QUANTUM THEORY

Focus 7

Elements of Physical Chemistry

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Quantum Theory

Quantum theory / mechanics / physics is the **latest theory** for description of ***the structure & properties of atoms and molecules***
(*"the currency of chemistry"*)

Quantum chemistry applies *quantum theory* to solve **problems in chemistry**

Quantum Chemistry

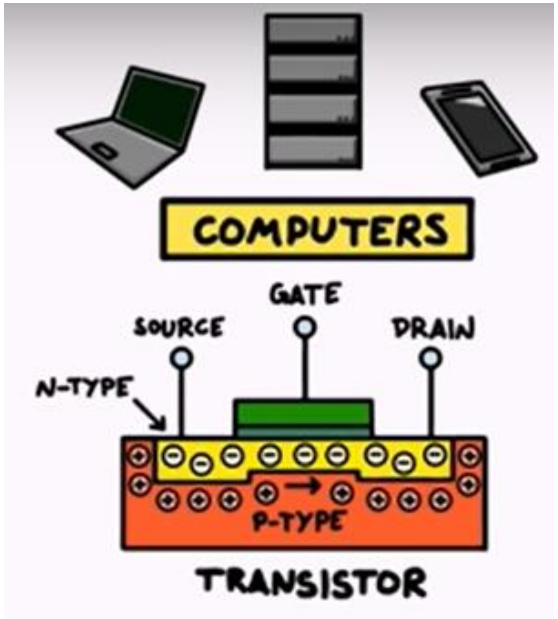
- To predict **molecular properties**, such as geometry, conformation, dipole moments, spectra…

- To study **chemical reactions,** predict properties of transition states and intermediates, to investigate the mechanisms

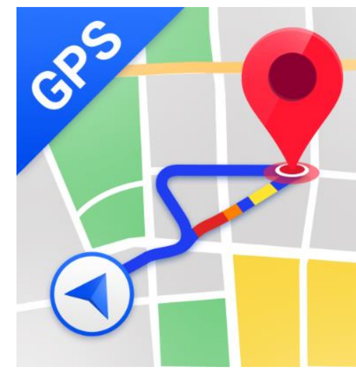
- To understand intermolecular forces and the behavior of molecules in **solutions**, **solids**, **biomolecules**

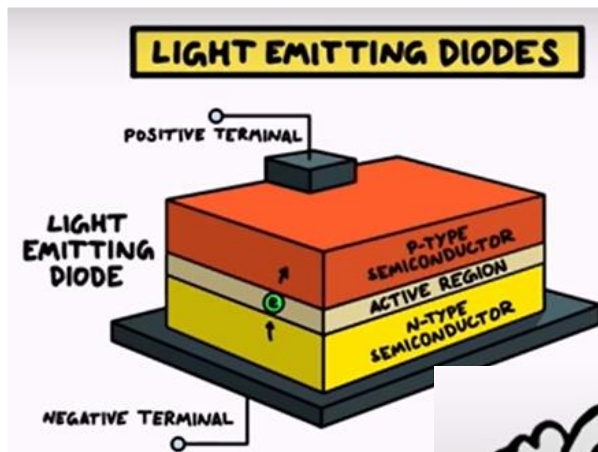
- To calculate **thermodynamic properties** (e.g., entropy, heat capacity)

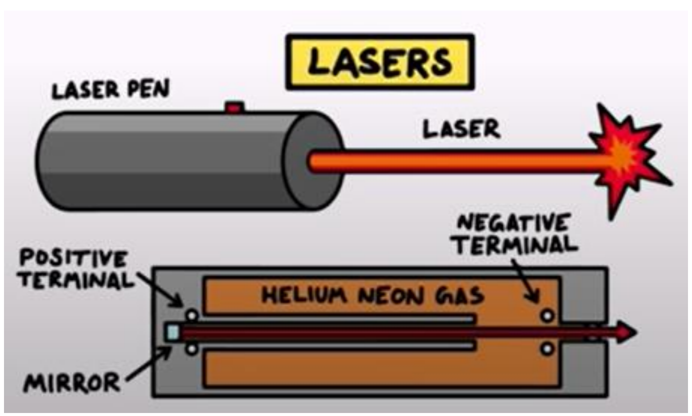
Without Quantum Mechanics, we could never have designed and built …

