BOHR MODEL

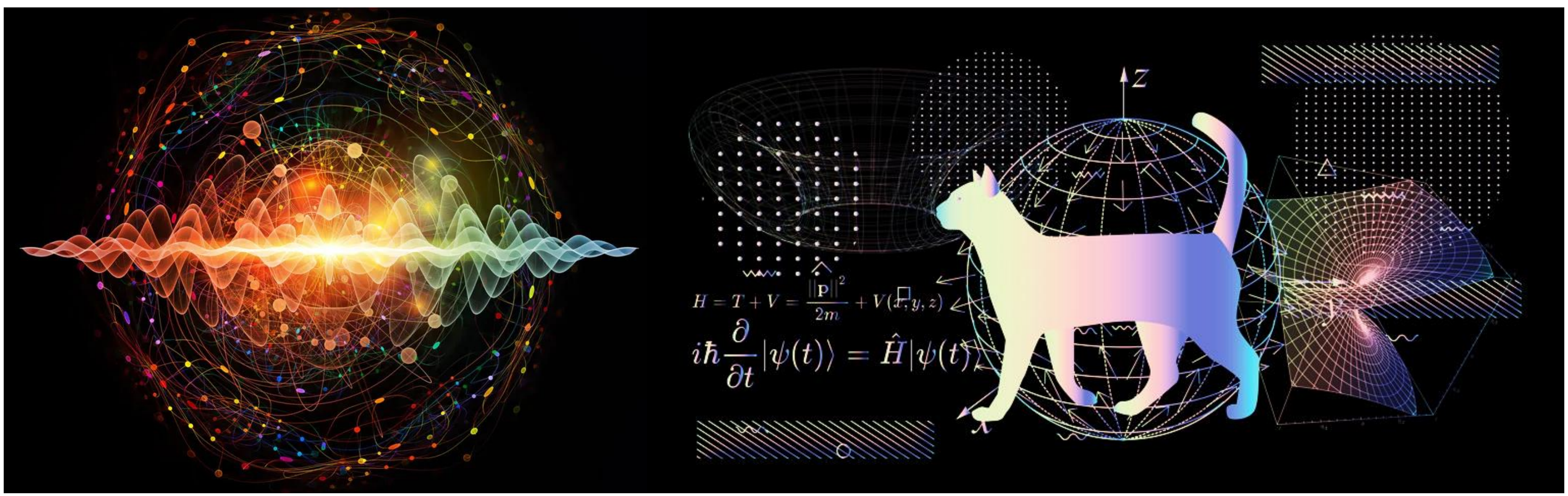
General Chemistry I, Lecture Series 4

Pengxin Liu

Reading:
OGB8 §§3.3, 4.1, 4.2, 4.3

Quantum mechanism

- Energy Quantization (能量非连续)
- Wave-particle duality (波粒二象性)



Syllabus

Week	Sunday	Monday	Wednesday	Friday
1			**Sept 18** Overview Formula	**Sept 20** Formula Nomenclature Q0
2		**Sept 23** Recitation		**Sept 27** Classical atoms Bonding & valence Q1
3				
4	**Oct 7** PS1 due			**Oct 11** Bohr model Q2
5	**Oct 13** Recitation	**Oct 14** Recitation	**Oct 16** Bohr model Quantum mechanics	**Oct 18** Quantum mechanics Hydrogen atom Q3
6	**Oct 20** PS2 due	**Oct 21** Recitation		**Oct 25** Hydrogen atom Review 1 Q4

Syllabus

- Week 4
  - Wave
  - Quantum mechanism of light (energy & particle-like behavior)
  - Bohr Model (to explain light-emitting observation)

light extends to matter

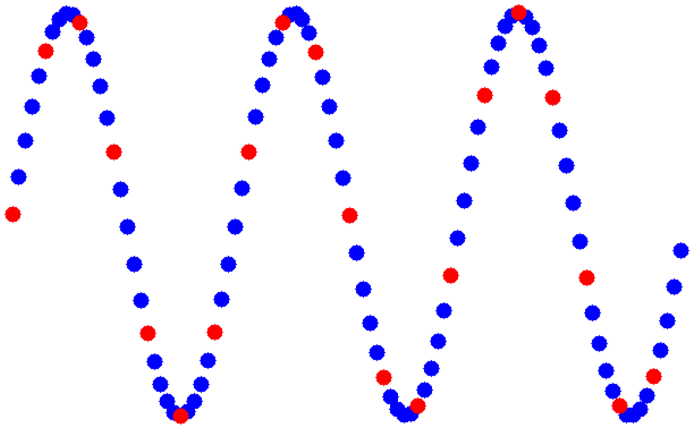
- Week 5
  - Matter waves (electrons)
  - Wave function (electron)

- Week 6
  - Wave function and its solution of H atom
  - Electron density, the shape and size

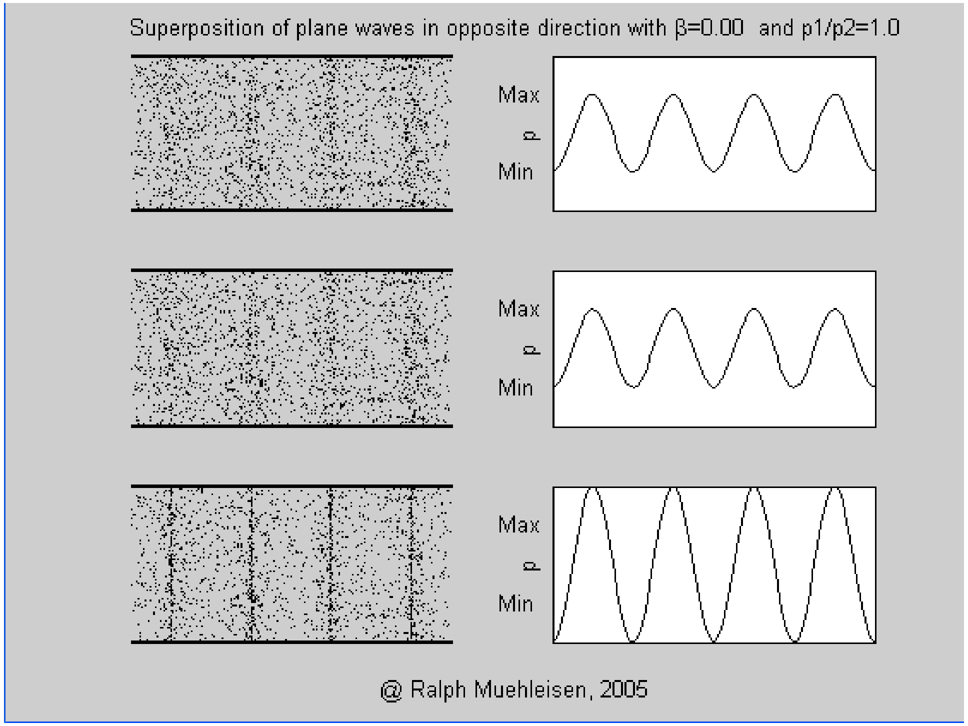
Outline

- Fundamentals of waves
- Light
  - Light is electromagnetic wave
  - Spectra
  - The particle nature of light (wave-particle duality)
  - Quantization of energy
- Flame Tests
- Balmer, Rydberg & Bohr
- The Bohr model
  - Quantization of energy in atoms

Wave: Basics

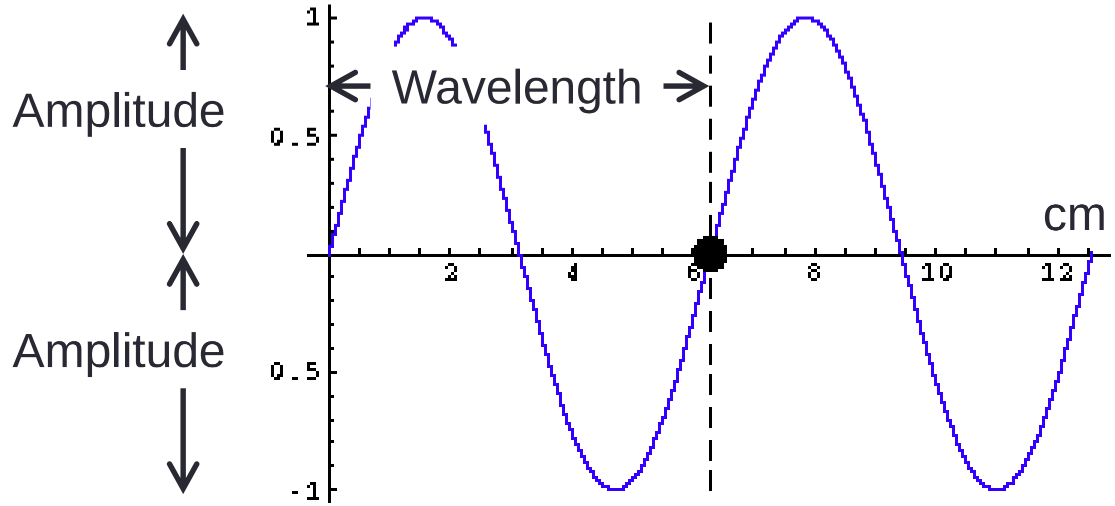


Traveling Waves 行波



Standing wave 驻波

Wave: Properties



Amplitude 振幅 $A = 1$

Wavelength 波长 $\lambda = 6.3$ cm ↔ Wavenumber 波数 $\tilde{\nu} = \lambda^{-1} \approx 0.16$ cm^{-1}

Period 周期 $T = 3.0$ s ↔ Frequency 频率 $\nu = T^{-1} \approx 0.33$ Hz

Speed 波速 $s = \lambda / T = \lambda\nu \approx 2.1\ \text{cm}\cdot\text{s}^{-1}$

$c_{vacuum} = 3.0\times10^{8}\ \text{m}\cdot\text{s}^{-1}$

For visible light, λ = 400–700 nm,

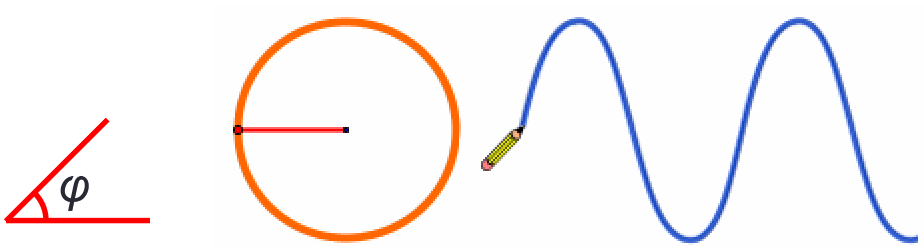
Wave: Phase 相位

Moon phases:

0 $\pi/2$ π $3\pi/2$ 2π

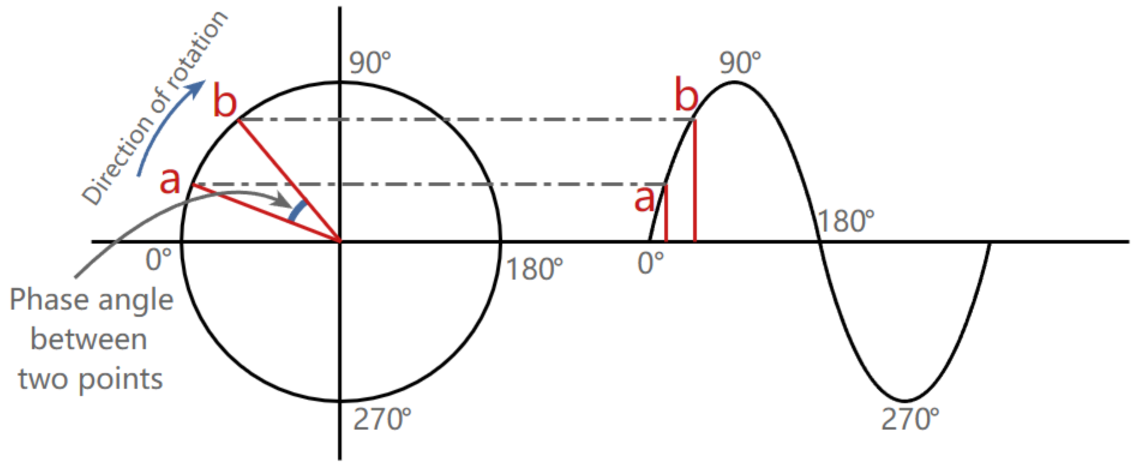
φ

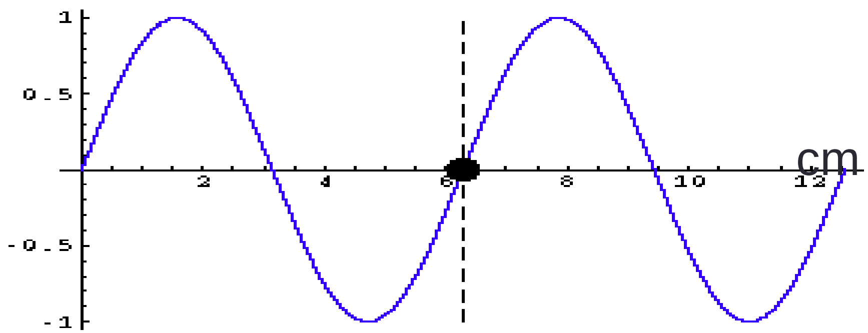
Wave phases:



$$y = A \sin\varphi$$

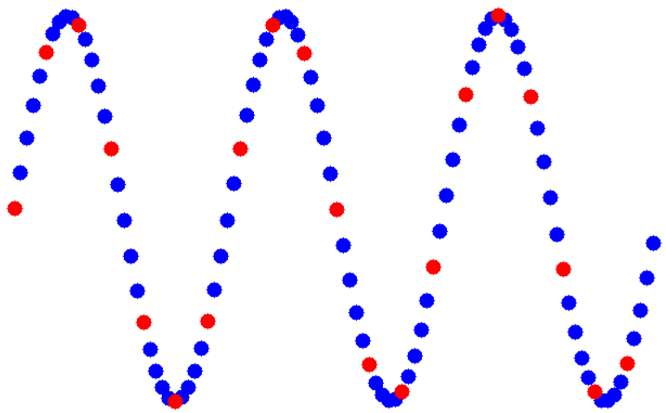
Wave: Phase 相位





Phase in Traveling Waves 行波

Phase propagates in both time and space.



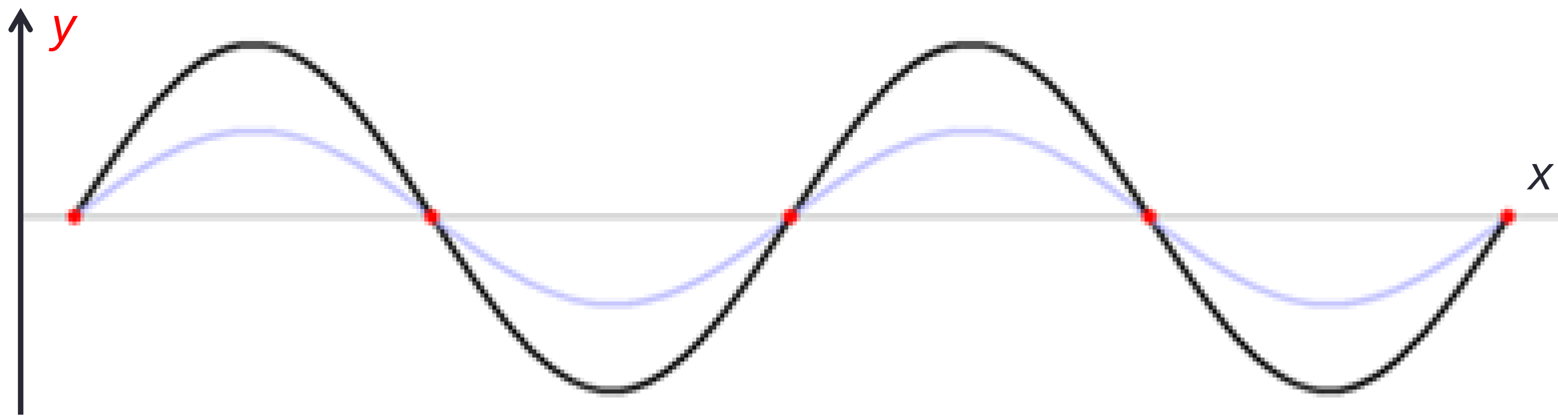
$$\varphi(x) = \frac{2\pi x}{\lambda} = 2\pi\tilde{\nu}x$$

$$\varphi(t) = -\frac{2\pi t}{T} = -2\pi\nu t$$

$$y(x,t) = A\sin[\varphi(x) + \varphi(t)] = A\sin\left[2\pi\left(\frac{x}{\lambda} - \frac{t}{T}\right)\right].$$

$$\text{speed} = \frac{\Delta x}{\Delta t} = \frac{\lambda}{T}$$

Standing Waves 驻波



- Equals the sum of two traveling waves in opposite directions;
- Does not propagate in either direction and fits in a confined space;

$$y(x,t) = \frac{A_0}{2}\sin\left[2\pi\left(\frac{x}{\lambda} - \frac{t}{T}\right)\right] + \frac{A_0}{2}\sin\left[2\pi\left(\frac{x}{\lambda} + \frac{t}{T}\right)\right]$$

$$\boxed{y(x,t) = A_0 \sin\left(2\pi\frac{x}{\lambda}\right)\cos\left(2\pi\frac{t}{T}\right).}$$

Summary

Properties of Wave

- A $\lambda, \tilde{\nu}$ T, ν s φ

Traveling wave

- Propagates in an open space

$$y(x,t) = A \sin\left[2\pi\left(\frac{x}{\lambda} - \frac{t}{T}\right)\right]$$

Standing wave

- Stays in a confined space
- Can be separated into an amplitude part and an oscillatory part

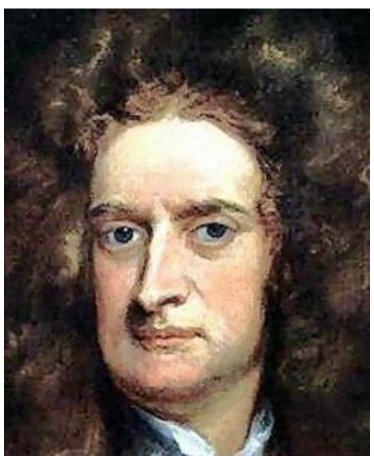
$$y(x,t) = A_0 \sin\left(2\pi\frac{x}{\lambda}\right) \cos\left(2\pi\frac{t}{T}\right)$$

Outline

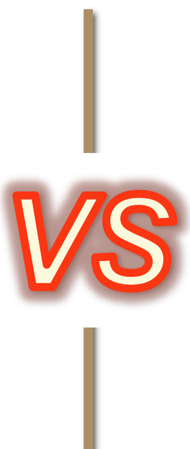
- Fundamentals of waves
- Light
  - Light is electromagnetic wave
  - Spectra
  - The particle nature of light (wave-particle duality)
  - Quantization of energy
- Flame Tests
- Balmer, Rydberg & Bohr
- The Bohr model
  - Quantization of energy in atoms

Light: Particle or Wave?

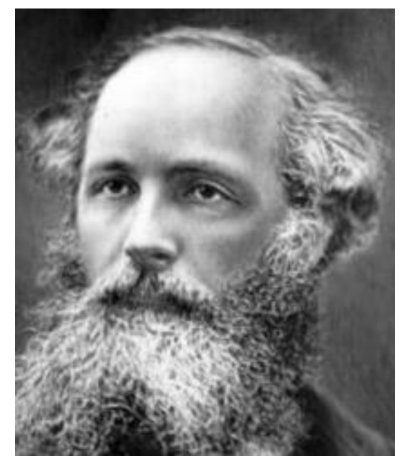
- 1850s, light is transverse wave (横波) carried by Ether.
- 1845, Faraday found magnetic field twisted light.
- 1864, Maxwell proposed visible light as a propagating wave of electromagnetic radiation.
- 1888, Hertz proved so.



Isaac Newton
(1643–1727)

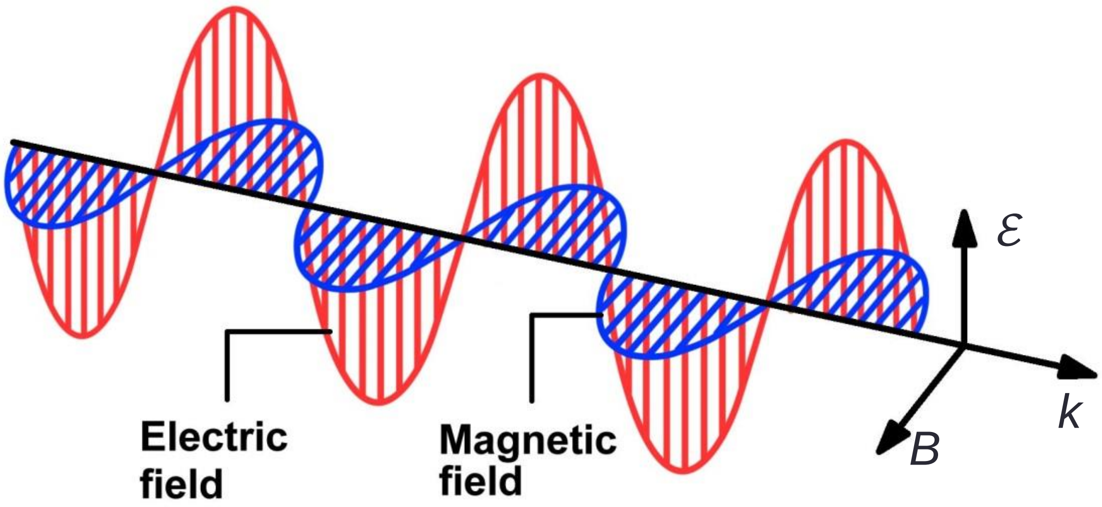


Christiaan Huygens
(1629–1695)

