its allowable energy states or levels to another, a photon is either absorbed (the electron makes a transition to a higher energy level) or is emitted (the electron makes a transition to a lower energy level). In either case, the magnitude of this \(E_{\text{photon}}\) equals \(\Delta E_{\text{electron}}\).

Thus:

\[
E_{\text{photon}} = |\Delta E_{\text{electron}}|
\]

This \(E_{\text{photon}}\) (according to Planck) \(= h\frac{c}{\lambda}\). This \(\lambda\) or \(\nu\) produces the specific emission or absorption whose “color” is the observed spectral line.

(b) Remember: for the hydrogen-like atom, \(B^{+4}\), \(Z = 5\), 5 protons in the nucleus and one (1) electron outside the nucleus.

Second line - Lyman - emission \(\square\) \(n_i = 3 \rightarrow n_f = 1\).

\[
\square E_e = \frac{hc}{\lambda} = Z^2 R_y \left[ \frac{1}{2} \right] \frac{1}{n_f} - \frac{1}{n_i} = (5)^2 (2.18 \times 10^{-18} \text{ J}) \frac{1}{3} \frac{1}{1} = 4.84 \times 10^{-17} \text{ J}
\]

Note: the \(\square\) sign indicates emission. However, \(\square\) is positive, so we “ignore” the minus sign.

\[
\square = \frac{hc}{\square E_e} = \frac{6.63 \times 10^{-34} \text{ J s}}{4.84 \times 10^{-17} \text{ J}} = 4.10 \times 10^9 \text{ m} \times \frac{1 \text{ nm}}{10^9 \text{ m}} = 4.10 \text{ nm}
\]
(c) For the hydrogen-like atom, B\(^{+4}\), \(Z = 5\), 5 protons in the nucleus and one (1) electron outside the nucleus.

Second line - Balmer - absorption

\[ n_i = 2 \rightarrow n_f = 4 \]

\[ E_e = \frac{\hbar c}{\lambda} = Z^2 R_y \left( \frac{1}{n_i^2} - \frac{1}{n_f^2} \right) = (5)^2 \left( 2.18 \times 10^{-18} \text{ J} \right) \left( \frac{1}{2^2} - \frac{1}{4^2} \right) \]

\[ E_e = \frac{\hbar c}{\lambda} = +1.02 \times 10^{-17} \text{ J} \]

Note: the (+) sign indicates absorption.

\[ \lambda = 1.95 \times 10^{-8} \text{ m} \times \frac{1 \text{ nm}}{10^{-9} \text{ m}} = 19.5 \text{ nm} \]

(d) For the hydrogen-like atom, B\(^{+4}\), \(Z = 5\), 5 protons in the nucleus and one (1) electron outside the nucleus.

Ionize from ground state

\[ n_i = 1 \rightarrow n_f = \infty \text{ (infinity)} \]

\[ E_e = Z^2 R_y \left( \frac{1}{n_i^2} - \frac{1}{n_f^2} \right) = (5)^2 \left( 2.18 \times 10^{-18} \text{ J} \right) \left( \frac{1}{1^2} - \frac{1}{\infty^2} \right) \]

\[ E_e = +5.45 \times 10^{-17} \text{ J} \]

Note: the (+) sign indicates absorption.

\[ E_e = \frac{1 \text{ eV}}{1.60 \times 10^{-19} \text{ J}} = 341 \text{ eV} \]

Since \( E_e = \hbar \frac{\omega}{c} \)

\[ \omega = \frac{E_e}{\hbar} = \frac{5.45 \times 10^{-17} \text{ J}}{6.63 \times 10^{-34} \text{ J s}} = 8.22 \times 10^{16} \text{ s}^{-1} \text{ or Hz} \]

(e) For the hydrogen-like atom, B\(^{+4}\), \(Z = 5\), 5 protons in the nucleus and one (1) electron outside the nucleus.