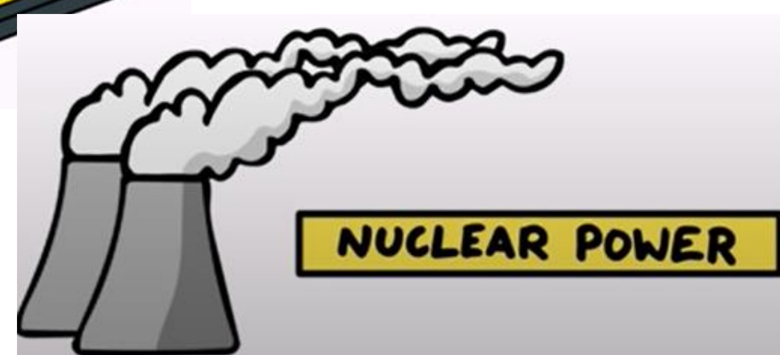


Semiconductor devices
Lasers
MRI
Nuclear Reactor
Atomic Clock



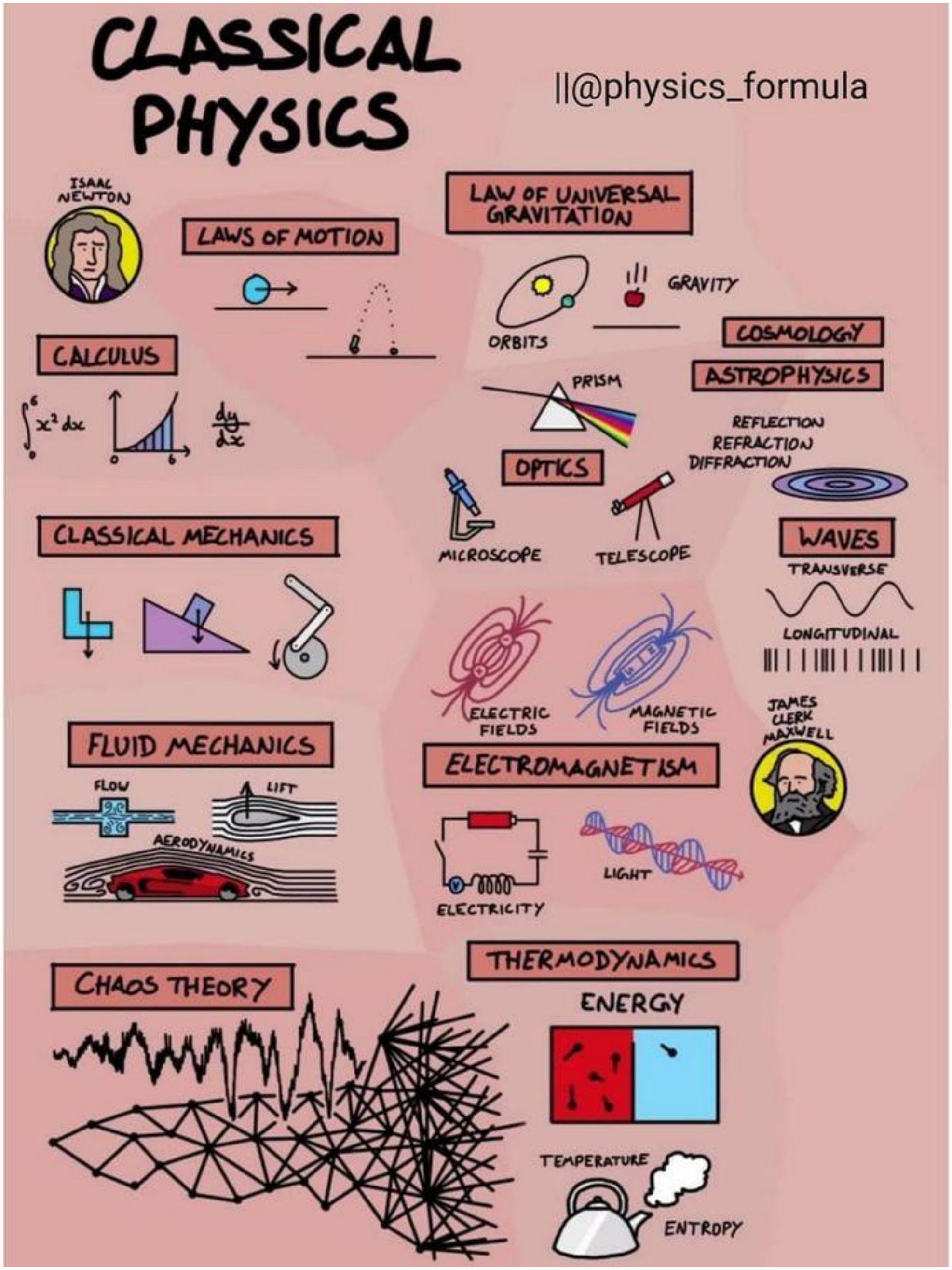






Dr. Dominic Walliman https://youtu.be/Usu9xZfabPM?si=ZZFrANPuK4JfUum7

The Emergence of Quantum Theory



https://images.app.goo.gl/WAaP2eYn67aBCwdB7

Classical mechanics

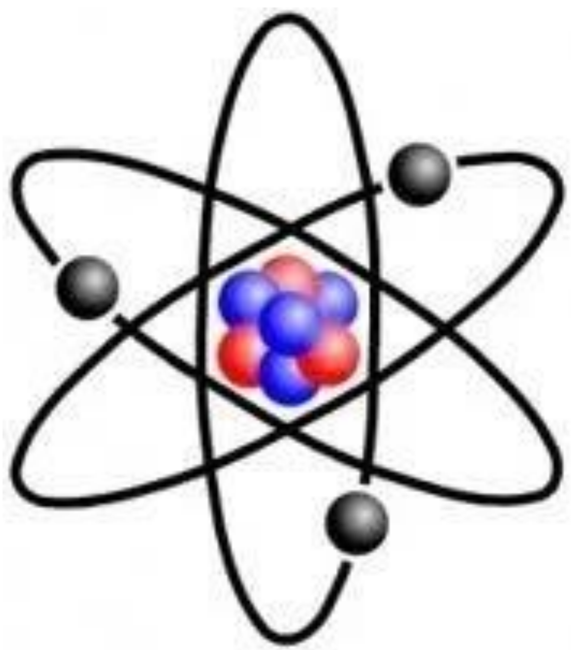
Galileo
Newton
Lagrange
Hamilton
Maxwell

Successfully describes laws of motion of macroscopic objects

The Emergence of Quantum Theory

Early 20th century, it was found that classical mechanics does not correctly describe behavior of objects of very small mass (microscopic objects)

- Stability of Atom

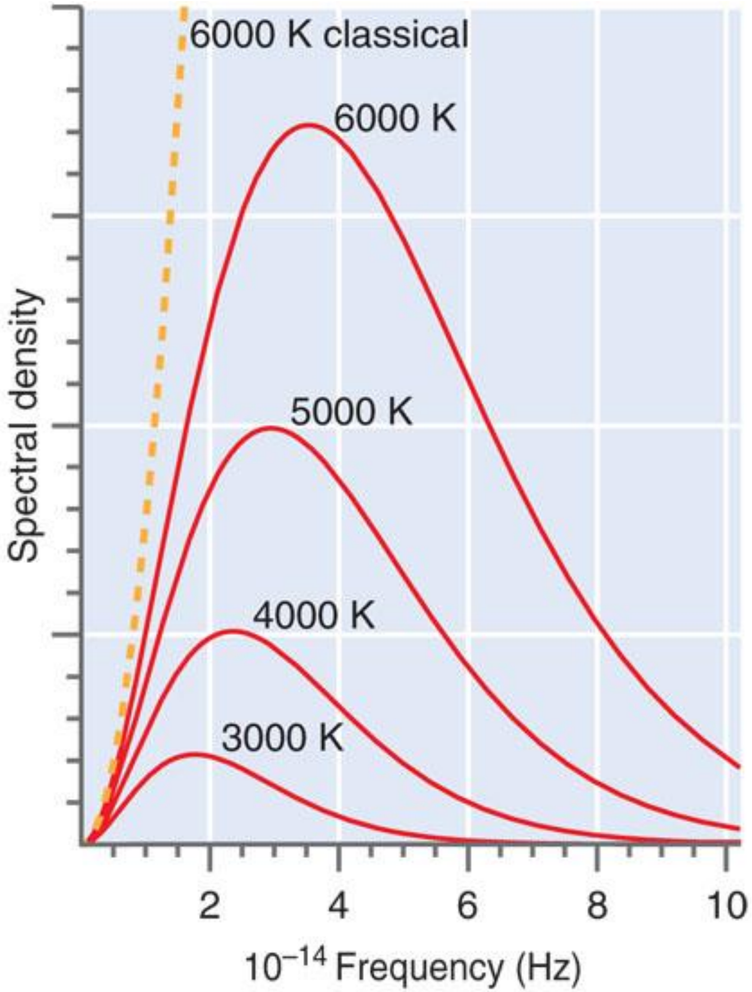


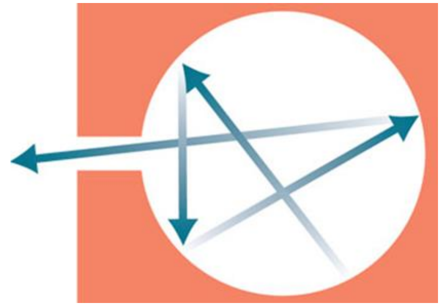
Accelerating electrons (charges) will emit electromagnetic radiation (energy) which would cause prompt decay of orbit

Atoms should disintegrate in nanoseconds!