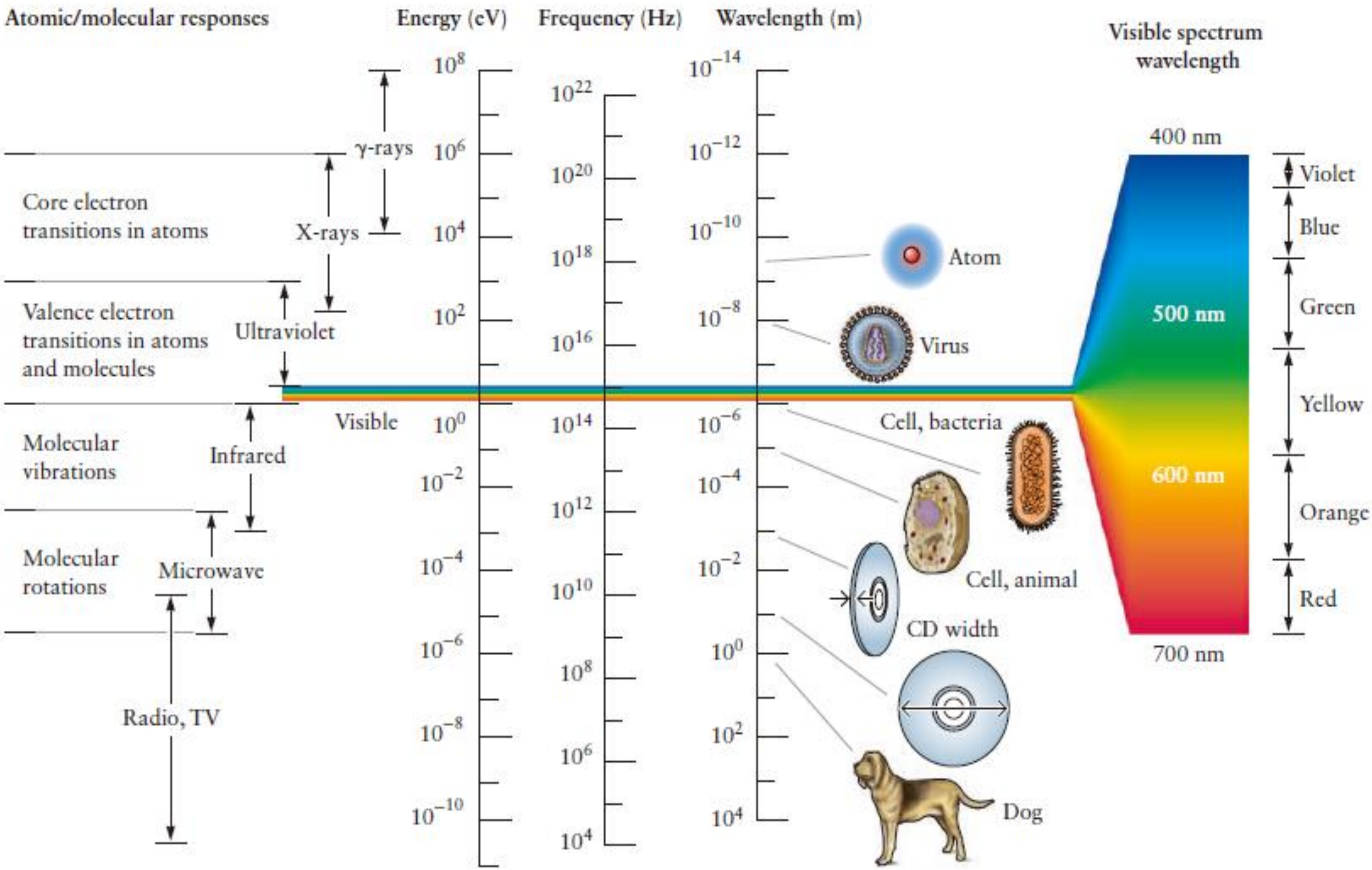


James C. Maxwell
(1831–1879)

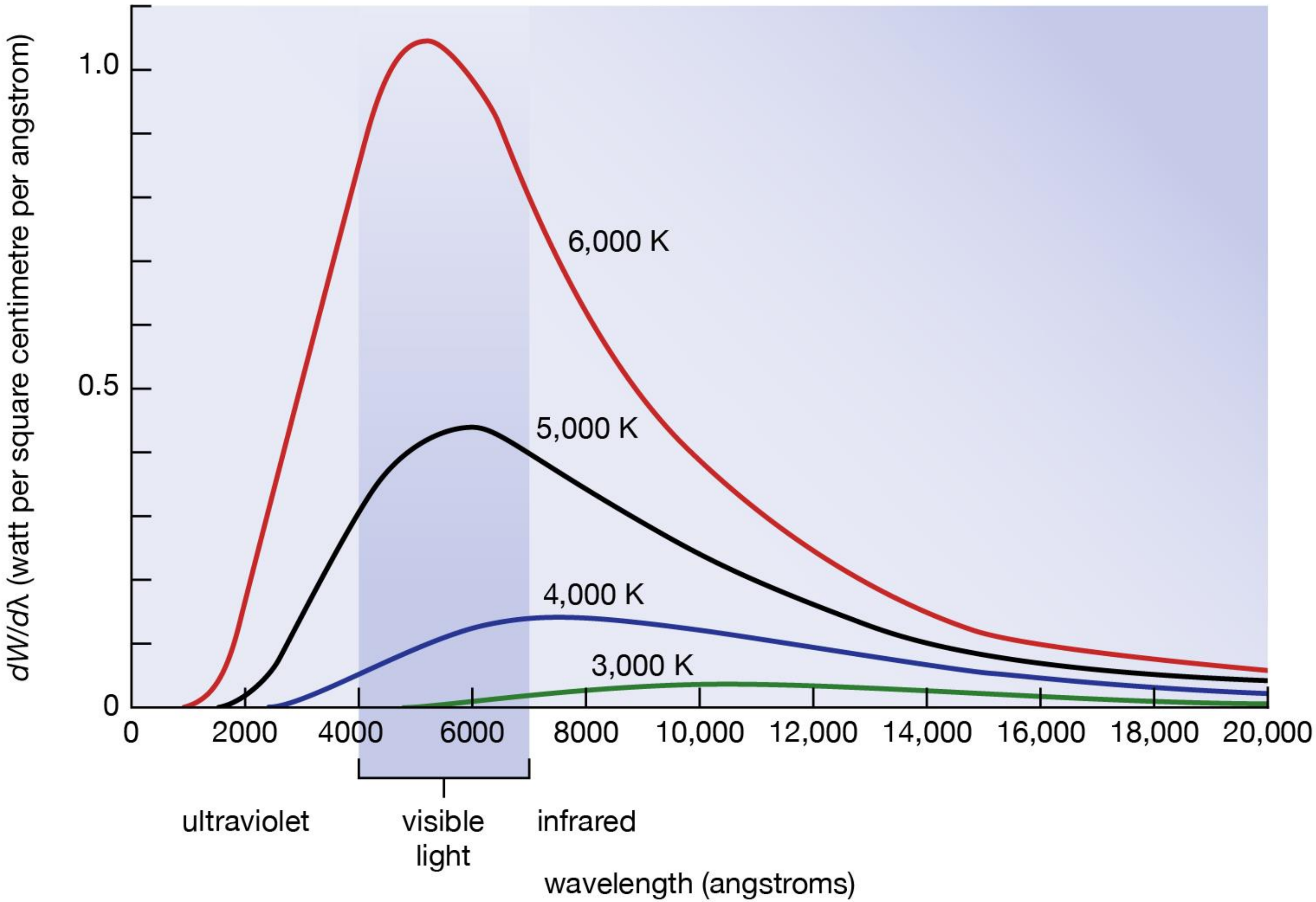
Electromagnetic Wave



- Light consists of oscillating electric and magnetic fields oriented perpendicular to each other.
- These fields are produced by the motion of charged particles in the source of the light.
- Not sustained by some propagating medium.

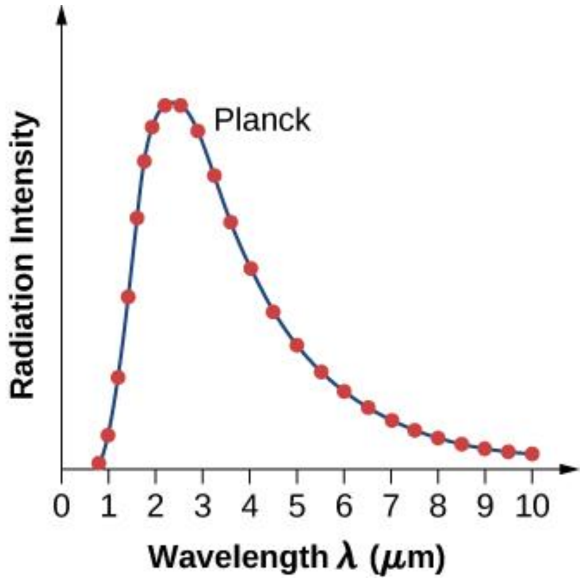

Atomic/molecular responses
Energy (eV)
Frequency (Hz)
Wavelength (m)
Visible spectrum wavelength
γ-rays
X-rays
Core electron transitions in atoms
Valence electron transitions in atoms and molecules
Ultraviolet
Visible
Molecular vibrations
Infrared
Molecular rotations
Microwave
Radio, TV
10^8
10^6
10^4
10^2
10^0
10^{-2}
10^{-4}
10^{-6}
10^{-8}
10^{-10}
10^{22}
10^{20}
10^{18}
10^{16}
10^{14}
10^{12}
10^{10}
10^8
10^6
10^4
10^{-14}
10^{-12}
10^{-10}
10^{-8}
10^{-6}
10^{-4}
10^{-2}
10^0
10^2
10^4
Atom
Virus
Cell, bacteria
Cell, animal
CD width
Dog
400 nm
500 nm
600 nm
700 nm
Violet
Blue
Green
Yellow
Orange
Red

Blackbody radiation



Blackbody radiation

- solved in 1900 by Max Planck
- Planck assumed that the energy of an oscillator (E_n) can have only discrete, or quantized, values:
    - $E_n = nh\nu$, where n=1,2,3,…



Light: Wave or Particle?

Max Planck
(Berlin, 1858–1947)

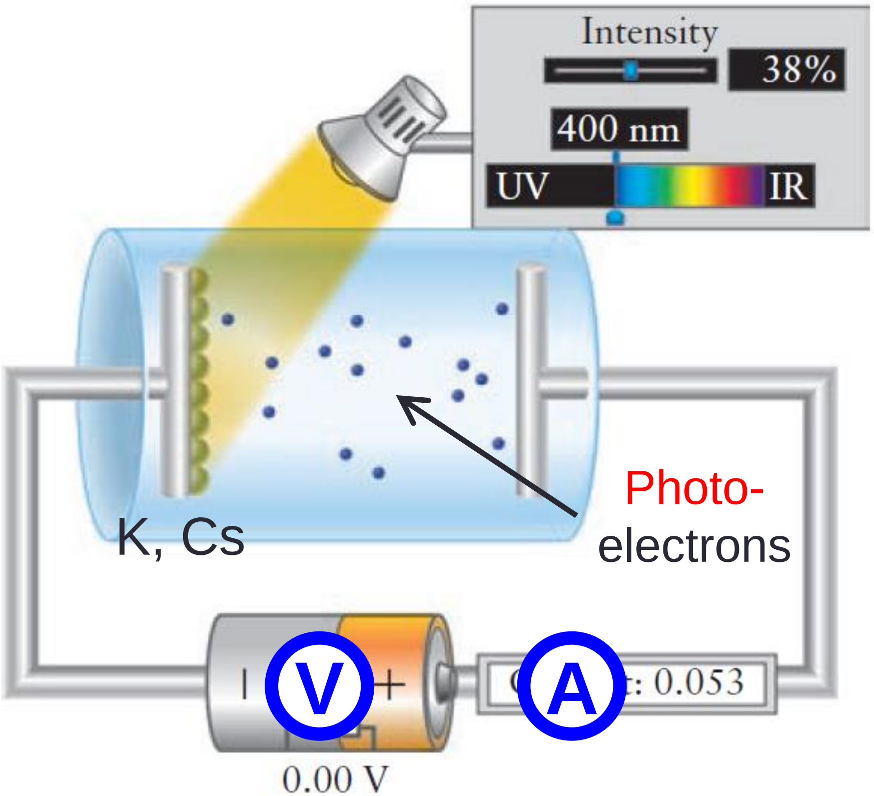
Albert Einstein
(Zürich, 1879–1955)

