Chapter 33

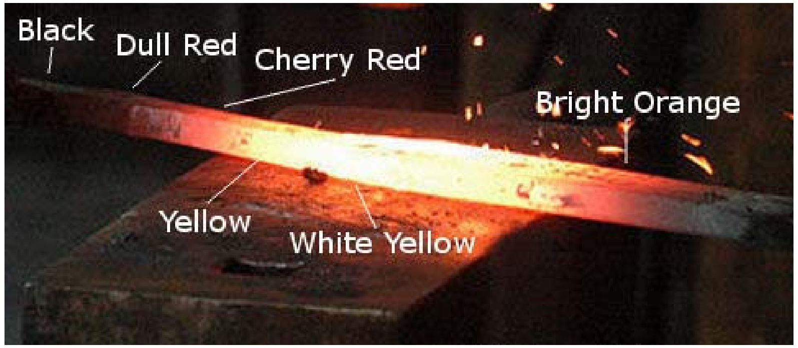
Early Quantum Theory & Models of Atom

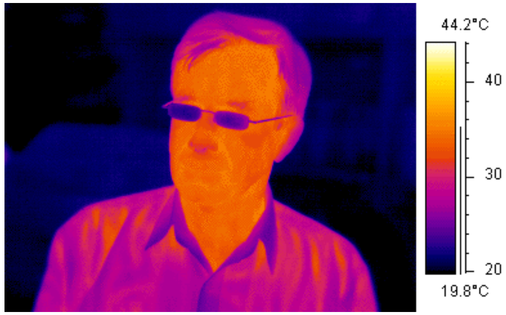
- Blackbody Radiation; Planck's Quantum Hypothesis
- Photon Theory of Light & the Photoelectric Effect
- Compton Effect
- Photon Interactions; Wave-Particle Duality
- Wave Nature of Matter
- Early Models of the Atom; Atomic Spectra
- The Bohr Model
- *de Broglie’s Hypothesis Applied to Atoms

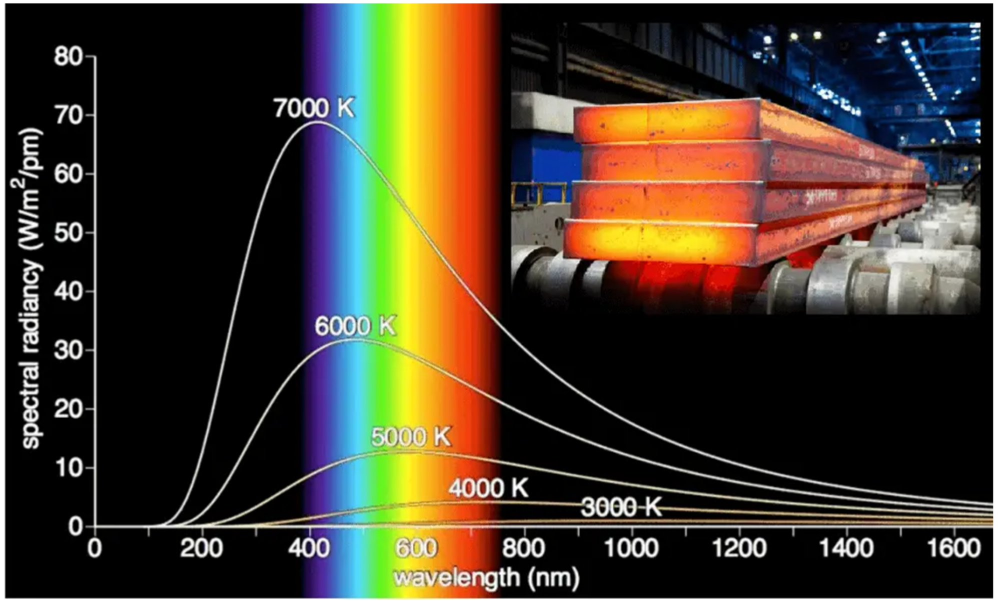
Thermal Radiation (due to thermal motion of atoms and molecules):

Planck's Law—Every object emits radiation at all times and at all wavelengths.

The characteristics of radiated electromagnetic waves are related to the temperature of the object







§ 31-1 Blackbody Radiation; Planck's Quantum Hypothesis

1. Blackbody radiation

Blackbody: absorbs all incident electromagnetic radiation, regardless of frequency or angle of incidence.

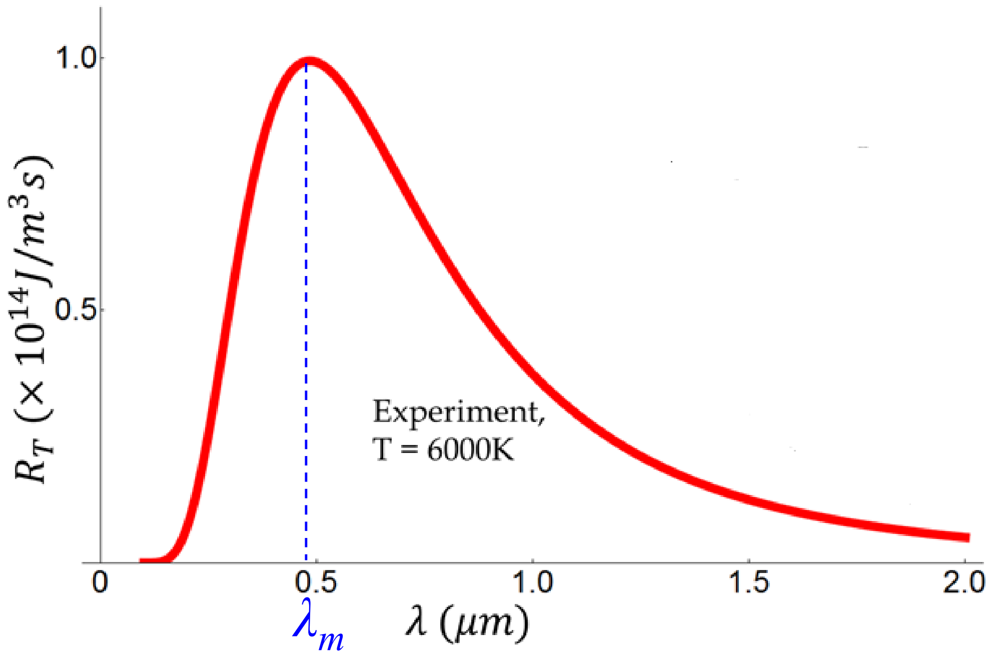
Wein's Law:

$$\lambda_m = \frac{2.898\times10^{-3}\ \ [\mathrm{m\cdot K}]}{T}$$

Stefan–Boltzmann Law: radiation energy transfer rate (W/m^2) from the object to its surroundings is

