QUANTUM THEORY OF THE ATOM

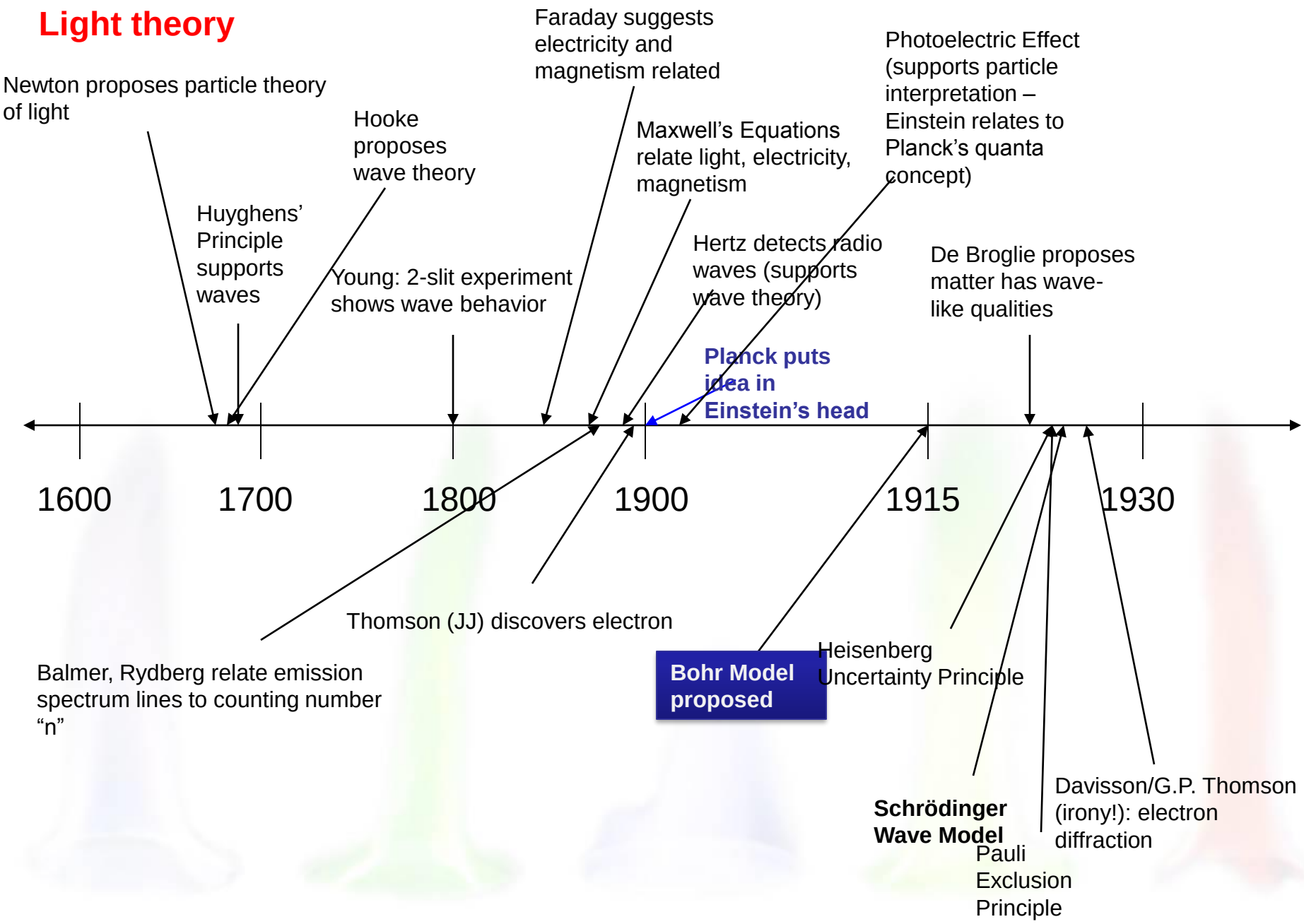
Contents and Concepts

Light Waves, Photons, and the Bohr Theory

To understand the formation of chemical bonds, you need to know something about the electronic structure of atoms. Because light gives us information about this structure, we begin by discussing the nature of light. Then we look at the Bohr theory of the simplest atom, hydrogen.