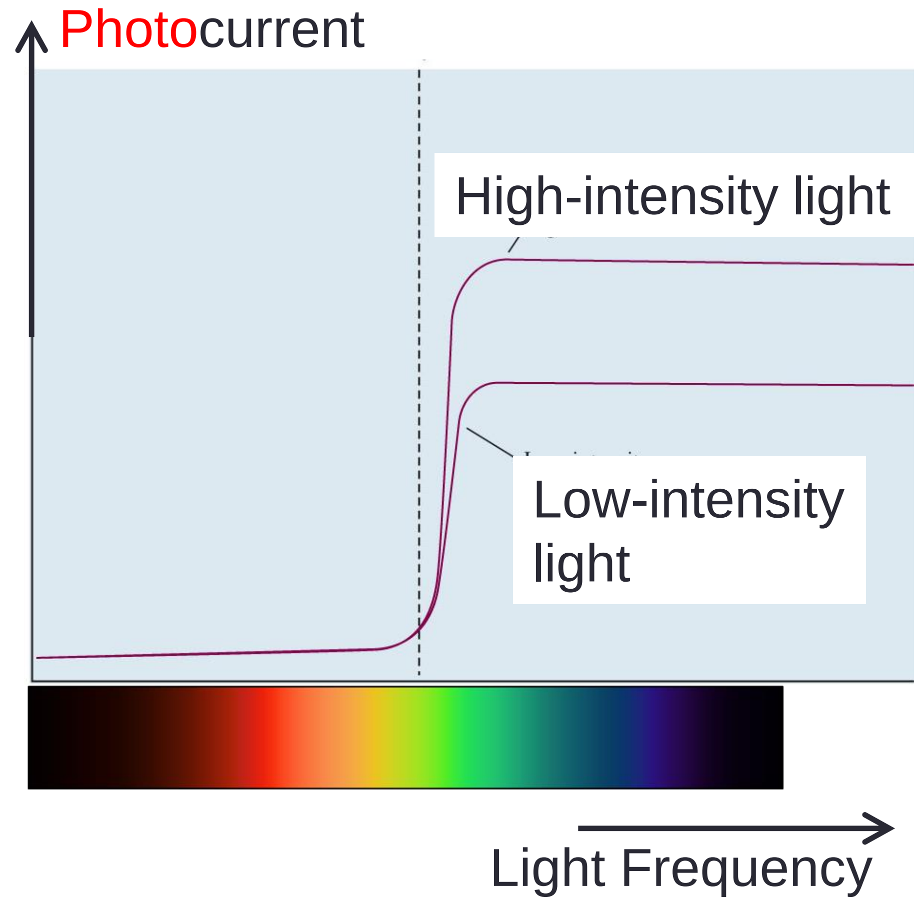
"Energy is quantized in matter but not in light."

"Light is also quantized."

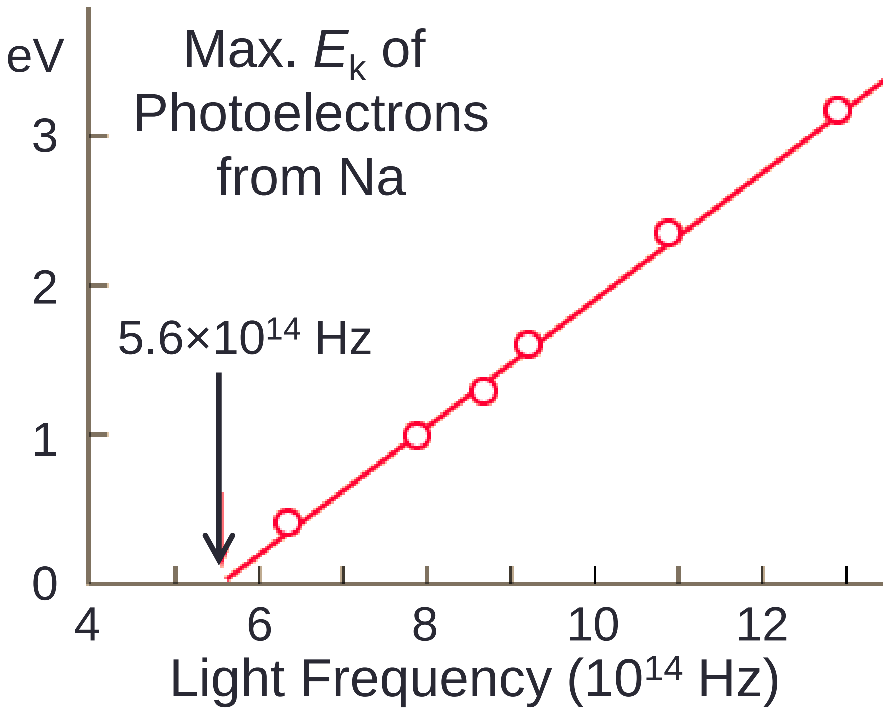
The Photoelectric Effect

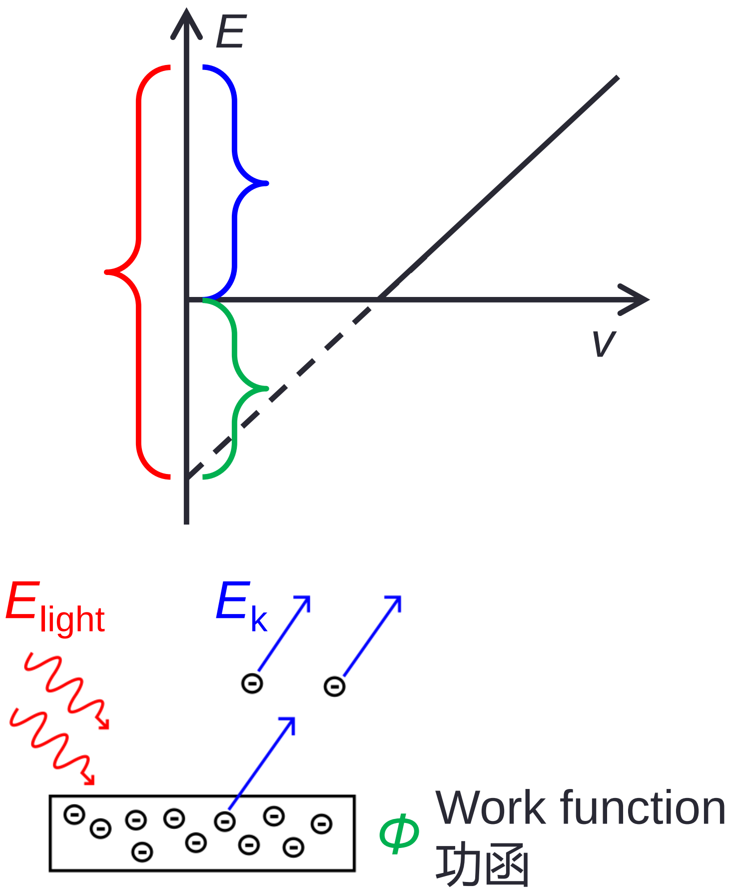
Photo- 光





Photon: The Energy Quanta of Light





Einstein 1905:

$$E_{k,max} + \Phi = E_{light} \propto \nu$$

$$E_{light} = h\nu$$

Light Also Bears Momentum

(1) Planck 1900, Einstein 1905:

$$E = h\nu$$

(2) Einstein 1916:

$$E = mc^2$$

(3) Definition of momentum

$$p = mv, \quad v = c \text{ for light}$$

(1)+(2)+(3)

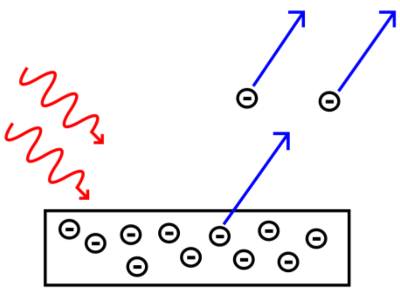
$$\boxed{p = \frac{h\nu}{c} = \frac{h}{\lambda}}$$

Photo- + -on = Photon 光子

Albert Einstein
(Zürich, 1879–1955)

Photon and Electromagnetic Wave

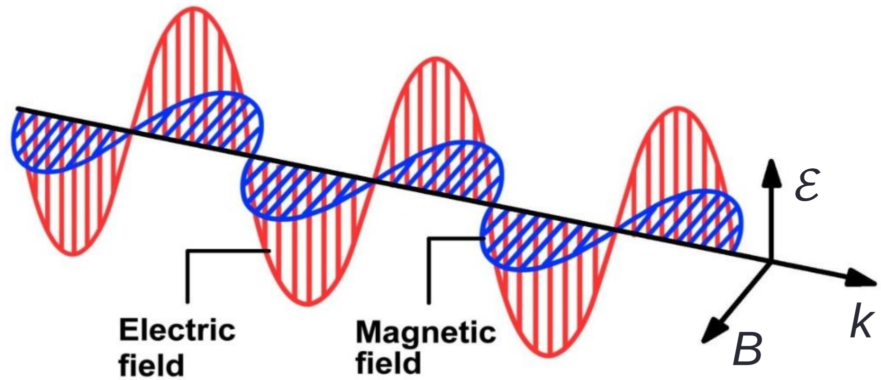
电磁波



Photoelectric effect

(1) $E_{\text{photon}} = hv$

VS



Electromagnetic wave

(2) $E_{\text{light}} \propto \mathcal{E}^2$

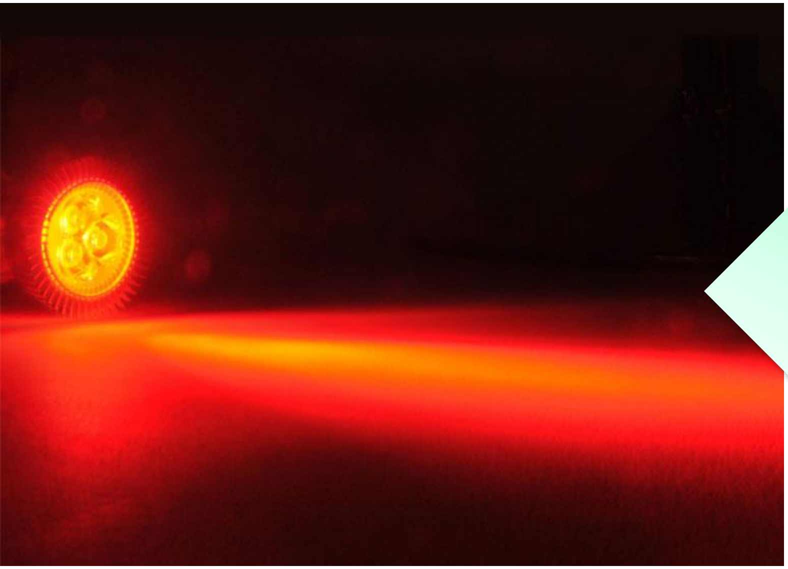
(1)+(2):

$N_{\text{photon}} \propto \mathcal{E}^2$

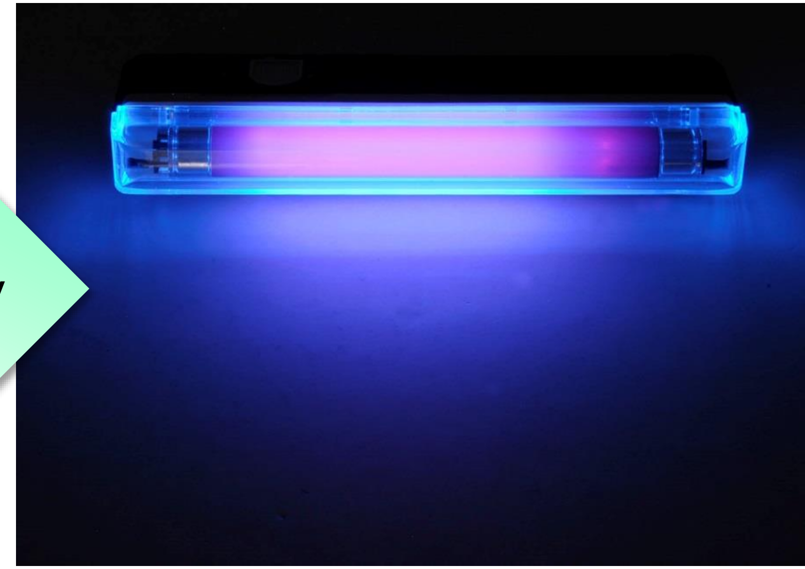
Light frequency → Energy of a single photon