$$Q = \sigma \cdot T^4$$

$$(\sigma = 5.670\times10^{-8}\ \ \mathrm{W\cdot m^{-2}\cdot K^{-4}})$$



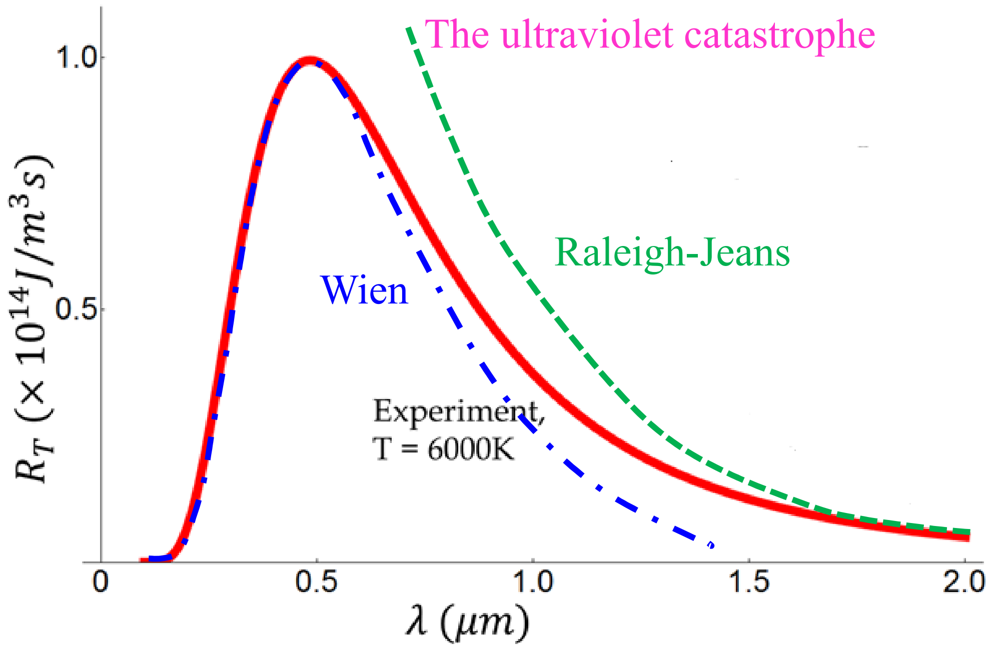
Spectrum function of blackbody radiation derived from classical theories:

Wien:

$$R_T(\lambda, T) = \frac{2\pi hc^2}{\lambda^5} \cdot e^{-\frac{hc}{\lambda kT}}$$

$$(k = 1.38 \times 10^{-23}\ J/K)$$

agrees with the experimental data at short wavelengths.



Rayleigh-Jeans:

$$R_T(\lambda, T) = \frac{2\pi kT}{\lambda^4}$$

Raleigh-Jeans's formula agrees with the experimental data at long wavelengths. This result is called the ultraviolet catastrophe.

2. Planck's quantum hypothesis

Planck assumed the energy exchanged between atoms and the electromagnetic radiation can only be an integer number of a minimum energy *hf* (f : the frequency of the radiation):

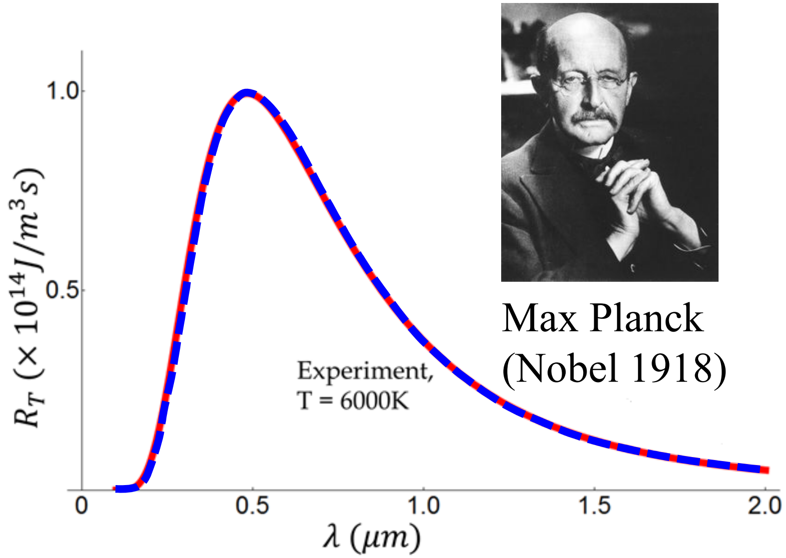
$$E = n \cdot hf$$

(n : quantum number; hf : quantum of energy)

and get the formula (1900):

$$R_T(\lambda, T) = \frac{2\pi hc^2}{\lambda^5} \cdot \frac{1}{e^{\frac{hc}{\lambda kT}} - 1}$$

Planck's constant: $h = 6.626 \times 10^{-34}\, J \cdot s$



Max Planck
(Nobel 1918)

Quantum → discrete amount

(a) (b)

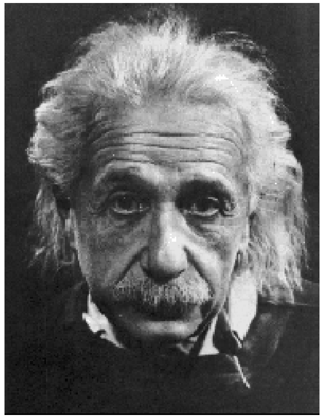
continuous discrete

§ 31-2 Photon Theory of Light & the Photoelectric Effect

1. Photon theory of light

The light ought to be emitted, transported, and absorbed as tiny particles (now we call photons), each with an energy:

$$\boxed{E = hf = \frac{hc}{\lambda}} \rightarrow \text{quantum of radiation}$$



Albert Einstein
(Nobel 1921)

Momentum of a photon:

$$\left.\begin{aligned} P &= mc \\ E &= hf = mc^2 \end{aligned}\right\} \Rightarrow \boxed{P = \frac{h}{\lambda} = \frac{hf}{c}}$$

Mass and rest mass of a photon:

$$\boxed{\begin{aligned} m_0 &= 0 \\ m &= \frac{E}{c^2} = \frac{hf}{c^2} \end{aligned}}$$

Energy of photon in visible region:

Example1: Calculate the energy of a photon with

$\lambda = 450$nm (blue light).

Solution:

$$E = \frac{hc}{\lambda} = 4.4 \times 10^{-19} J = 2.7eV$$

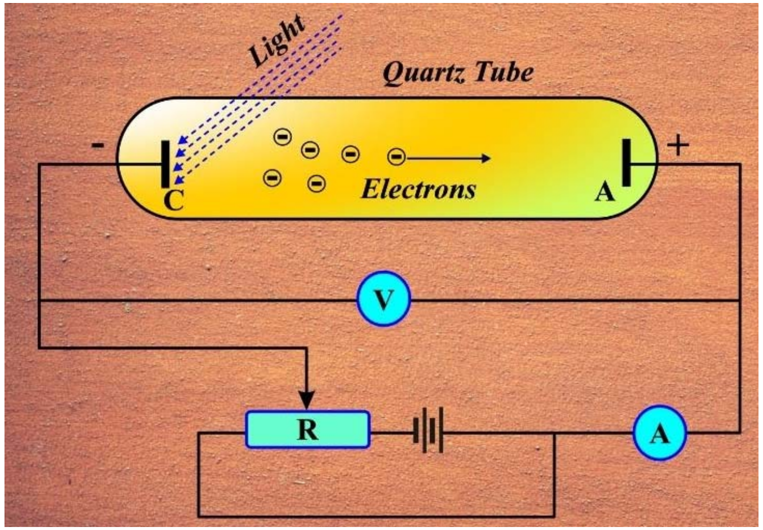
Example2: Estimate the number of visible light photons per sec in radiation of 50W light bulb.