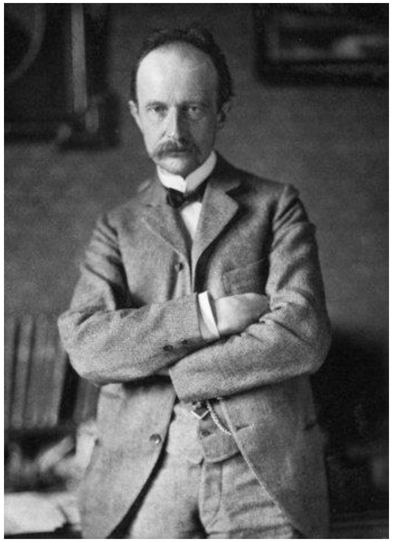
The Emergence of Quantum Theory

- Black-body Radiation





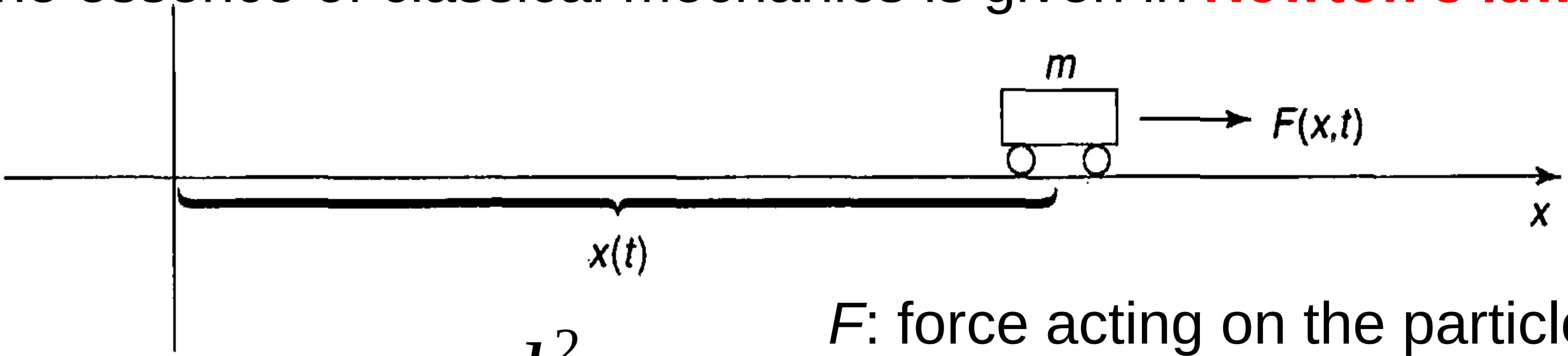
Classical theory suggested a "UV catastrophe," leading to infinite energy radiating from hot body.



Max Planck solved this problem by postulating light quanta.

Classical Mechanics

The essence of classical mechanics is given in **Newton's laws**



$$F = ma = m\frac{d^2x}{dt^2}$$

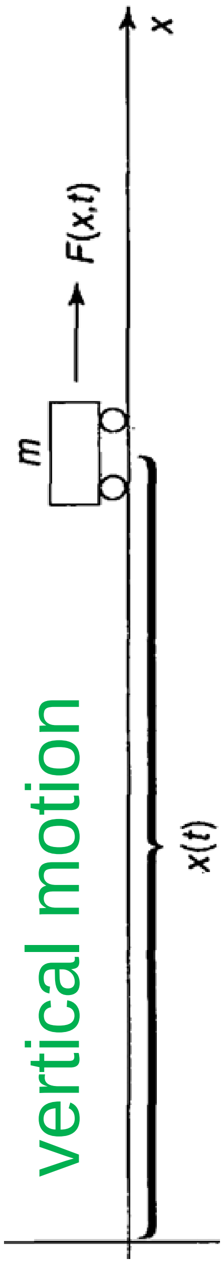
F: force acting on the particle,
m: its mass, *t*: the time,
acceleration: $a = dv/dt = d^2x/dt^2$,
v: the velocity.

Solution: $x = g(t, c_1, c_2)$, c_1 and c_2 are constants

Addn. conditions: $x_0 = g(t_0, c_1, c_2)$ $v_0 = \left.\frac{d}{dt}\, g(t, c_1, c_2)\right|_{t=t_0}$

Knowing the position x_0 and velocity v_0 at present time t_0, we can predict the future position of the particle.

Example…



$$F = -mg = m\frac{d^2x}{dt^2} \Rightarrow \frac{d^2x}{dt^2} = -g$$

$$dx/dt = -gt + c_1$$

If at t = t_0 the particle had v = v_0, then

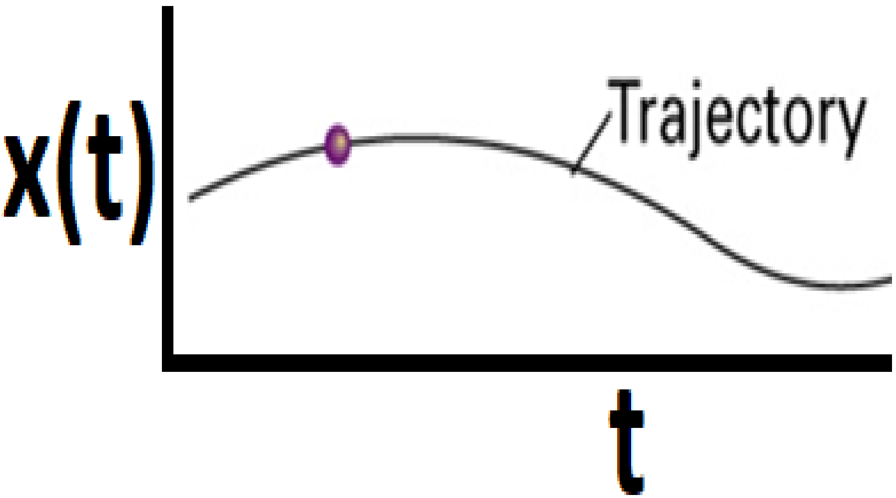
$$c_1 = v_0 + gt_0.$$

$$x = -\tfrac{1}{2}gt^2 + (gt_0 + v_0)t + c_2.$$

If at t = t_0, position x = x_0, then

$$c_2 = x_0 - \tfrac{1}{2}gt_0^2 - v_0t_0.$$

Given the position (x_0) and the velocity (v_0) at present time (t_0), future position x(t) is known.



What about properties??

$$F = -\partial V / \partial x$$
$$F = \partial p / \partial t$$

PE = V = mgx

KE = $mv^2/2 = p^2/2m = (Ft)^2/2m$

Classical Mechanics

For a given force, **if the initial position and the velocity of the particle is known**, all physical quantities such as position, momentum, angular momentum, energy etc. **at all subsequent times** can be calculated.