Light intensity → Number of photons

Light and Rain: An Analogy



Equal Intensity



Equal
precipitation

Summary

- Wave–particle duality
  - Light can behave like particles
  - Energy is quantized in light.

$$\boxed{E_{\text{photon}} = h\nu}$$

$$\boxed{p_{\text{photon}} = \frac{h}{\lambda}}$$

Brief history of Early Quantum Mechanics

- **On light**
- 1900 Max Planck: $E_n = nh\nu$
- 1905 Albert Einstein: $E = mc^2$ $\quad p_{\text{photon}} = \frac{h}{\lambda}$
- 1913 Niels Bohr: The Bohr Model for H

- **On matter**
- 1924 Louis de Broglie: $p = m_e v = \frac{h}{\lambda}$
- 1926 Erwin Schrödinger: Schrödinger Equation
- 1926 Max Born: $P(x) = |\psi(x)|^2$

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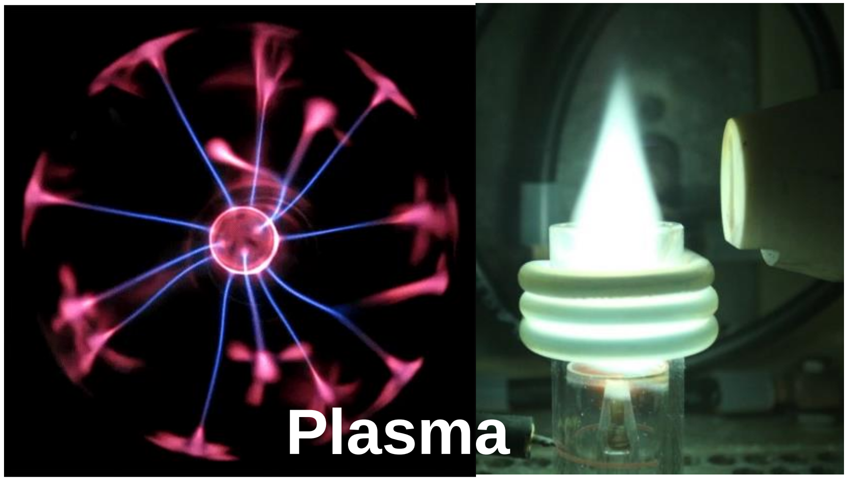
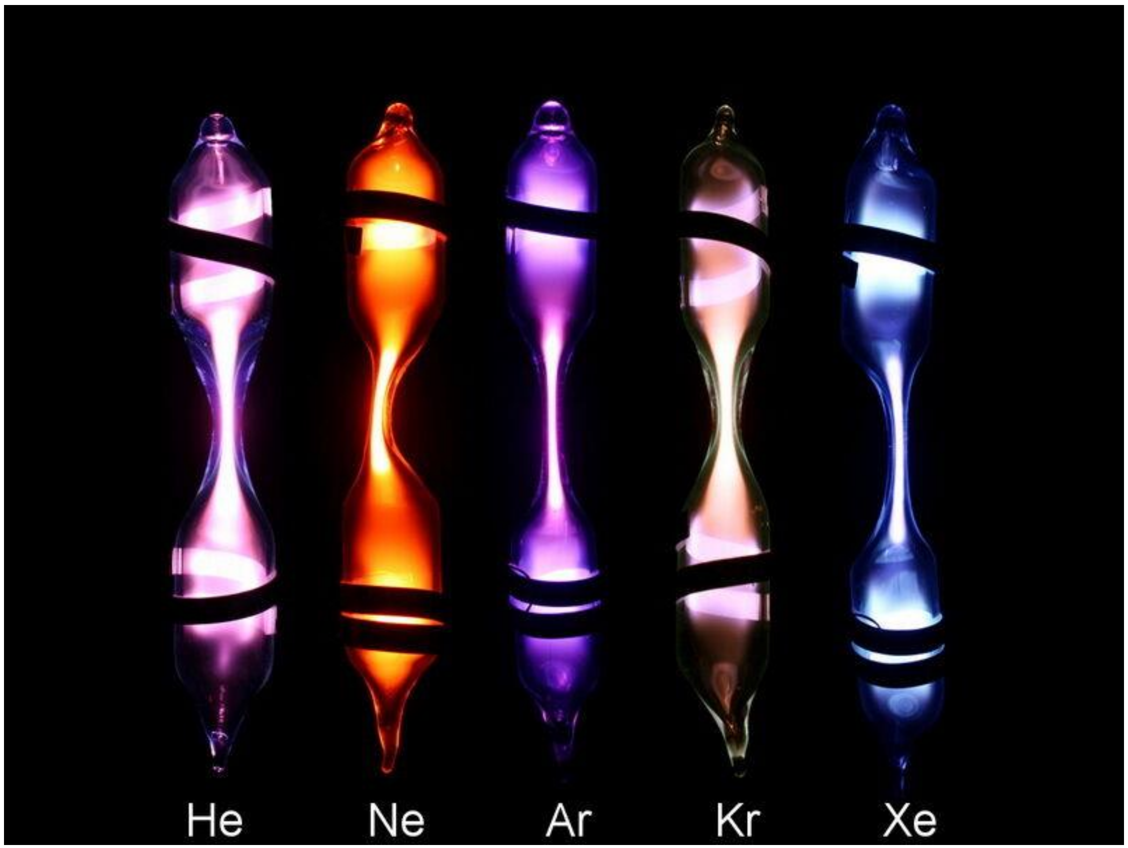
Flame Tests



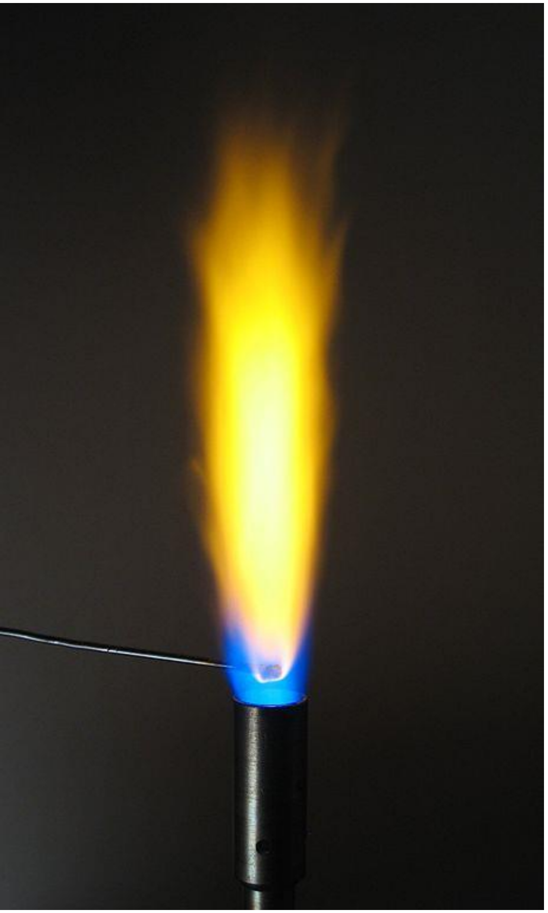
Gas Discharge Tubes



Xenon lamp 氙灯

Neon lamp 氖(霓虹)灯

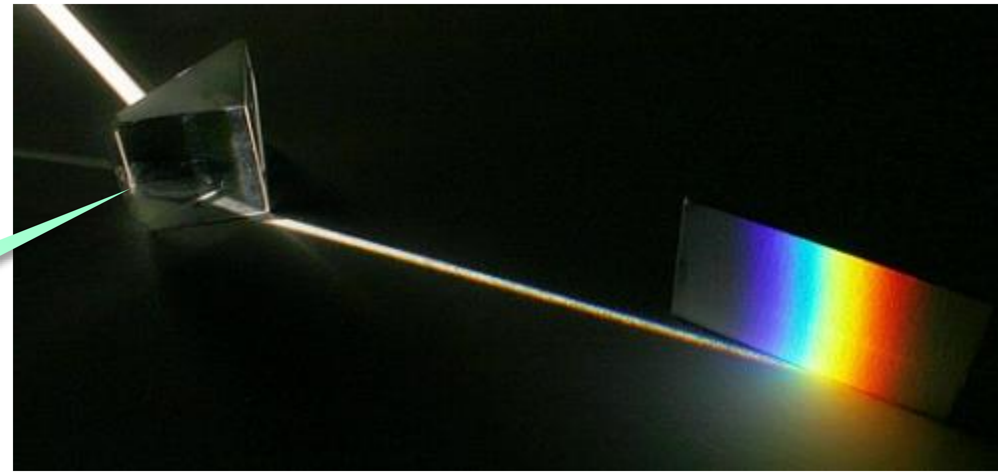
Sodium Flames and Sodium Lamps



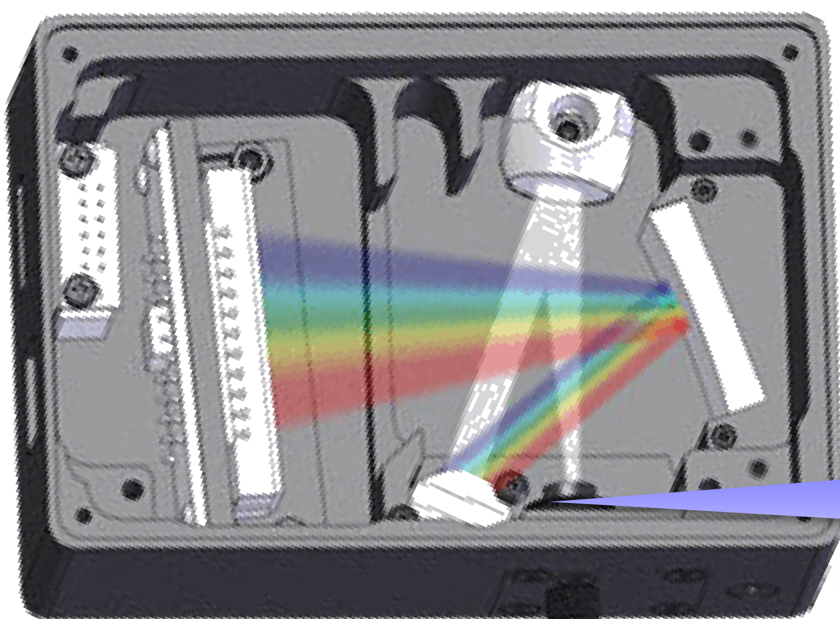
NaCl
Soda-lime glass
Sweat
…

An element in various compounds shows the same flame color.