Solution: Average wavelength:

$$\bar{\lambda} \approx 550nm$$

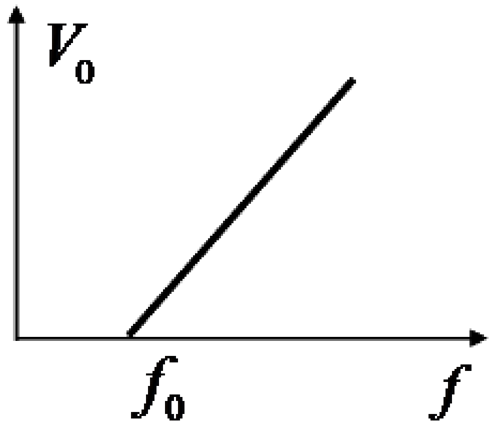
$$n = P \Big/ \frac{hc}{\bar{\lambda}} = 1.4 \times 10^{20}$$ invisible light photons?

2. The photoelectric effect



Photoelectric effect: when shined by light, a metal surface will emit electrons (photoelectrons).

Stopping voltage V_0: the reverse voltage applied until no photoelectrons reach the anode A. The maximum kinetic energy of the photoelectrons is:



$$E_{k\,\max} = \frac{1}{2}mv^2 = eV_0$$

Experimental results:

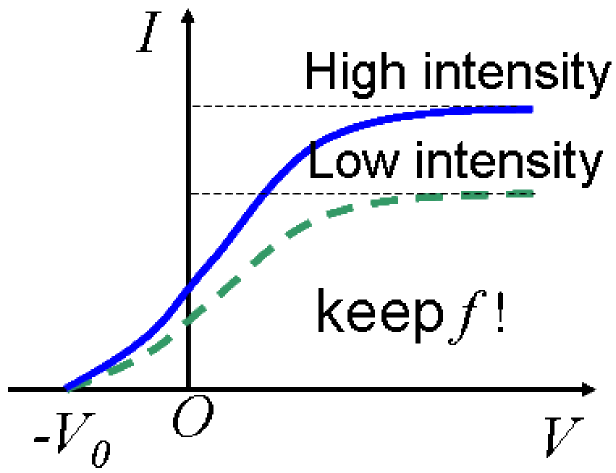
(1) $E_{k\max} \propto f$, but independent of the light intensity;

(2) When $f < f_0$ (cutoff frequency), no photoelectrons emitted;

(3) Increasing V, I increases, but it will become saturated;

(4) The saturated current I_s is proportional to the light intensity;

(5) Instant emission: Photoelectrons emit in extremely short time $\sim 10^{-9}$s.



Comparison between experiment and classical prediction:

Items	Experimental results	Classical predictions
E_{kmax}	Independent on intensity	Dependent on intensity
	Dependent on f	Independent on f
f	Existence of cutoff f_0	No cutoff f_0
Time of emission	$\sim 10^{-9}$s	$\sim 10^{-6}$s

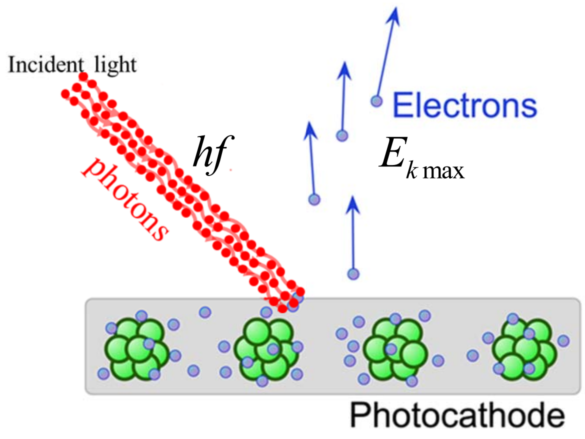
Fail!

Explanation by photon theory:

(1) A photon collides with an electron;

(2) All photon energy is transferred to the electron;

(3) Work function W_0: minimum energy required to get an electron out of the metal.



Energy conservation: $\boxed{hf = E_{k\,max} + W_0}$ ——Photoelectric equation

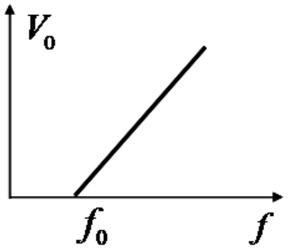
Compare with experiment:

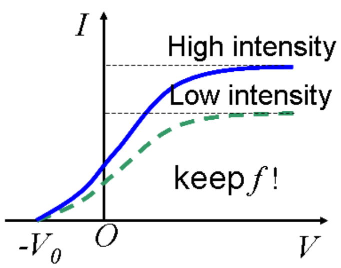
(1) V_0 vs f:

$$V_0 = \frac{h}{e} f - \frac{W_0}{e}$$

(2) $E_{kmax} > 0$:

$$f > \frac{W_0}{h}, \quad f_0 = \frac{W_0}{h}$$





(3) Fix f, I increases, photon number increases, saturated current I_s increases.

Example3: The threshold wavelength for a metal surface is 350 nm. What is the $E_{k\max}$ when the wavelength changes to (a) 280 nm, (b) 380 nm?

Solution: $hf = E_{k\max} + W_0, \quad W_0 = hf_0 = hc/\lambda_0$

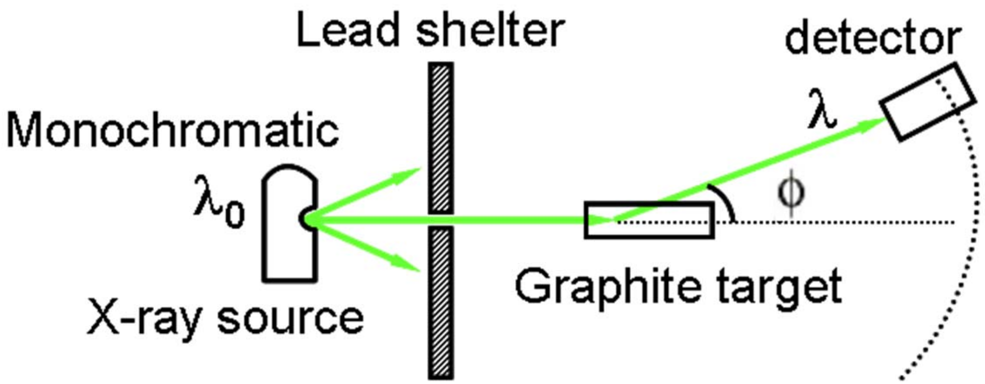
$$\therefore \quad E_{k\max} = \frac{hc}{\lambda} - \frac{hc}{\lambda_0}$$

(a) $\lambda = 280nm, \quad E_{k\max} = 1.4\times10^{-19} J \ = 0.89eV$

(b) $\lambda = 380nm > 350nm$ No ejected electrons!