DETERMINISTIC

A super-being able to know the state of the universe at any instant could, in principle, calculate all future motions

...*Laplace* (1749-1827)

Classical mechanics (Summary)

- A particle travels in a **trajectory** (a path with a precise position and momentum) at each instant.

- Any type of motion can be excited to a state of arbitrary energy.

- Waves and particles are distinct concepts.

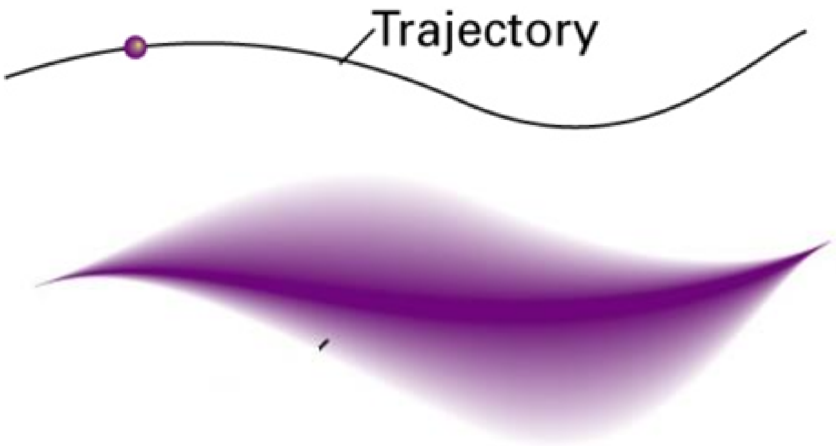
These conclusions agree with everyday experience.

However, everyday experience does not extend to individual atoms & subatomic particles.

Position-momentum uncertainty relation:

$$\Delta p_x \, \Delta x \geq \hbar / 2$$

An uncertainty of ~10^{-8} *m* in position of an electron means an uncertainty of ~10^4 m/s in its speed.



Classical mechanics fails when

- Applied to individual atoms and subatomic particles
- The transfer of energy is very small

Experimental results that overthrew the concepts of classical physics….

- Energy can be transferred between systems only in discrete amounts.

- Light behaved like a stream of particles.

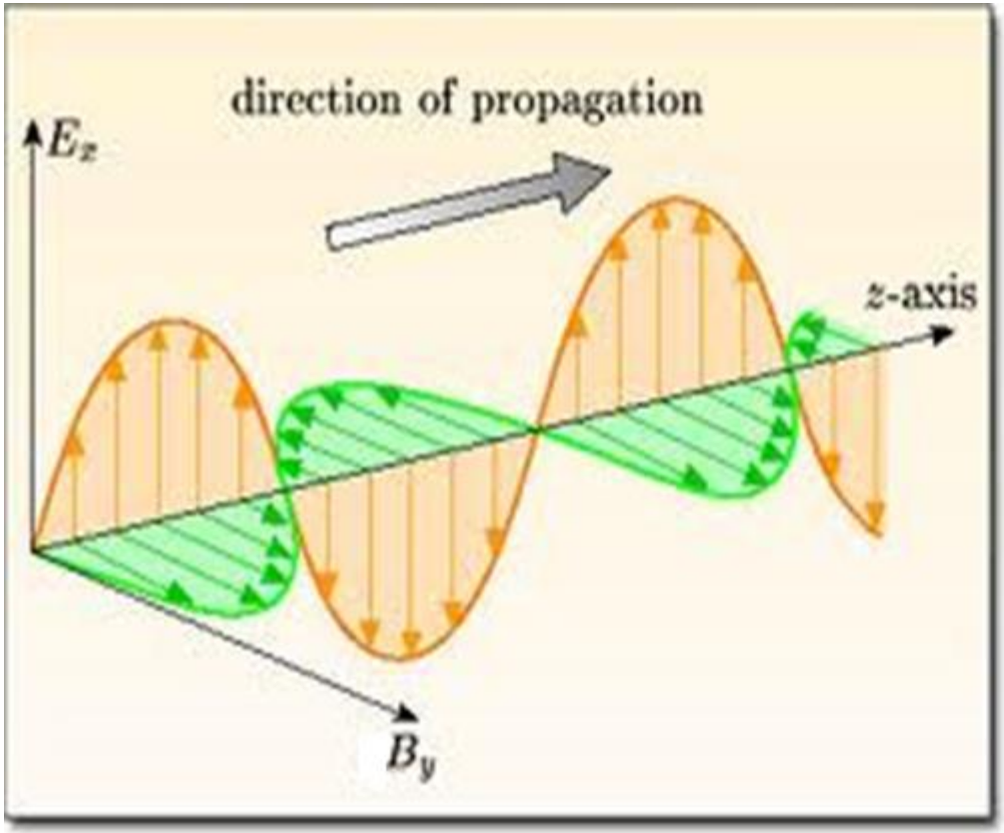
- Electrons behaved like waves.

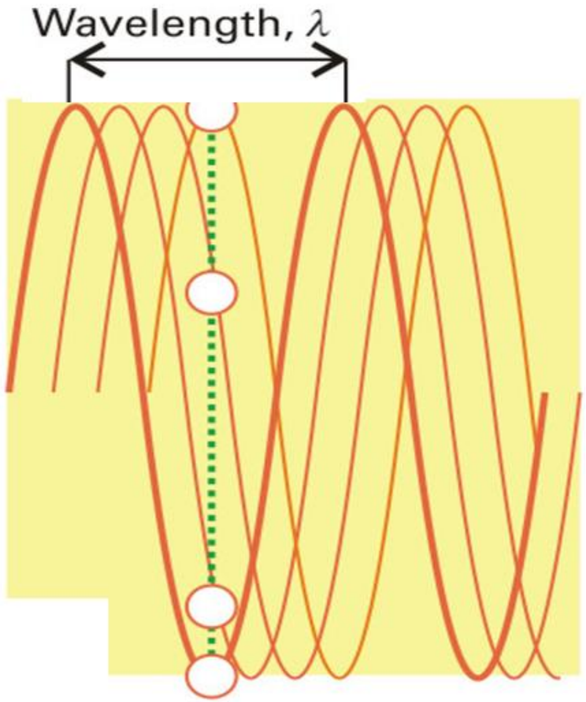
More Examples:

- Heat capacities
- Photoelectric effect
- Compton effect

Properties of Light

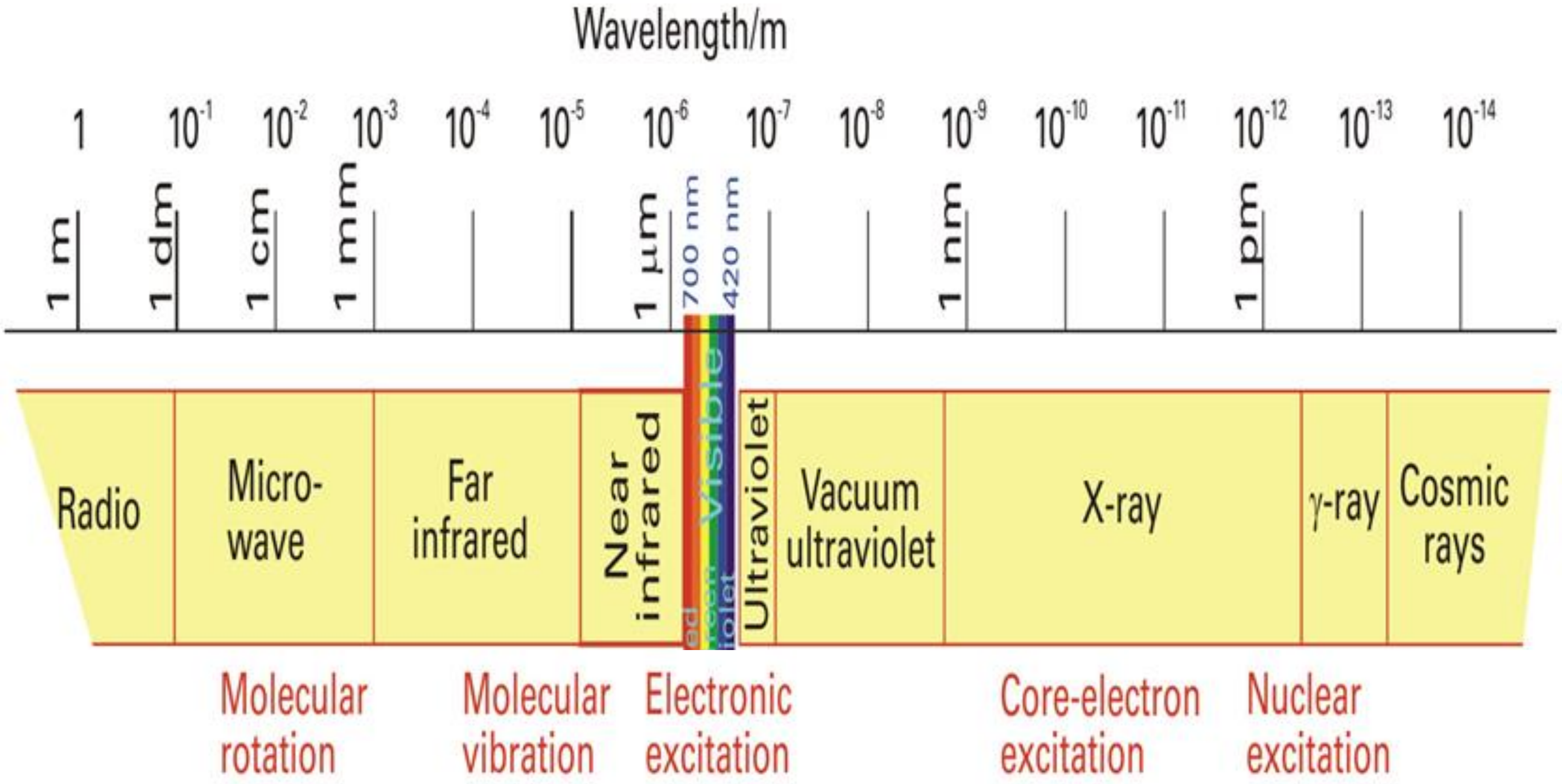
In classical physics, light is described as an electromagnetic radiation travelling at a speed of c = 2.997 924 58 x10^8 m s^{-1}, characterized by wavelength (λ) and frequency (ν): $\lambda\nu = c$