From Colors to Spectra

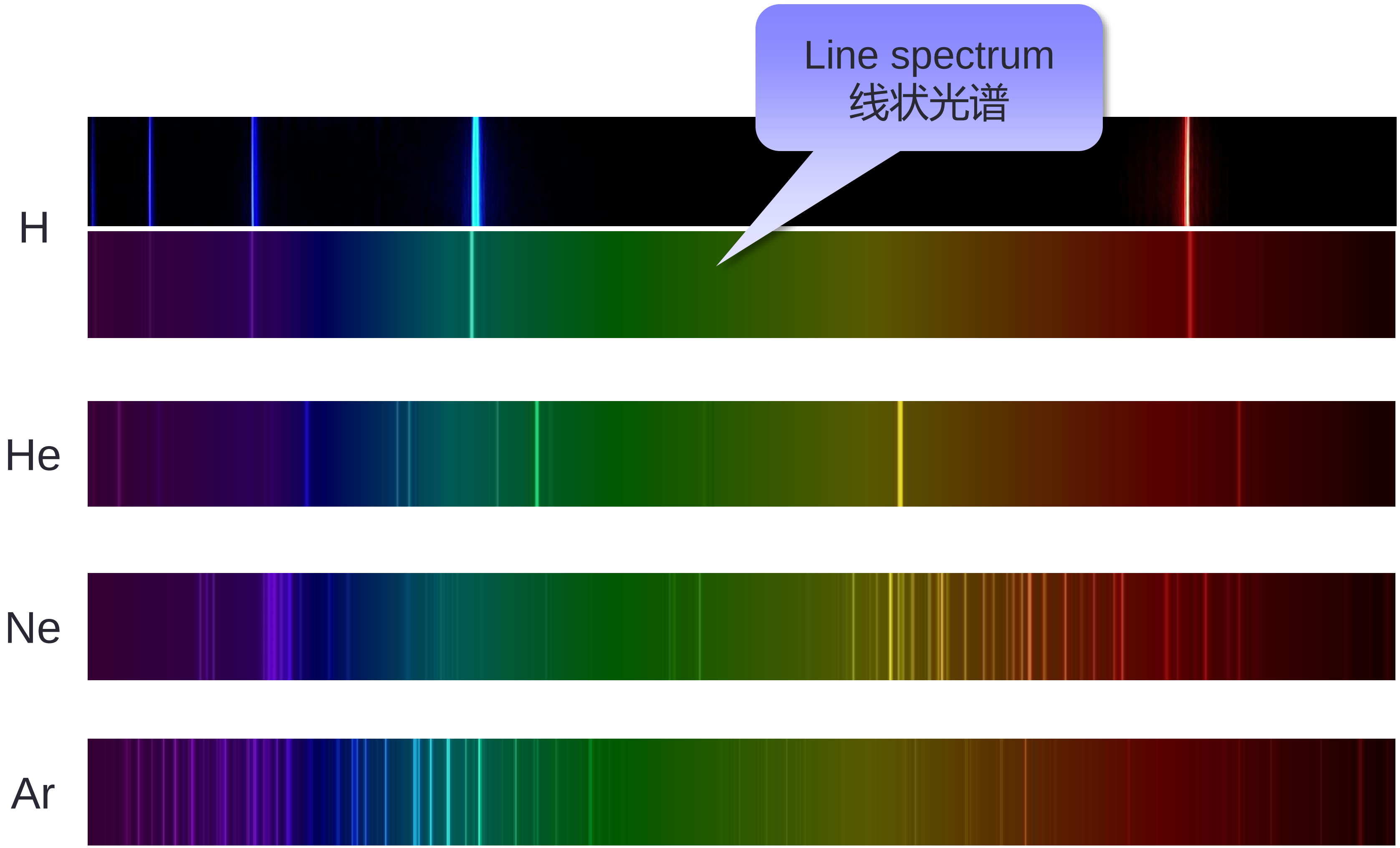


Prism 棱镜

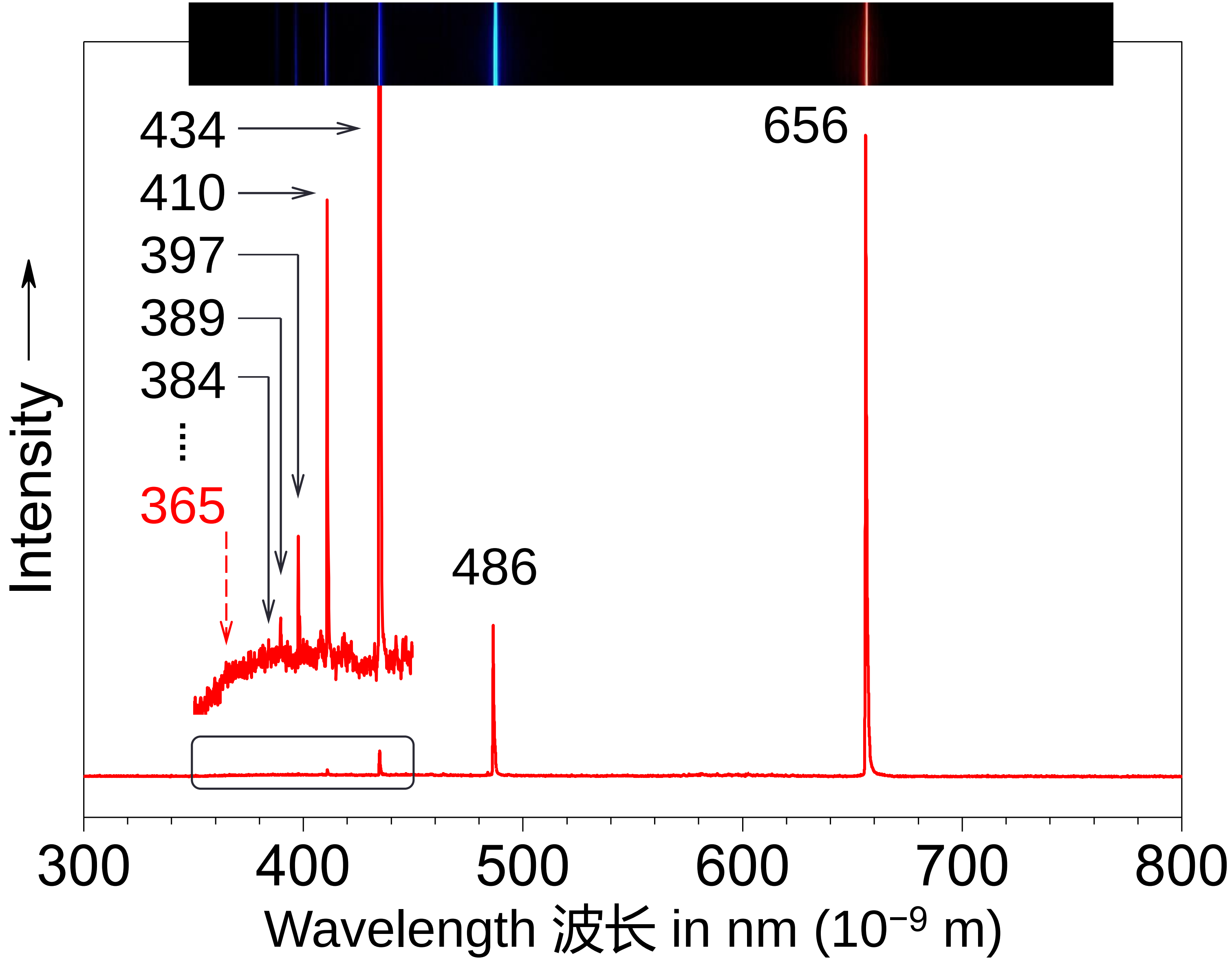


Grating 光栅

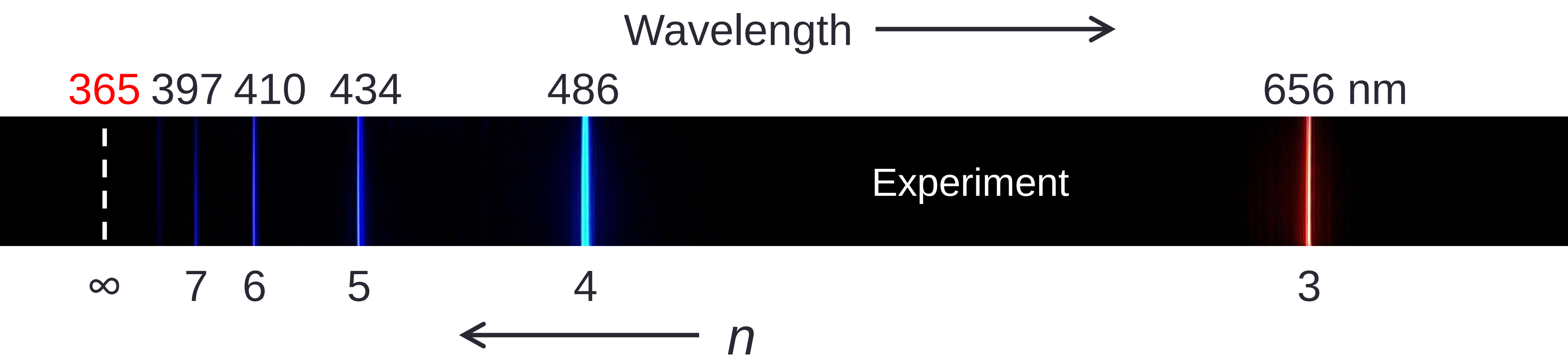
Gas Discharge Spectra



Experimental H Spectrum (1860s)



The Balmer Formula (1885)



$$\frac{656}{365} \approx 1.80 = \frac{9}{5} = \frac{9}{9-4}$$

$$\frac{486}{365} \approx 1.33 = \frac{4}{3} = \frac{16}{16-4}$$

$$\Longrightarrow \lambda_n = B\frac{n^2}{n^2-4}, \quad B = 365 \text{ nm}, \quad n = 3,4,5\ldots$$

The Balmer Formula (1885)

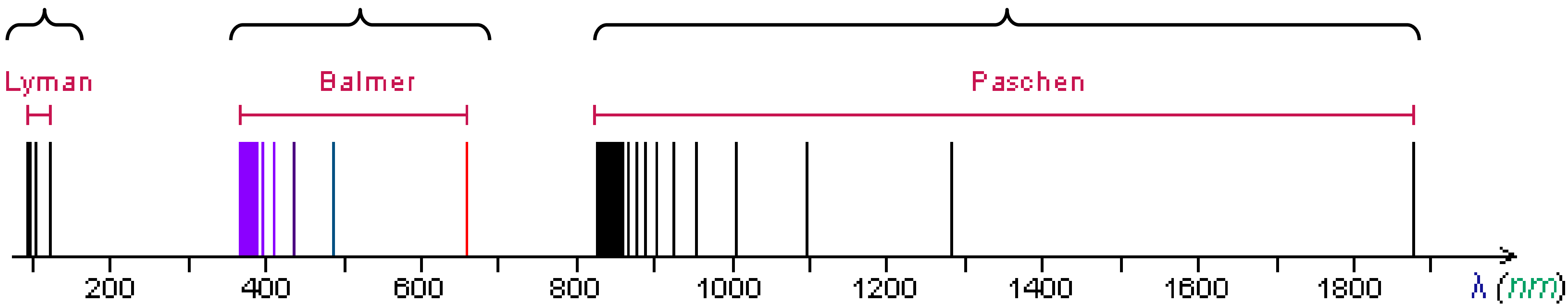
TABLE II.—BALMER'S SERIES OF LINES IN THE ARC SPECTRUM OF HYDROGEN.