Emission

\( n_i > n_f \)  
Energy released \( n_f \) negative energy change.

\[ n_i = n = ? \rightarrow n_f = 2 \text{ (first excited state)} \]
\[ E_{\text{photon}} = \frac{hc}{\lambda} = \frac{(6.63 \times 10^{34} \text{ J s})}{17.38 \times 10^{9} \text{ m}} = 1.144 \times 10^{17} \text{ J}. \]

Since we have emission \( \Box \), \( \Box E_e = \Box 1.144 \times 10^{17} \text{ J} \)

\( \Box E_e = \Box 1.144 \times 10^{17} \text{ J} = Z^2 R_y \left( \frac{1}{n_i^2} - \frac{1}{n_f^2} \right) \)

\( \Box 1.144 \times 10^{17} \text{ J} = (5)^2 (2.18 \times 10^{18} \text{ J}) \left( \frac{1}{n_i^2} - \frac{1}{2^2} \right) \); solving for “n”

\[ \frac{1}{n^2} = \frac{\Box 1.144 \times 10^{17} \text{ J}}{(5)^2 (2.18 \times 10^{18} \text{ J})} + \frac{1}{2^2} = \Box 0.210 + 0.250 = +0.04 \]

\[ n = \sqrt{1.04} = 5. \quad \Box n = 5 \quad \text{fourth excited state.} \]

(f) Be has \( Z = 4 \). So, the hydrogenic Be cation is Be\(^{+3} \).

The magnitude of the photon energy (i.e., \( |E_{\text{photon}}| \)) can be easily obtained.

\[ |E_{\text{photon}}| = \frac{hc}{\lambda} = \frac{(6.63 \times 10^{34} \text{ J s}) (3.00 \times 10^8 \text{ m/s})}{(30.4 \times 10^9 \text{ m})} \]

\( |E_{\text{photon}}| = 6.543 \times 10^{18} \text{ J} \)

**IMPORTANT...** Since this photon is emitted, it represents energy released by the electron when it undergoes the transition. Thus, \( E_{\text{photon}} \) is a negative number (energy released). Without the minus (\( \Box \)) sign, the incorrect \( n_i \) will result. Be careful.

\( E_{\text{photon}} = \Box 6.543 \times 10^{18} \text{ J} = \Box E_e = Z^2 R_y \left( \frac{1}{n_i^2} - \frac{1}{n_f^2} \right) \). Here, \( Z = 4 \).

Also, \( n_f = 2 \). This is true for all Balmer emissions.

Solving for \( \frac{1}{n_i^2} \):

\[ \frac{1}{n_i^2} = \frac{\Box (6.543 \times 10^{18} \text{ J})}{(4)^2 (2.18 \times 10^{18} \text{ J})} + \frac{1}{2^2} = \Box 0.1876 + 0.25 = 0.0624 \]
\[ n_i = + \sqrt{\frac{1}{0.0624}} \quad \text{must round to whole number} \]

The electron transition that corresponds to the listed emission is:
\[ n_i = 4 \quad \rightarrow \quad n_f = 2 \]

**Extra Credit**: The lines listed in a series are numbered sequentially - beginning with the smallest \( \Delta E_c \) (i.e., smallest \( E_{\text{photon}} \)). This transition gives rise to the photon that produces the first line in the series. Hence,

- \( n_i = 3 \rightarrow n_f = 2 \) corresponds to the **first Balmer emission line**.
- \( n_i = 4 \rightarrow n_f = 2 \) corresponds to the **second Balmer emission line**.
- \( n_i = 5 \rightarrow n_f = 2 \) corresponds to the **third Balmer emission line**.
- \( n_i = 6 \rightarrow n_f = 2 \) corresponds to the **fourth Balmer emission line**.

and so on. The following diagram may make it clear.

```
<table>
<thead>
<tr>
<th>2nd Balmer emission line</th>
<th>1st Balmer emission line</th>
</tr>
</thead>
<tbody>
<tr>
<td>electron transition</td>
<td>electron transition</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>n = 4</td>
<td>n = 4</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>n = 3</td>
<td>n = 3</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>n = 2</td>
<td>n = 2</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>n = 1</td>
<td>n = 1</td>
</tr>
</tbody>
</table>
```

Thus, the transition from \( n_i = 4 \rightarrow n_f = 2 \) corresponds to the **second Balmer emission line for the Be\(^{+3} \) cation**.