Wavenumber = $1/\lambda$

The electromagnetic spectrum

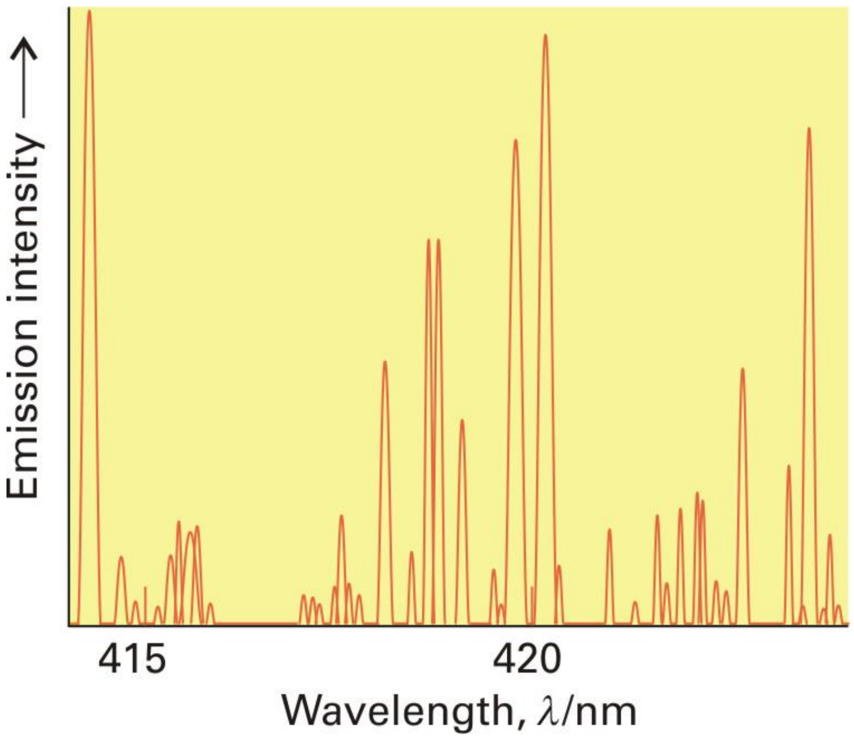


1 μm (micron) = 10^{-6} m; 1 nm (nano) = 10^{-9} m; 1 pm (pico) = 10^{-12} m

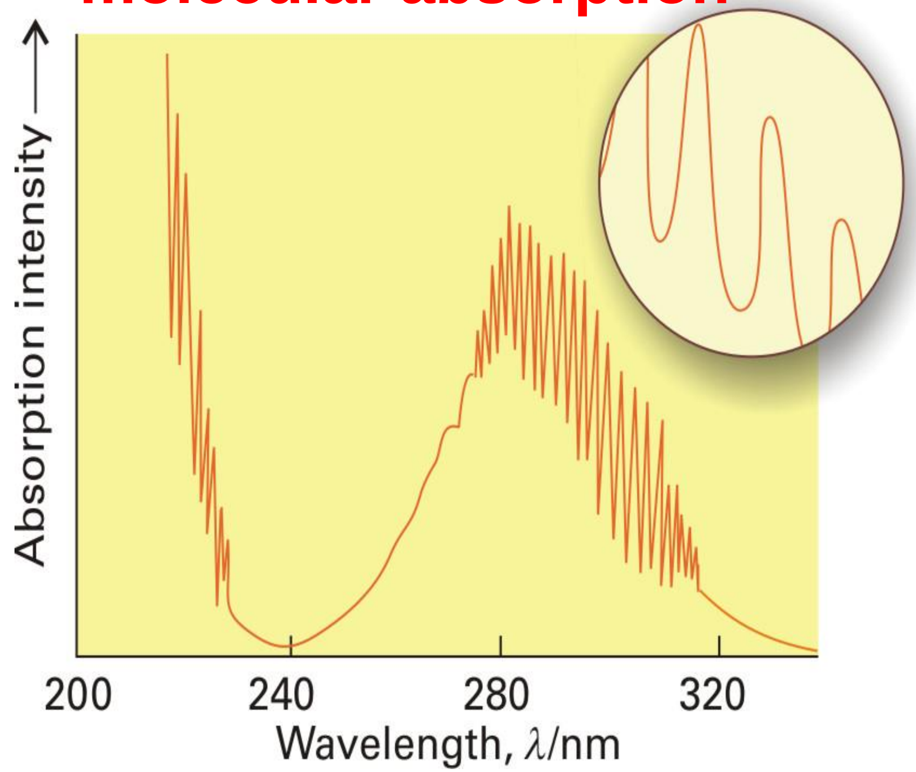
Evidence for discrete energy transfer

A **spectrum** is a display of the frequencies (or wavelengths) of electromagnetic radiation that are absorbed / emitted / scattered by an atom or molecule.

atomic emission



molecular absorption



Radiation is emitted or absorbed at a series of discrete wavelengths / frequencies.

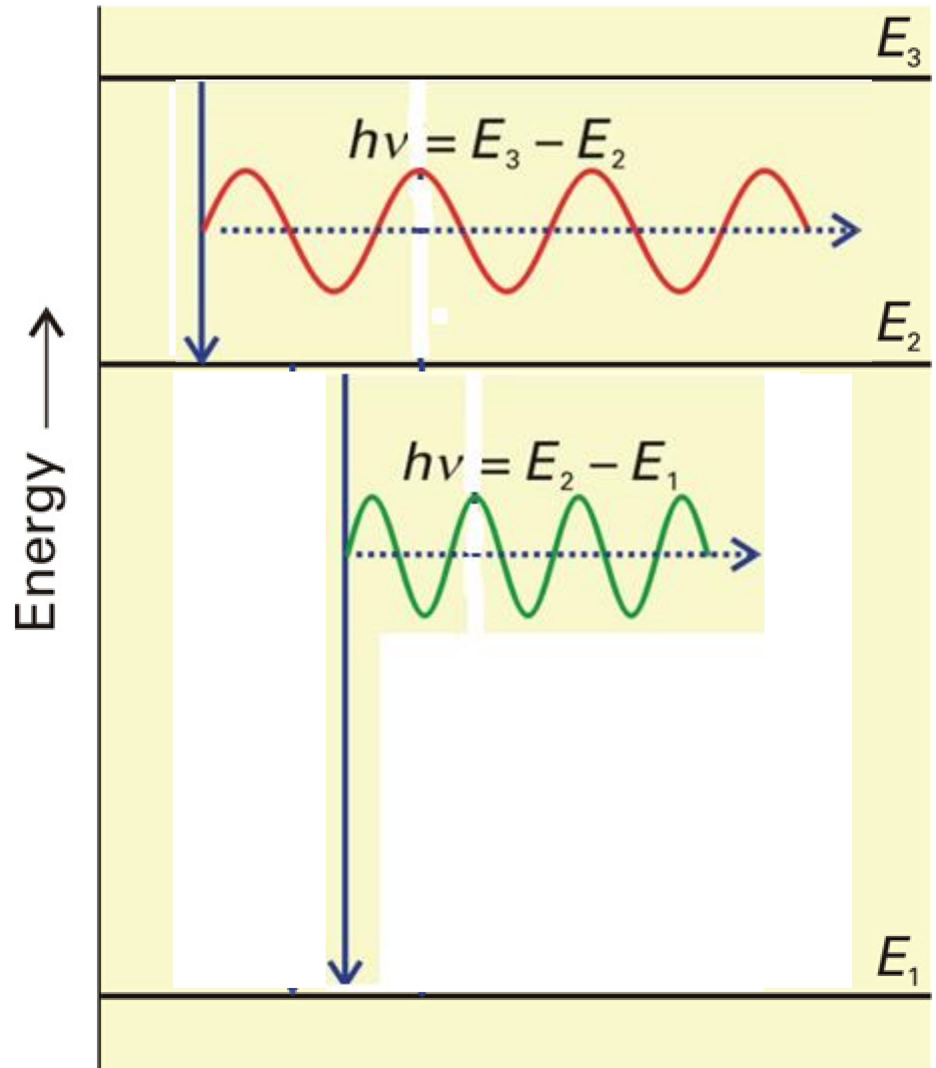
Atomic and molecular spectra

Conclusion: the energy of the atoms/molecules is **quantized**, i.e. confined to discrete values.

Energy can be discarded or absorbed only in discrete amounts

$$h\nu = \Delta E = |E_U - E_L|$$

Bohr frequency condition



Quantization of Energy

The limitation of energies to discrete values is called the quantization of energy.

The permitted energies of an electromagnetic wave of frequency ν are integer multiples of $h\nu$.

$$E = nh\nu, \quad n = 1, 2, \ldots$$

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

These particles of electromagnetic radiation are called **quanta / photons**.

The recognition that energy changes in discrete quanta at the atomic level marked the beginning of Quantum Theory…

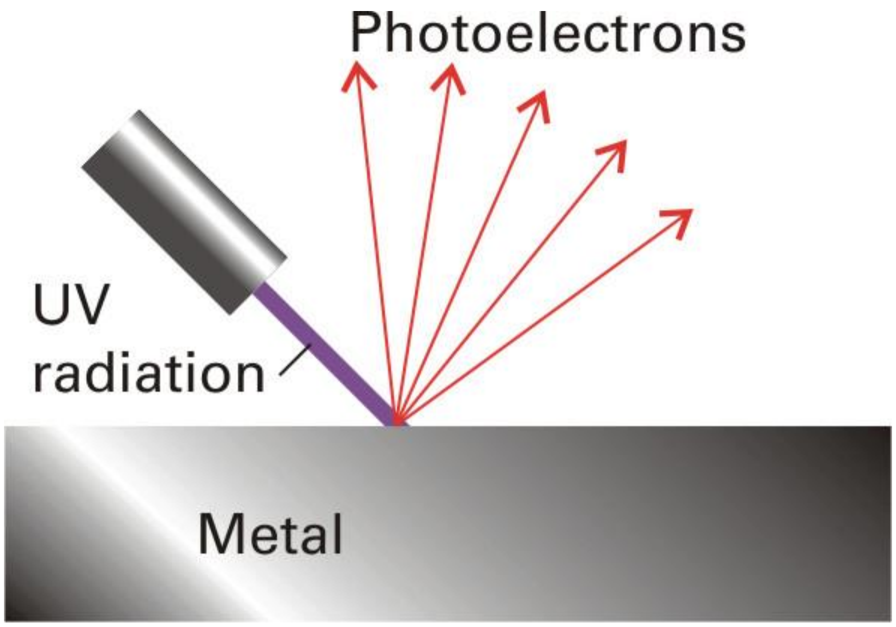
Max Planck

(1858-1947)

Nobel Prize in Physics 1918

Evidence for radiation as particles

Under the right circumstances light can be used to push electrons, freeing them from the surface of a solid.