§ 31-3 Compton Effect

Compton's x-ray scattering experiment (Nobel 1927):



Classical theory prediction:

- Electrons undergo forced vibration driven by EM waves;
- Vibration frequency equals to the EM wave frequency;
- Electrons emit EM waves of the same frequency as the vibration;

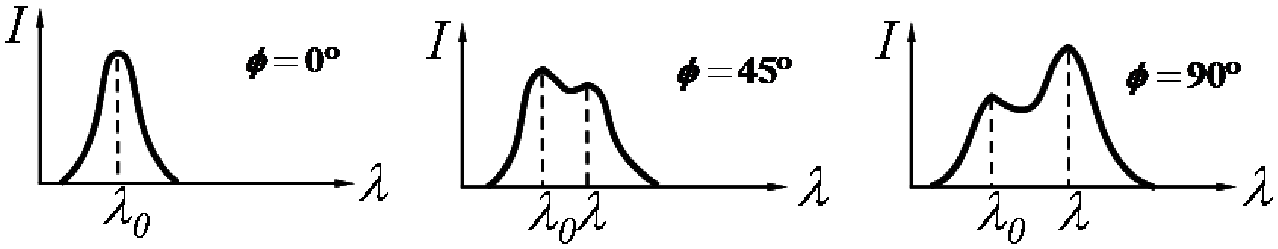
Therefore,

$$f = f_0, \quad \lambda = \lambda_0$$

Experimental results:

(1) Besides λ_0, scattered light has longer wavelengths λ ($\lambda > \lambda_0, f < f_0$);

(2) $\Delta\lambda = \lambda - \lambda_0$ depends only on the scattering angle ϕ.



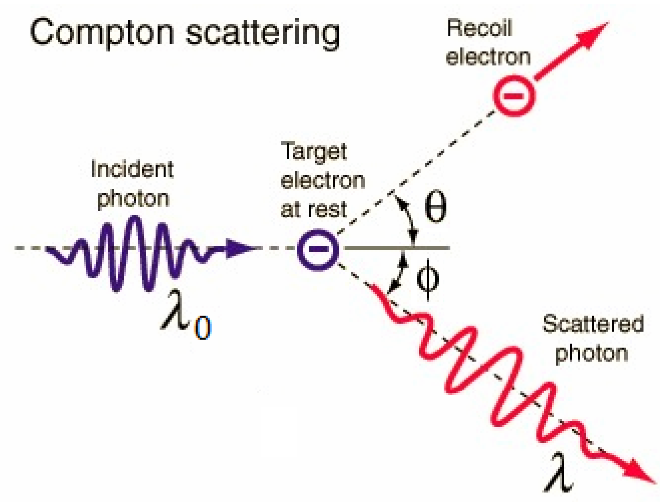
Explanation by photon theory:

(1) A photon collides with an electron (free, at rest) elastically;

(2) Energy is conserved;

(3) Momentum is conserved.

Photon: Energy loss $\rightarrow f < f_0 \rightarrow \lambda > \lambda_0$



(4) Compton shift

Conservation of energy:

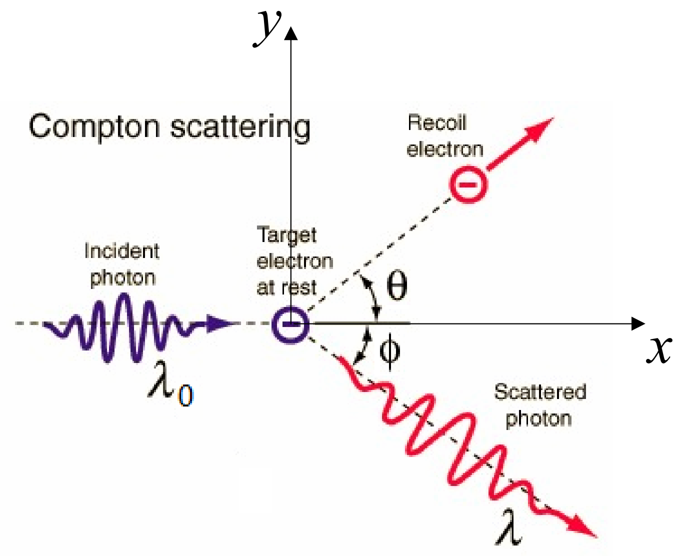
$$\frac{hc}{\lambda_0} + m_0 c^2 = \frac{hc}{\lambda} + mc^2$$

Conservation of momentum:

$$\begin{cases} x: & \dfrac{h}{\lambda_0} = \dfrac{h}{\lambda}\cos\phi + mv\cos\theta \\ y: & 0 = mv\sin\theta - \dfrac{h}{\lambda}\sin\phi \end{cases}$$

Relativistic mass:

$$m = \frac{m_0}{\sqrt{1 - v^2/c^2}}$$



$$\Rightarrow \quad \boxed{\Delta\lambda = \lambda - \lambda_0 = 2\lambda_C \sin^2\frac{\phi}{2}}$$

Compton shift

$$\boxed{\lambda_C = \frac{h}{m_0 c} = 2.43\times10^{-12}\,\mathrm{m}}$$

Compton wavelength

Maximum wavelength: $\lambda_{\max} = \lambda_0 + 2\lambda_C = \lambda_0 + 4.86\times10^{-12}\,m$

Example4: X-rays with λ_0= 0.2 nm are scattered from a material. Calculate the wavelength of the x-rays at scattering angle (a) 45° and (b) 90° .

Solution:

$$\Delta\lambda = \lambda - \lambda_0 = 2\lambda_C \sin^2\frac{\phi}{2} = \lambda_C(1-\cos\phi)$$

$$\lambda = \lambda_0 + \Delta\lambda = \lambda_0 + \frac{h}{m_0 c}(1-\cos\phi)$$

$$(a) \quad \phi = 45^\circ: \ \lambda = 0.2007\text{nm}$$

$$(b) \quad \phi = 90^\circ: \ \lambda = 0.2024\text{nm}$$

Maximum shift?

Some questions:

(1) Why there is still a peak of λ_0 ?

Photons scattered from very tightly bound electrons.

(2) What is the difference from photoelectric effect?

Photon collides with free electron, and photon collides with bound electron.

(3) Why not absorb the photon ?

Forbidden by the law of momentum conservation.

(4) Why not consider $\vec{p}$ in photoelectric effect?

Bound electron attracted by the atom, net force is not zero.

§ 31-4 Photon Interactions; Wave-Particle Duality

1. Photon interactions

(1) Knocks an electron out of an atom, then disappears (absorbed);

(2) Scattered from an electron, and lose some energy (still exists);

(3) Knock an atom-electron from low energy state to higher energy state, then disappears (Absorbed by an atom);

(4) Pair production: the photon disappears in the process of creating the electron-positron pair (create matter, $E=mc^2$).

Inverse process : annihilation of a pair electron-positron → photon.

2. Wave-particle duality

The nature of light?

- Sometimes light behaves like a wave;
- Sometimes it behaves like a stream of particles.

"They could but make the best of it and went around with woebegone faces, sadly complaining that on Mondays, Wednesdays, and Fridays, they must look on light as a wave; on Tuesdays, Thursdays, and Saturdays, as a particle. On Sundays, they simply prayed."——The Strange Story of the Quantum

Bohr's principle of complementarity:

To understand any given experiment of light, we must use either the wave or the photon theory, but not both.