H line.	n	Wave-length, λ. in Å (10^{-10} m)		Difference.
		Calculated.	Observed.	
H_α or C	3	6564·96	6564·97	+0·01
H_β or F	4	4862·93	4862·93	—
H_γ or G	5	4341·90	4342·00	—0 1
H_δ or h	6	4103·10	4103·11	+0·01
H_ϵ or H	7	3971·4	3971·4	—
H_ζ or α	8	3890·3	3890·3	—
H_η or β	9	3836·7	3836·8	+0·1
H_θ or γ	10	3899·2	3799·2	—
H_ι or δ	11	3771·9	3771·9	—
H_κ or ϵ	12	3751·4	3751·3	—0·1
H_λ or ζ	13	3735·6	3735·3	—0·3
H_μ or η	14	3723·2	3722·8	—0·4
H_ν or θ	15	3713·2	3712·9	—0·3

1. J. S. Ames, *Philosophical Magazine*, **1890**, *30*, 33.

The Rydberg Formula (1888)

$$\lambda_n \propto \frac{n^2}{n^2 - 1} \qquad \lambda_n \propto \frac{n^2}{n^2 - 4} \qquad \lambda_n \propto \frac{n^2}{n^2 - 9}$$



$$\lambda_n = B\frac{n^2}{n^2-4}$$

$$\Rightarrow \quad \frac{1}{\lambda_n} = \frac{1}{B}\left(1 - \frac{4}{n^2}\right)$$

$$\Rightarrow \quad \frac{1}{\lambda_n} = \frac{4}{B}\left(\frac{1}{2^2} - \frac{1}{n^2}\right)$$

$$\boxed{\frac{1}{\lambda} = R_H\left(\frac{1}{m^2} - \frac{1}{n^2}\right),\ m < n.}$$

R_H: Rydberg's constant

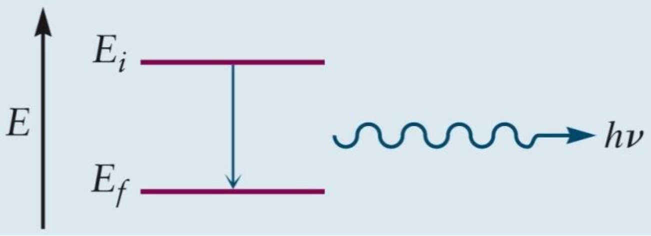
Bohr's Interpretation (1913)

$$\frac{1}{\lambda} = R_H\left(\frac{1}{m^2} - \frac{1}{n^2}\right),\ m < n.$$

$$h\nu = \Delta E = E_{\text{final}} - E_{\text{initial}}$$

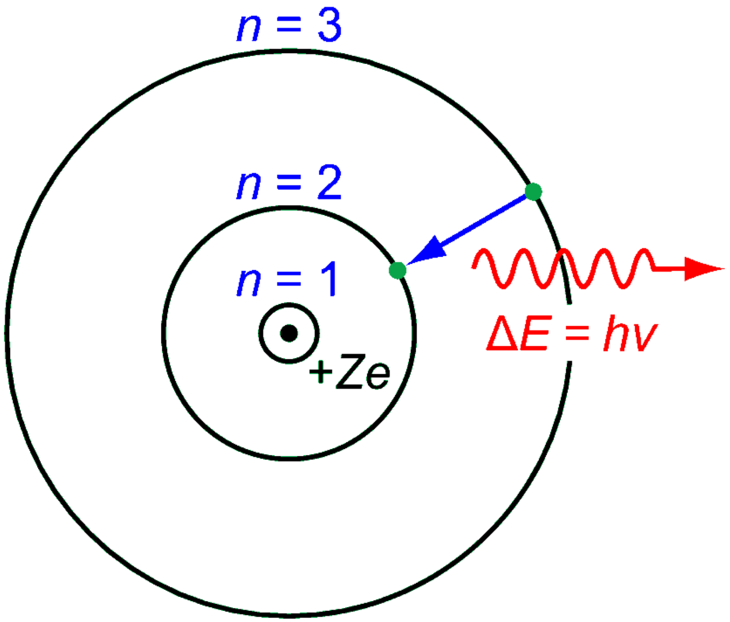
Niels Bohr (Copenhagen, Cambridge, 1885–1962)

- In an atom, there are various states 能态 of fixed, discrete energy.
- Emission or absorption of light results from a transition 跃迁 between two of these states.

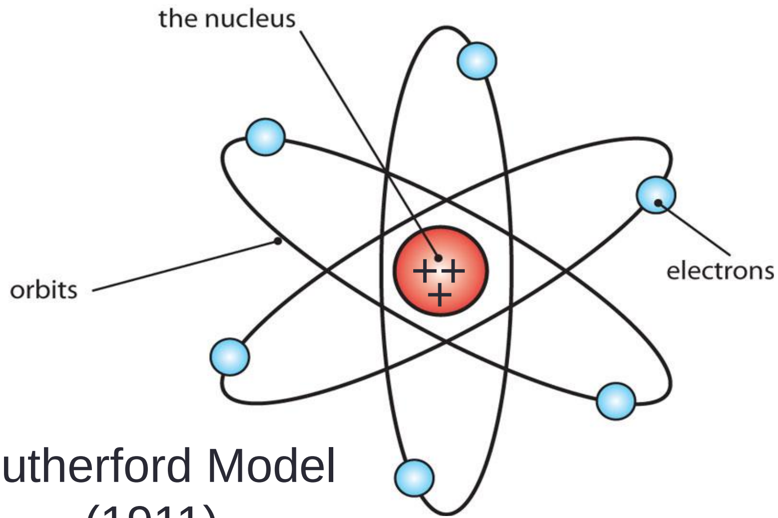


- The energy quantum $h\nu$ of the absorbed/emitted light equals the transition energy.

The Bohr Model for H



- The electron orbits the nucleus.
- Each orbit is a circle specified by an angular momentum $L = nh/2\pi$ ($n \in \mathbb{N}$).
- The electron is stable in these orbits, but gains or loses energy when jumping between the orbits.



Rutherford Model (1911)

Shanghai Synchrotron (2009)

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The Virial Theorem for Circular Orbits

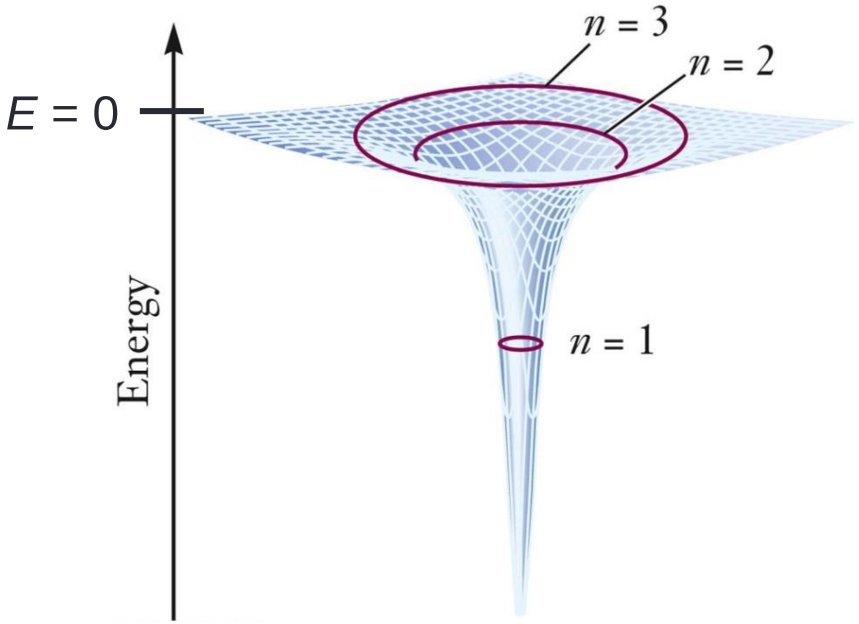
- Coulomb attraction = centripetal force 向心力

$$F = \frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r^2} = m_e\frac{v^2}{r}$$

$$\Longrightarrow \quad \frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r} = m_e v^2$$

$$\Longrightarrow \quad \frac{1}{8\pi\varepsilon_0}\frac{Ze^2}{r} = \frac{1}{2}m_e v^2 = E_k$$

Because $V = -\frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r}$,

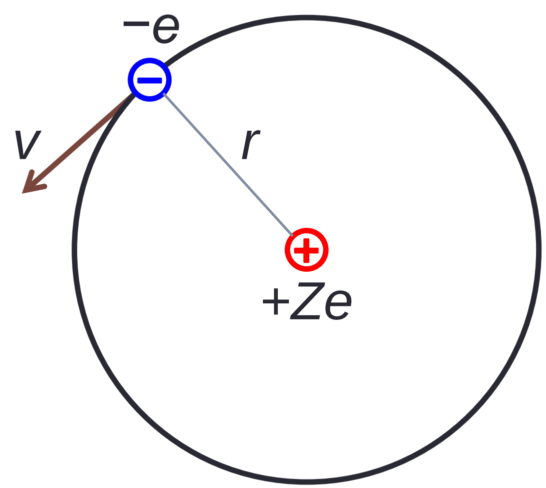


$$\boxed{E_k = -\frac{V}{2}, \quad E = E_k + V = \frac{V}{2}.}$$

The Quantization Condition

- Coulomb attraction = centripetal force 向心力

(1) $$F = \frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r^2} = m_e\frac{v^2}{r}$$



- Discrete orbits

(2) $$E = \frac{V}{2} = -\frac{1}{8\pi\varepsilon_0}\frac{Ze^2}{r}$$

(3) $$E \propto \frac{1}{n^2},\ n \in \mathbb{N}$$

(2)+(3) $\Longrightarrow r \propto n^2$

(1) becomes $F \propto \frac{1}{n^4} \propto \frac{v^2}{n^2} \Longrightarrow v \propto \frac{1}{n}$

Therefore $L = m_e v \cdot r \propto n$

$$\boxed{L = m_e vr = n\frac{h}{2\pi} = n\hbar,\ n \in \mathbb{N}}$$

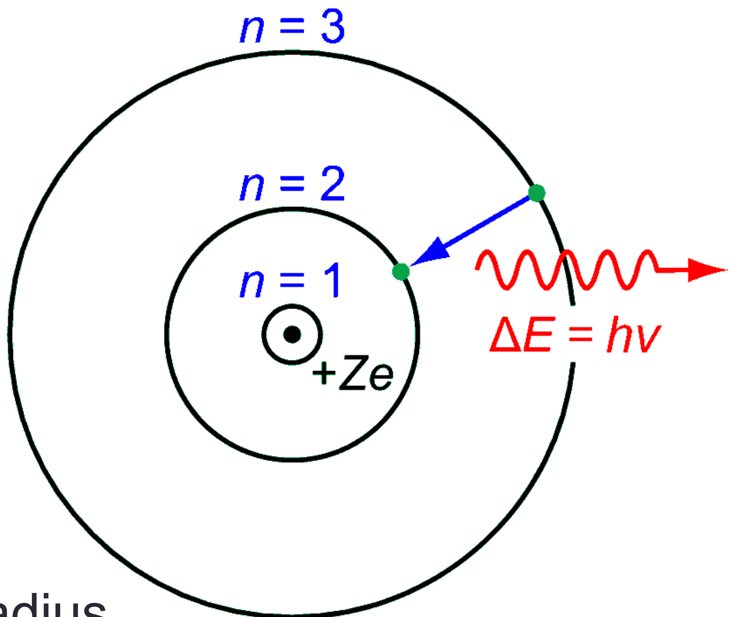
Solving the Unknowns: *r* and *v*

- Coulomb attraction = centripetal force

(1) $$F = \frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r^2} = m_e\frac{v^2}{r}$$

- Quantized angular momentum L

(2) $$L = m_e v \cdot r = n\frac{h}{2\pi},\ n \in \mathbb{N}$$



(1)+(2)

$$r = \frac{n^2}{Z}\frac{\varepsilon_0 h^2}{\pi e^2 m_e} = \frac{n^2}{Z}a_0,$$ a_0 = 52.9 pm is Bohr radius.