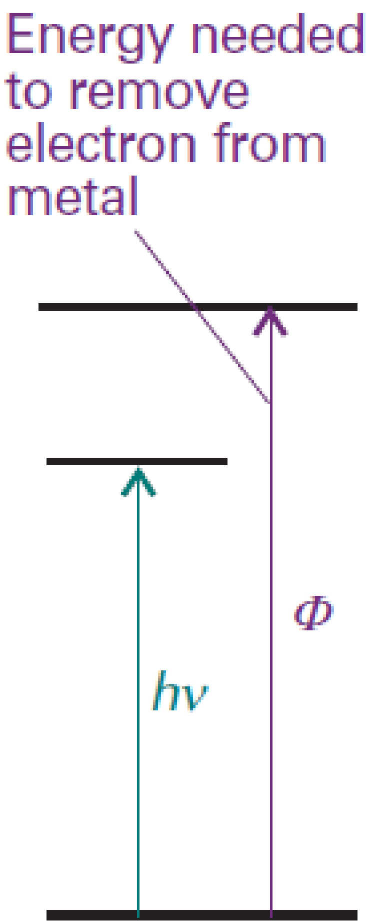


H. Hertz (1887)

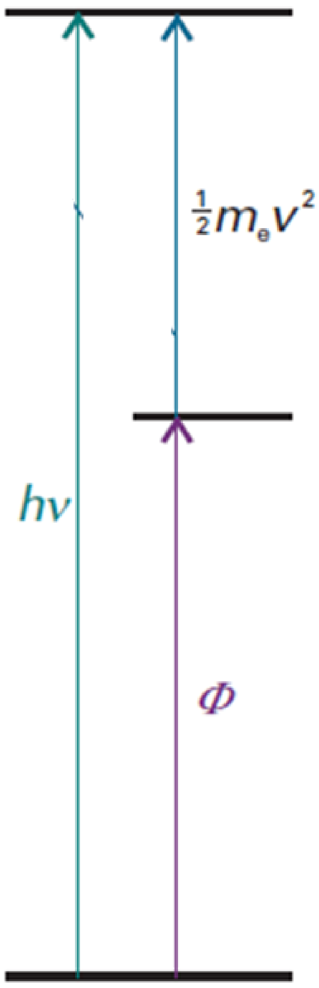
This process is called the photoelectric effect (or photoelectric emission or photoemission)

Features of Photoelectric Effect

Classically
$E_{EMW} \propto A^2$



- No electrons are ejected, unless the frequency exceeds a threshold value
- Even at low light intensities, electrons are ejected immediately if the frequency is above the threshold value
- The kinetic energy of the ejected electrons varies linearly with the frequency of the incident radiation



$$\frac{1}{2}m_e v^2 = h\nu - \Phi$$

The Photoelectric Effect

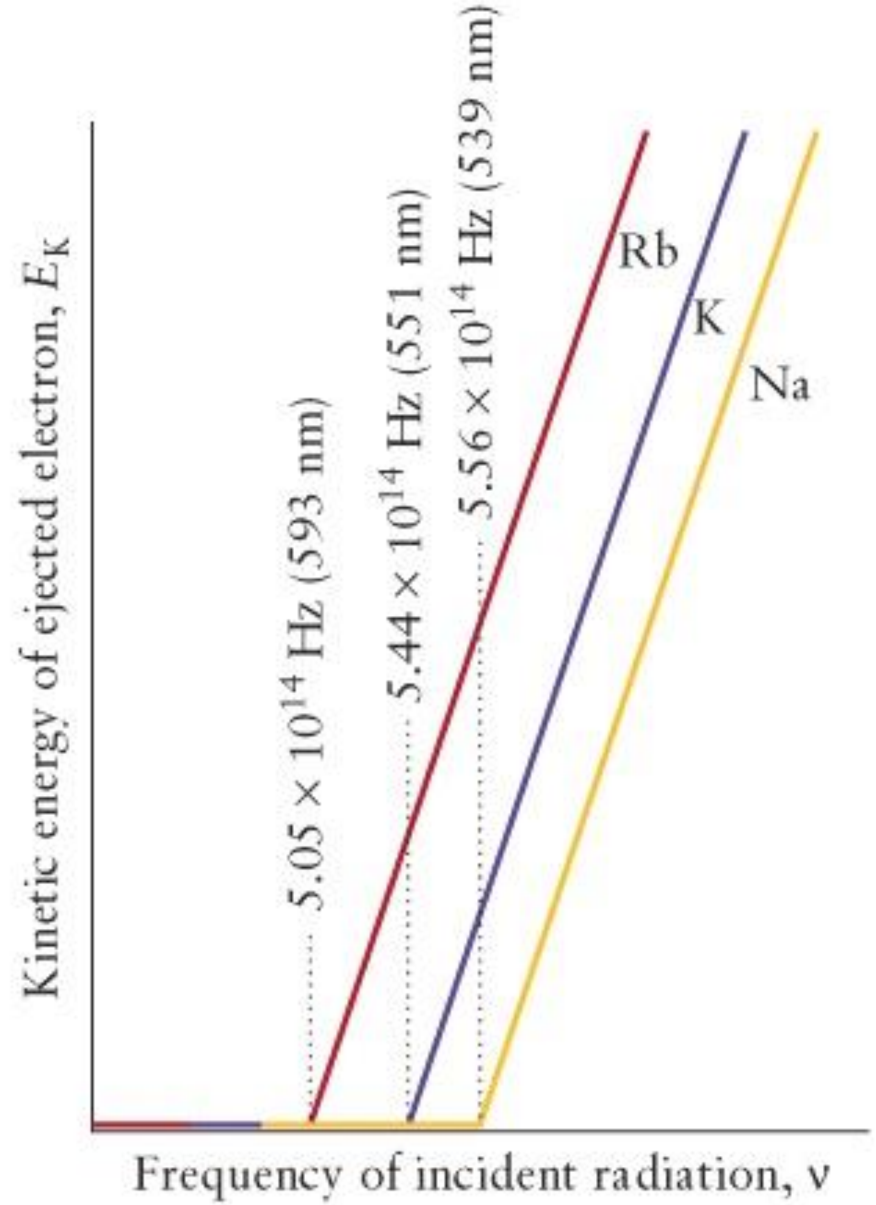
$$E_K = \frac{1}{2}m_e v^2 = h\nu - \Phi$$