Physicists' final conclusion: **Wave-particle duality**

§ 31-5 Wave Nature of Matter

de Broglie's hypothesis: **a matter particle in motion is also associated with waves.**

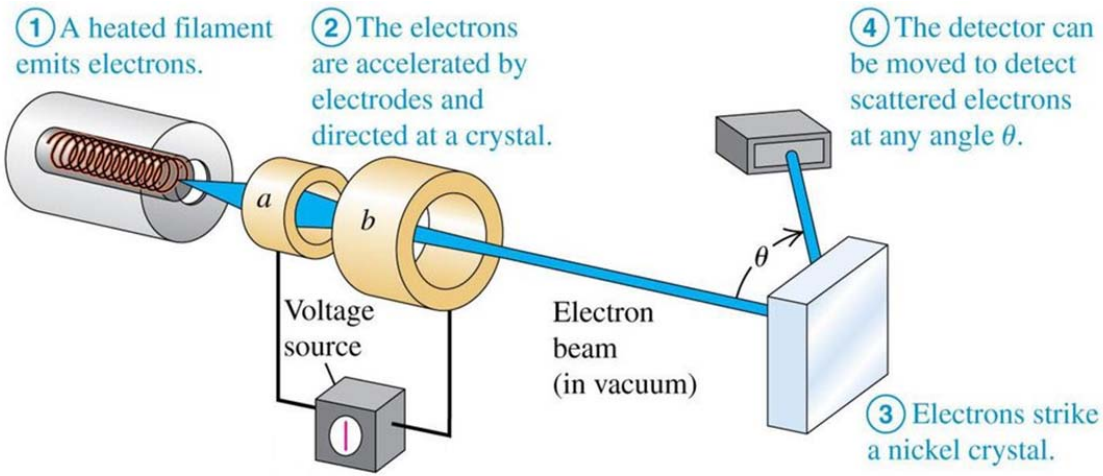
L. de Broglie
(Nobel 1929)

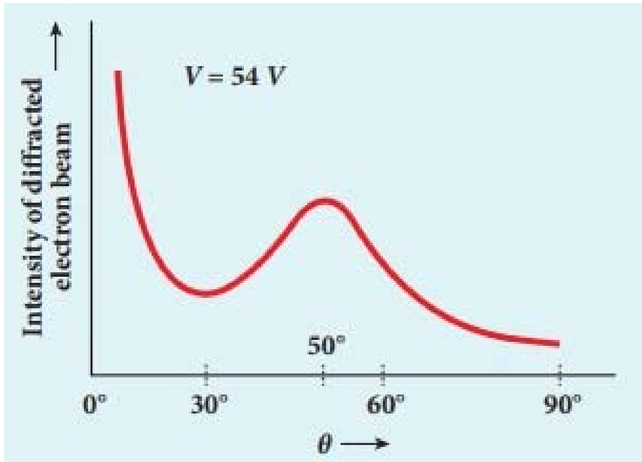
$$\boxed{\lambda = \frac{h}{p} = \frac{h}{mv}}$$

de Broglie wave

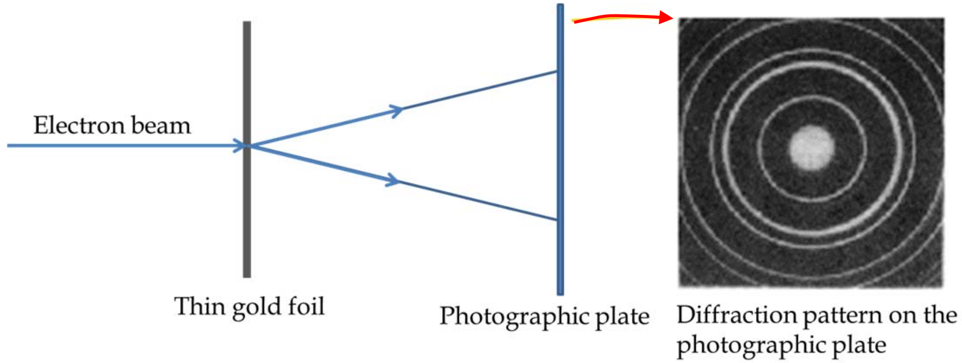
or matter wave

Experimental proof (Davisson-Germer, Nobel 1937):





Experimental proof (G.P. Thomson, Nobel 1937):



What is an electron?

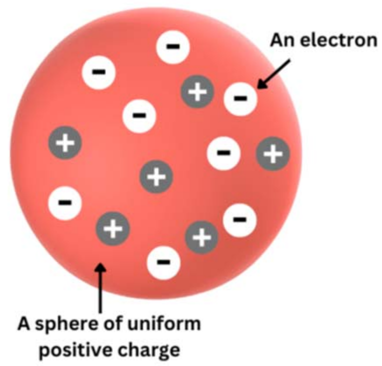
No one sees an electron directly. All the electrons we think of are models we use to picture it based on the properties it displays.

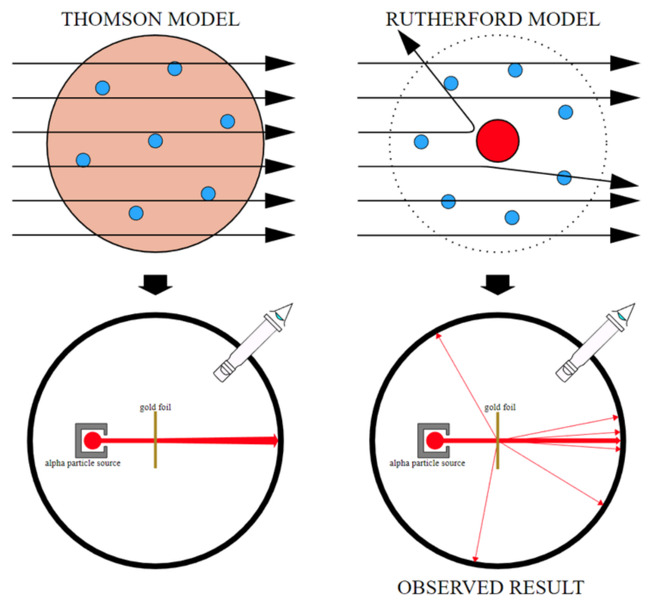
- An electron is neither a wave nor a particle;
- It is the set of its properties that we can measure;
- "A logical construction" —— B. Russell;
- de Broglie wave → a wave of probability.

§ 31-6 Early Models of the Atom; Atomic Spectra

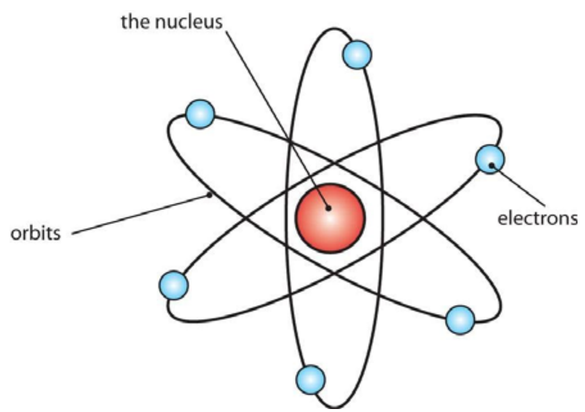
1. Early models of the atom

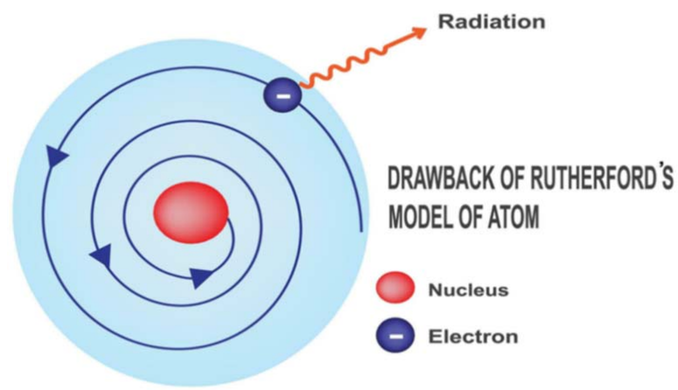
(1) Plum-pudding Model (J. J. Thomson)