For hydrogen atom (Z = 1),

$n = 1,\ r = a_0 = 52.9$ pm;

$n = 2,\ r = 4a_0 = 212$ pm;

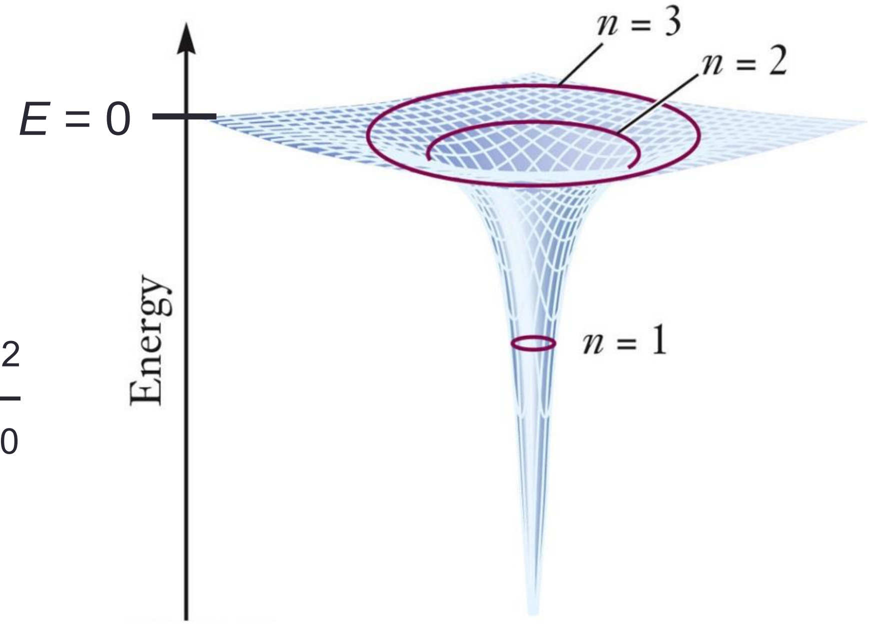
$n = 3,\ r = 9a_0 = 476$ pm.

$$\boxed{r = \frac{n^2}{Z}a_0}$$

Orbital Energies

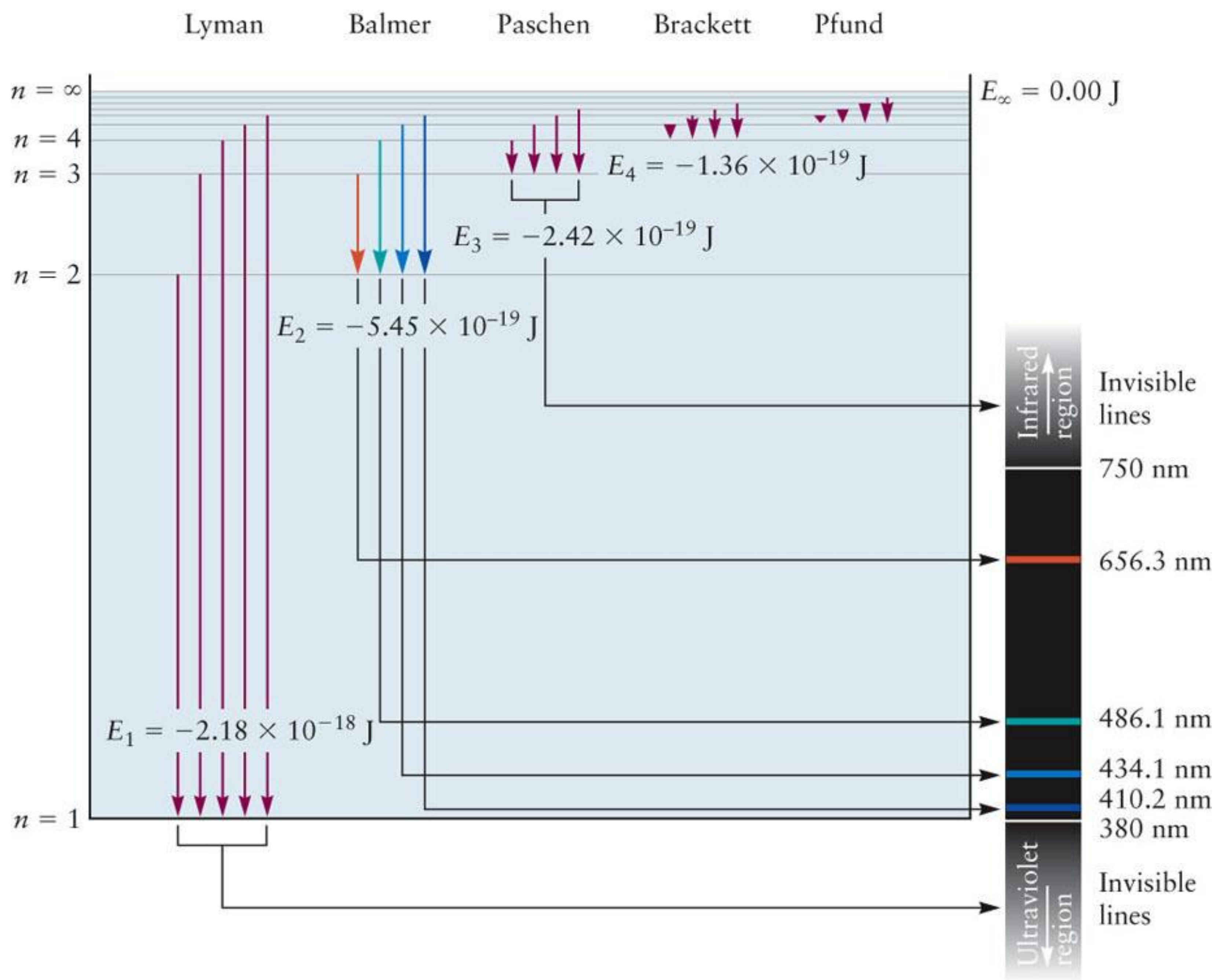
From previous pages:

$$\left.\begin{aligned} E &= -\frac{1}{8\pi\varepsilon_0}\frac{Ze^2}{r} \\ r &= \frac{n^2}{Z}a_0 \end{aligned}\right\} \Longrightarrow E = -\frac{1}{8\pi\varepsilon_0}\frac{Z^2e^2}{n^2a_0}$$

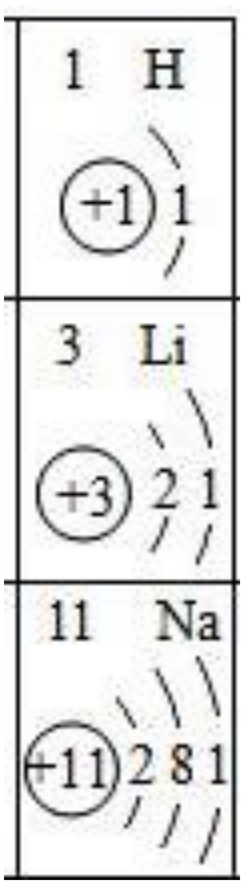


$$E = -\mathrm{Ry}\frac{Z^2}{n^2},\ \mathrm{Ry} = 2.18\times10^{-18}\ \mathrm{J} = 13.6\ \mathrm{eV}$$

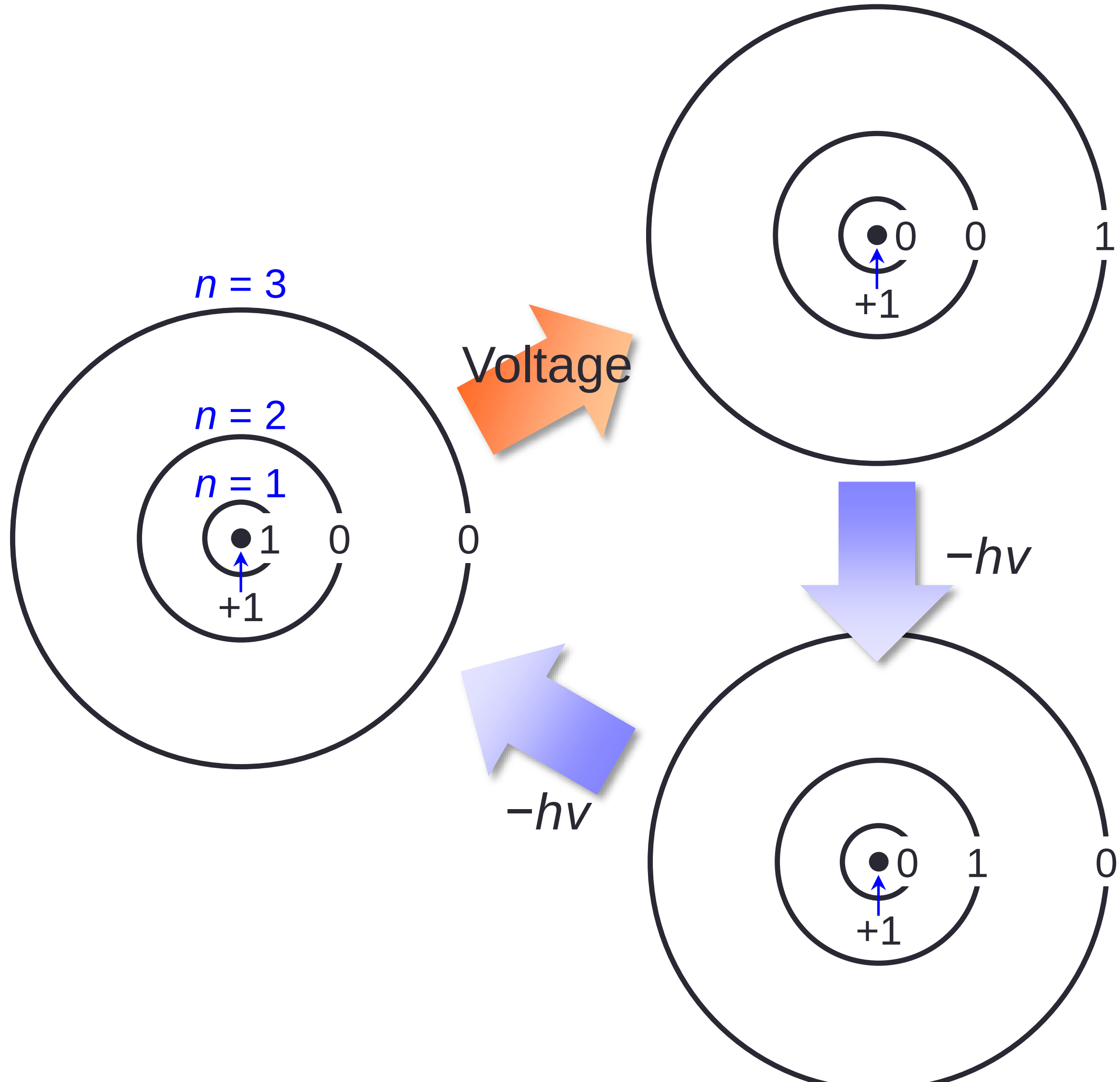
Ry: Rydberg energy


Lyman
Balmer
Paschen
Brackett
Pfund
$n = \infty$
$n = 4$
$n = 3$
$n = 2$
$n = 1$
$E_\infty = 0.00$ J
$E_4 = -1.36 \times 10^{-19}$ J
$E_3 = -2.42 \times 10^{-19}$ J
$E_2 = -5.45 \times 10^{-19}$ J
$E_1 = -2.18 \times 10^{-18}$ J
Infrared region
Invisible lines
750 nm
656.3 nm
486.1 nm
434.1 nm
410.2 nm
380 nm
Ultraviolet region
Invisible lines

Bohr Model and Electron Orbits

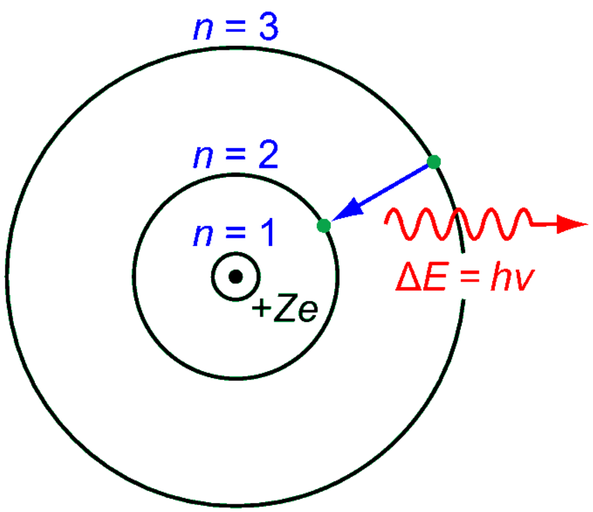


VS



Summary for the Bohr Model

- Stable orbits / states of H atom
- Transitions between the orbits
- Quantized orbital angular momentum
- “Old quantum theory”



But the Bohr model doesn’t work for the He atom at all!

Next lecture series: Quantum Mechanics

Reading: OGB8 §4