Kinetic energy, $E_K = eV_S$

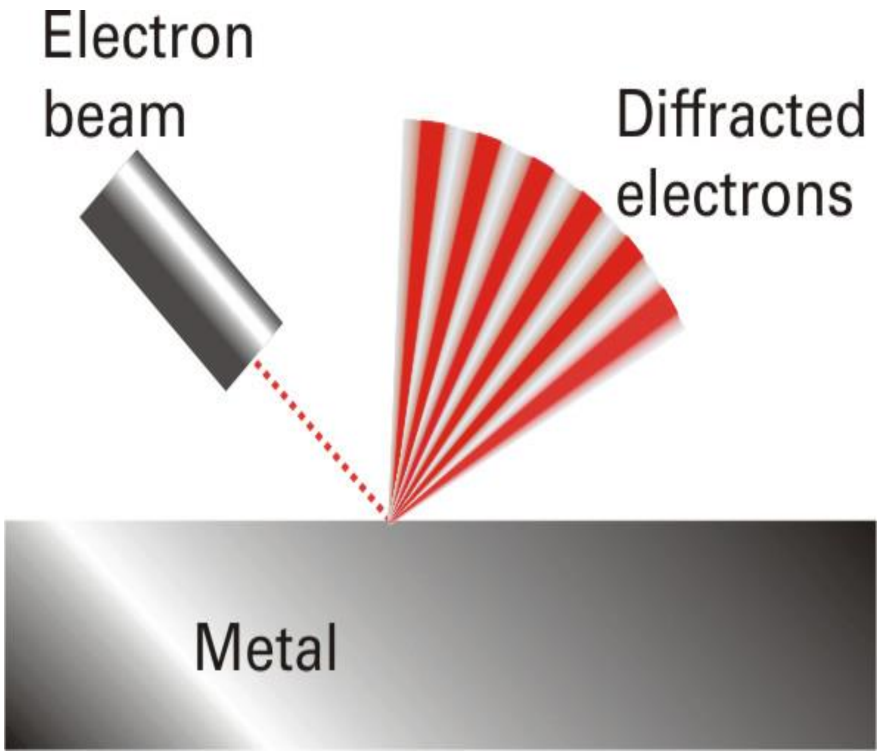
V_S: Stopping potential

work function, $\Phi = h\nu_0$

Photoelectric effect confirmed that radiation can be interpreted as a stream of particles.

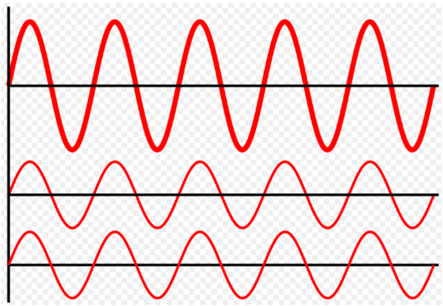


Evidence for particles as waves

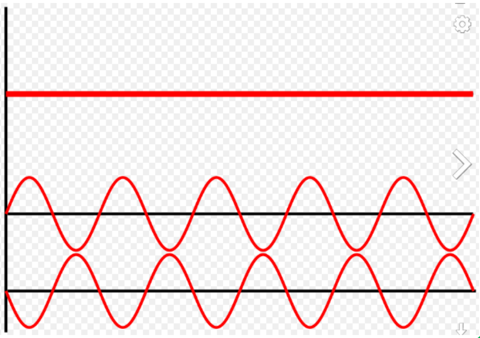


C. Davisson, L. Germer (1952)

The scattering of an electron beam from a nickel crystal shows a variation of intensity characteristic of a diffraction experiment.



Diffraction: waves interfere constructively (left) and destructively (right) in different directions.



Evidence for particles as waves

Diffraction is a typical characteristic of wave.

The Davisson–Germer experiment has been repeated with other particles (including molecular hydrogen and C_{60}), shows clearly that particles have wave-like properties.

In fact, the diffraction of neutrons is now a well-established technique for investigating the structures and dynamics of condensed phases.

<u>Wave-Particle duality</u>

Particles have wave-like properties and waves have particle-like properties <u>when examined on an atomic scale.</u>

(i.e. the concepts of particle and wave melt together)

This joint wave-particle character of matter and radiation is called **wave-particle duality.**

Wave-Particle Duality

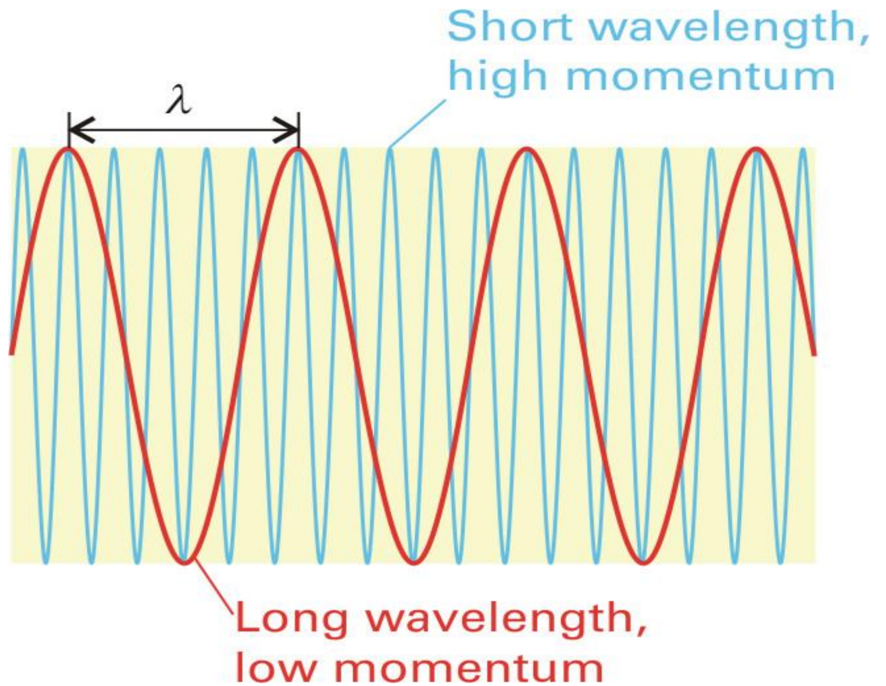
Phenomenon	Can be explained in terms of waves.	Can be explained in terms of particles.
Reflection	∿ ✓	•→ ✓
Refraction	∿ ✓	•→ ✓
Interference	∿ ✓	•→ ⊗
Diffraction	∿ ✓	•→ ⊗
Polarization	∿ ✓	•→ ⊗
Photoelectric effect	∿ ⊗	•→ ✓
Compton scattering	∿ ⊗	•→ ✓

How to describe wave-particle duality?

de Broglie relation

Wavelength of a travelling particle is inversely related to its linear momentum

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



Classical mechanics	**Quantum mechanics**
➢ Governed by Newton's law	➢ Governed by Schrodinger equation
➢ Deterministic	➢ Probabilistic
➢ Continuous energy	➢ Discrete energy
➢ Wave & particle are different concepts	➢ Wave-particle duality