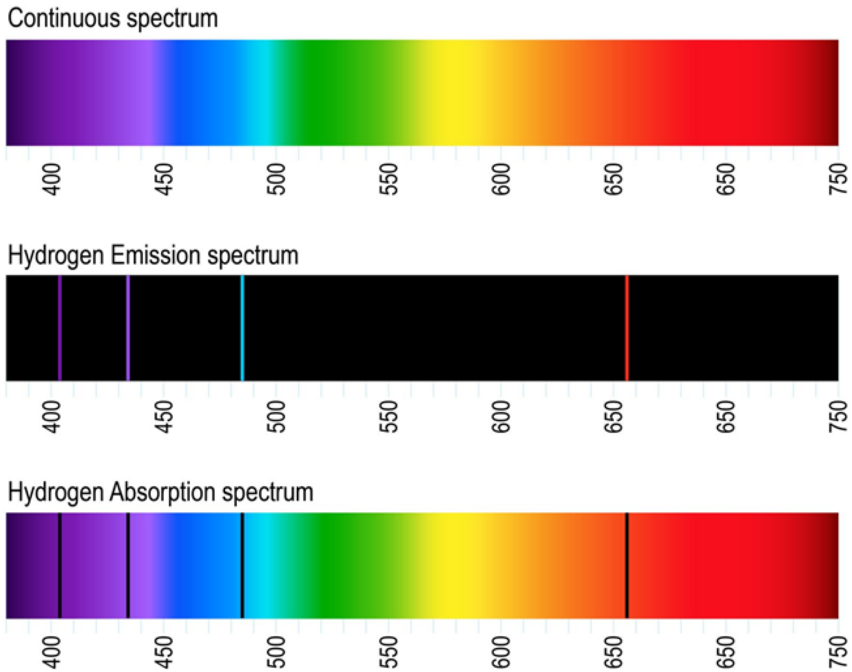
(2) Rutherford's planetary model (nuclear model)





2. Atomic spectrum

- An atomic spectrum is a line spectrum—only certain frequencies appear;
- The emission and absorption spectrum is characteristic of the material and can serve as "fingerprint" for identification of the gas.



Spectrum of Hydrogen:

(1) Balmer series（1885）

$$\frac{1}{\lambda}=R\left(\frac{1}{2^2}-\frac{1}{n^2}\right),\quad n=3,4,\ldots$$

Visible light

Rydberg constant: $R=1.097\times10^{7}\,\mathrm{m}^{-1}$

(2) General formula of Hydrogen's spectrum

There were other series of lines in the UV and IR regions found experimentally. Balmer's formula could be extended to these series:

$$\boxed{\frac{1}{\lambda} = R\left(\frac{1}{k^2} - \frac{1}{n^2}\right), \quad (n = k+1,\ k+2,\ \cdots\ )}$$

$\boldsymbol{k = 1} \rightarrow$ Lyman series (ultraviolet)

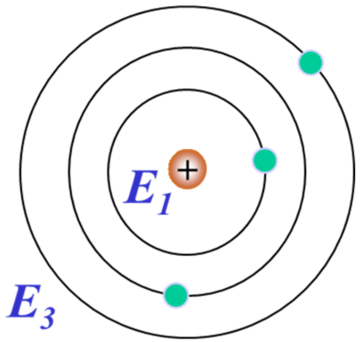
$\boldsymbol{k = 2} \rightarrow$ Balmer series (visible)

$\boldsymbol{k = 3} \rightarrow$ Paschen series (infrared) $\cdots\cdots$

Note: Rutherford's atom model contradicted the line spectrum of the atom.

§ 31-7 The Bohr Model

1. Bohr's three postulates



Neils Bohr
(Nobel 1922)

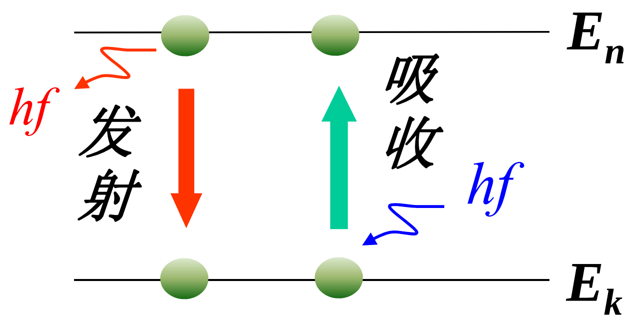
(1) Stationary states:

stable & discrete energy level.

(2) Quantum transition: ("jump")

emit or absorb a photon:

$$hf = E_n - E_k$$

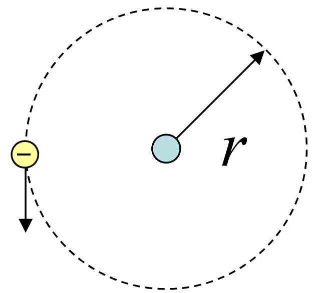


(3) Quantum condition: (for angular momentum)

$$L = mvr = n\hbar, \ n = 1, \ 2, \ \cdots \qquad (\hbar = \frac{h}{2\pi})$$

2. Bohr model

Rutherford model + quantum idea = semi-classical



$$\left.\begin{array}{l}\dfrac{e^2}{4\pi\varepsilon_0 r^2} = m\dfrac{v^2}{r} \\ L = mvr = \dfrac{nh}{2\pi}\end{array}\right\} \Rightarrow \left\{\begin{array}{l} r_n = n^2 \cdot \dfrac{\varepsilon_0 h^2}{\pi m e^2} = n^2 r_1, \quad (n = 1,\ 2,\ \cdots) \\ r_1 = \dfrac{\varepsilon_0 h^2}{\pi m e^2} = 0.529\times 10^{-10}\,\mathrm{m} \end{array}\right.$$

(Bohr radius)

The orbital radius of electron is quantized

Kinetic energy: $E_k = \frac{1}{2}mv^2 = \frac{e^2}{8\pi\varepsilon_0 r_n}$

Potential energy: $U = -eV = -\frac{e^2}{4\pi\varepsilon_0 r_n}$

Total energy:

$$E = E_k + U = \frac{-e^2}{8\pi\varepsilon_0 r_n} = -\frac{1}{n^2}\left(\frac{me^4}{8\varepsilon_0{}^2 h^2}\right) = -\frac{13.6\ \mathrm{eV}}{n^2}$$

Energy is also quantized

(1) Energy levels

$$\boxed{E_n = \frac{-13.6\text{eV}}{n^2}, n = 1,\ 2,\ \cdots}$$

Negative energy due to bound state

(a) Quantization of energy (energy levels)

$n = 1$, ground state, $r = r_1$, $E_1 = -13.6\text{eV}$;

$n = 2$, 1^{st} exited state, $r = 4r_1$, $E_2 = -3.4\text{eV}$;

$n = 3$, 2^{nd} exited state, $r = 9r_1$, $E_3 = -1.51\text{eV}$;

……

(b) Binding / ionization energy

$$\Delta E = E_\infty - E_1 = -E_1 = 13.6\ \text{eV}$$

is precisely equal to the measured ionization energy of hydrogen.

(2) Transition & radiation

Jumping from upper state n to lower state k :

$$E_n = -\frac{1}{n^2}\left(\frac{me^4}{8\varepsilon_0{}^2 h^2}\right)$$

$$h\frac{c}{\lambda} = hf = E_n - E_k = \frac{me^4}{8\varepsilon_0{}^2 h^2}\left(\frac{1}{k^2} - \frac{1}{n^2}\right)$$

$$\Rightarrow \quad \frac{1}{\lambda} = \frac{me^4}{8\varepsilon_0{}^2 h^3 c}\left(\frac{1}{k^2} - \frac{1}{n^2}\right)$$

Experiment :

$$\frac{1}{\lambda} = R\left(\frac{1}{k^2} - \frac{1}{n^2}\right)$$

$$R = 1.097 \times 10^7\,\mathrm{m}^{-1}$$

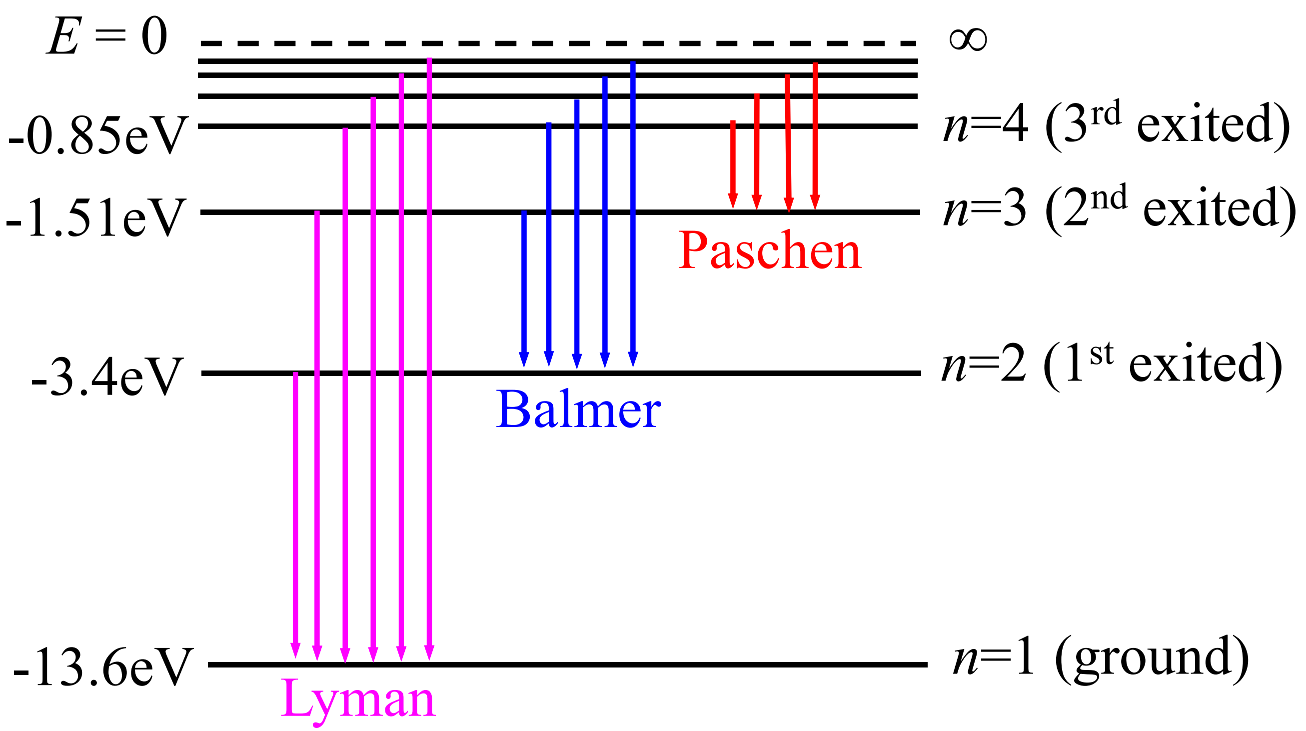
Theoretical value of *R* :

$$R = \frac{me^4}{8\varepsilon_0{}^2 h^3 c} = 1.097 \times 10^7\,\mathrm{m}^{-1}$$

In accord with the experimental value!

(3) Energy level diagram

$$E_n = \frac{-13.6\text{eV}}{n^2}, \qquad f = \frac{E_n - E_k}{h}, \qquad \frac{1}{\lambda} = R\left(\frac{1}{k^2} - \frac{1}{n^2}\right)$$



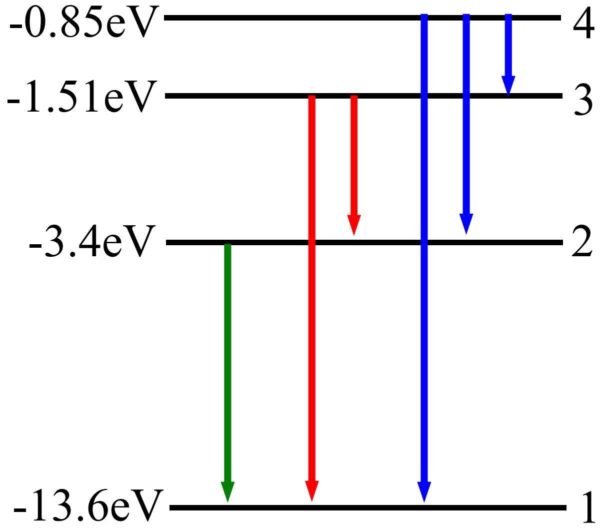
Example6: Hydrogen atom in 3rd excited state, (a) how many types of photon can it emit? (b) What is the maximum wavelength?

Solution: (a) $n = 4$

6 types of photon

(b) $\frac{1}{\lambda} = R(\frac{1}{3^2} - \frac{1}{4^2})$

$\Rightarrow \lambda = 1.9\mu m$



Single-electron ions:

Example7: Calculate (a) the ionization energy of He^+; (b) radiation energy when jumping from n=6 to n=2. (c) Can that photon be absorbed by H?

Solution: (a) For single-electron ions:

$$\frac{Ze^2}{4\pi\varepsilon_0 r^2} = m\frac{v^2}{r} \qquad (e^2 \to Ze^2,\ \text{Z: number of proton})$$

$$E_n = -\frac{1}{n^2}\left(\frac{me^4}{8\varepsilon_0{}^2 h^2}\right) \ \Rightarrow\ E_n' = Z^2 E_n$$

$$\Rightarrow\ E_{ion}' = 4\times 13.6 = 54.4\text{eV}$$

(b) radiation energy if jumping from n=6 to n=2

$$E_n' = Z^2 E_n, \qquad E_n = \frac{-13.6\text{eV}}{n^2}$$

$$\Rightarrow \ \Delta E = 4\times 13.6\times\left(\frac{1}{2^2}-\frac{1}{6^2}\right) = 12.09\text{eV}$$

(c) Can that photon be absorbed by H?

$$\Delta E = 4\times 13.6\times\left(\frac{1}{2^2}-\frac{1}{6^2}\right) = 13.6\times\left(1-\frac{1}{3^2}\right)$$

So it can be absorbed by Hydrogen atom

Success of Bohr's theory:

(1) Explained the line spectrum of atom;

(2) Accurately predicts the light wavelengths emitted by hydrogen;

(3) Accurately predicts the ionization energy of 13.6 eV for hydrogen;

(4) Explained the absorption spectrum;

(5) Ensures the stability of atoms;

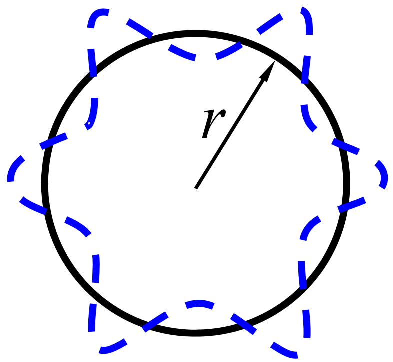
(6) Concept of stationary states, the ground state, and transitions between states.

Limitations of Bohr's theory:

- Cannot applied to other atoms (with more than one electron);
- Cannot give the intensity of the spectrum lines;
- Cannot explain the fine structure of the line spectrum of atoms;
- It's semi-classical, not a complete quantum theory.

§ 31-8 *de Broglie's Hypothesis Applied to Atoms

Stable orbit for electron → "standing wave"



de Broglie wave: $\lambda = \dfrac{h}{mv}$

Circular standing wave:

$$2\pi r = n\lambda, \quad (n = 1, 2, 3, \cdots)$$

Combine two equations:

$$L = mvr = \frac{nh}{2\pi} = n\hbar, \quad (n = 1, 2, 3, \cdots)$$

It is just the quantum condition by Bohr!

Summary

1. Wein's Law:

$$\lambda_m = \frac{2.898\times10^{-3}\ \ [\mathrm{m\cdot K}]}{T}$$

2. Planck's quantum hypothesis

$$E = n\cdot hf$$

(n : quantum number; hf : quantum of energy)

3. Photon theory of light

$$\boxed{E = hf = \frac{hc}{\lambda}}$$

$$\boxed{P = \frac{h}{\lambda} = \frac{hf}{c}}$$

$$\boxed{\begin{aligned} &m_0 = 0 \\ &m = \frac{E}{c^2} = \frac{hf}{c^2} \end{aligned}}$$

4. The photoelectric effect (**photon collides inelastically with bound electron**)

$$E_{k\,\max} = \frac{1}{2}mv^2 = eV_0$$

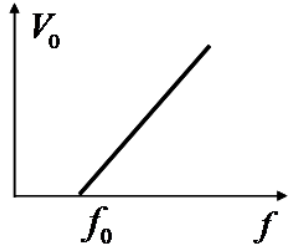
Stopping voltage: V_0

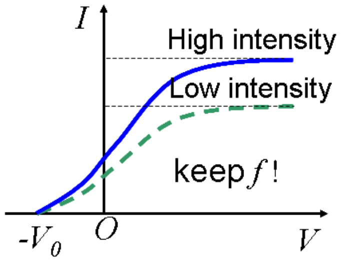
$$\boxed{hf = E_{k\,\max} + W_0}$$

Work function W_0

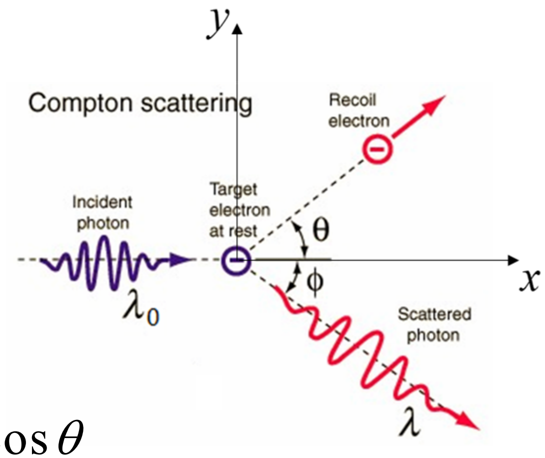
$$f_0 = \frac{W_0}{h}$$

Cutoff frequency





5. Compton effect (**photon collides elastically with free electron**)



$$\boxed{\Delta\lambda = \lambda - \lambda_0 = 2\lambda_C \sin^2\frac{\phi}{2}}$$

$$\boxed{\lambda_C = \frac{h}{m_0 c} = 2.43\times 10^{-12}\,\mathrm{m}}$$

$$\boxed{\lambda_{\max} = \lambda_0 + 2\lambda_C = \lambda_0 + 4.86\times 10^{-12}\,m}$$

$$\frac{hc}{\lambda_0} + m_0 c^2 = \frac{hc}{\lambda} + mc^2$$

$$\begin{cases} x: & \dfrac{h}{\lambda_0} = \dfrac{h}{\lambda}\cos\phi + mv\cos\theta \\ y: & 0 = mv\sin\theta - \dfrac{h}{\lambda}\sin\phi \end{cases}$$

6. de Broglie wave

$$\boxed{\lambda = \frac{h}{p} = \frac{h}{mv}}$$

7. Atomic spectrum

$$\boxed{\frac{1}{\lambda} = R\left(\frac{1}{k^2} - \frac{1}{n^2}\right), \quad (n = k+1,\ k+2,\ \cdots\ )}$$

$$(Rydberg\ constant : R = 1.097\times 10^{7}\,\mathrm{m}^{-1})$$

$\boldsymbol{k = 1} \longrightarrow$ Lyman series (ultraviolet)

$\boldsymbol{k = 2} \longrightarrow$ Balmer series (visible)

$\boldsymbol{k = 3} \longrightarrow$ Paschen series (infrared) $\cdots\cdots$

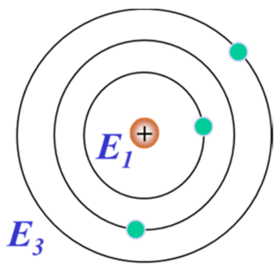
8. Bohr's three postulates

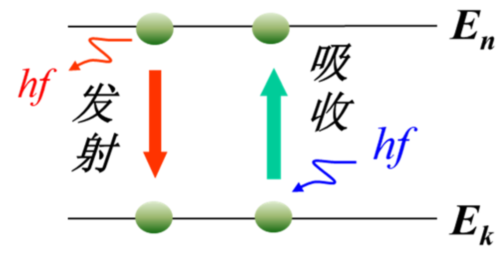
(1) Stationary states;

(2) Quantum transition: ("jump") $hf = E_n - E_k$

(3) Quantum condition: (for angular momentum)

$$L = mvr = n\hbar,\ n = 1,\ 2,\ \cdots$$

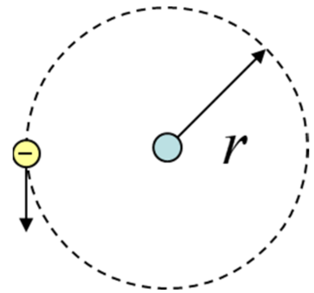




9. Bohr model

$$\left.\begin{aligned} \frac{e^2}{4\pi\varepsilon_0 r^2} &= m\frac{v^2}{r} \\ L = mvr &= \frac{nh}{2\pi} \end{aligned}\right\}$$

$$\boxed{E_n = \frac{-13.6\text{eV}}{n^2},\ n = 1,\ 2,\ \cdots}$$



10. Energy level diagram

$$E_n = \frac{-13.6\text{eV}}{n^2}, \qquad f = \frac{E_n - E_k}{h}, \qquad \frac{1}{\lambda} = R\left(\frac{1}{k^2} - \frac{1}{n^2}\right)$$