1. The Wave Nature of Light
2. Quantum Effects and Photons
3. The Bohr Theory of the Hydrogen Atom

Light theory



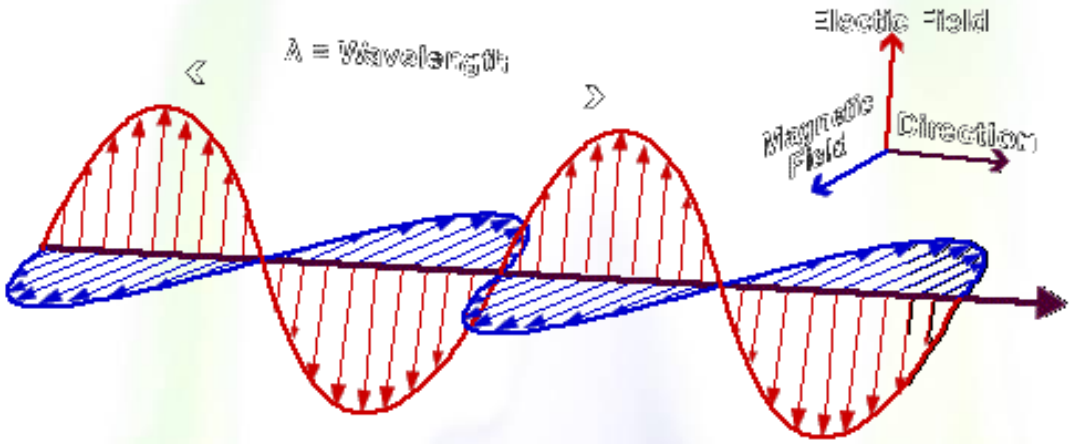
Quantum Mechanics and Quantum Numbers

The Bohr theory firmly establishes the concept of energy levels but fails to account for the details of atomic structure. Here we discuss some basic notions of quantum mechanics, which is the theory currently applied to extremely small particles, such as electrons in atoms.

4. Quantum Mechanics
5. Quantum Numbers and Atomic Orbitals

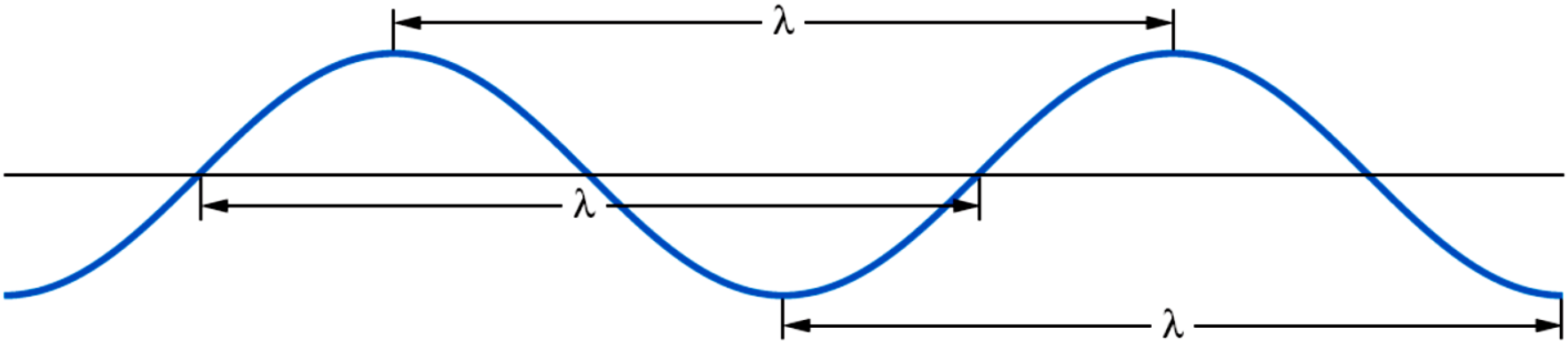
A **wave** is a continuously repeating change or oscillation in matter or in a physical field.

Light is an **electromagnetic wave**, consisting of oscillations in electric and magnetic fields traveling through space.

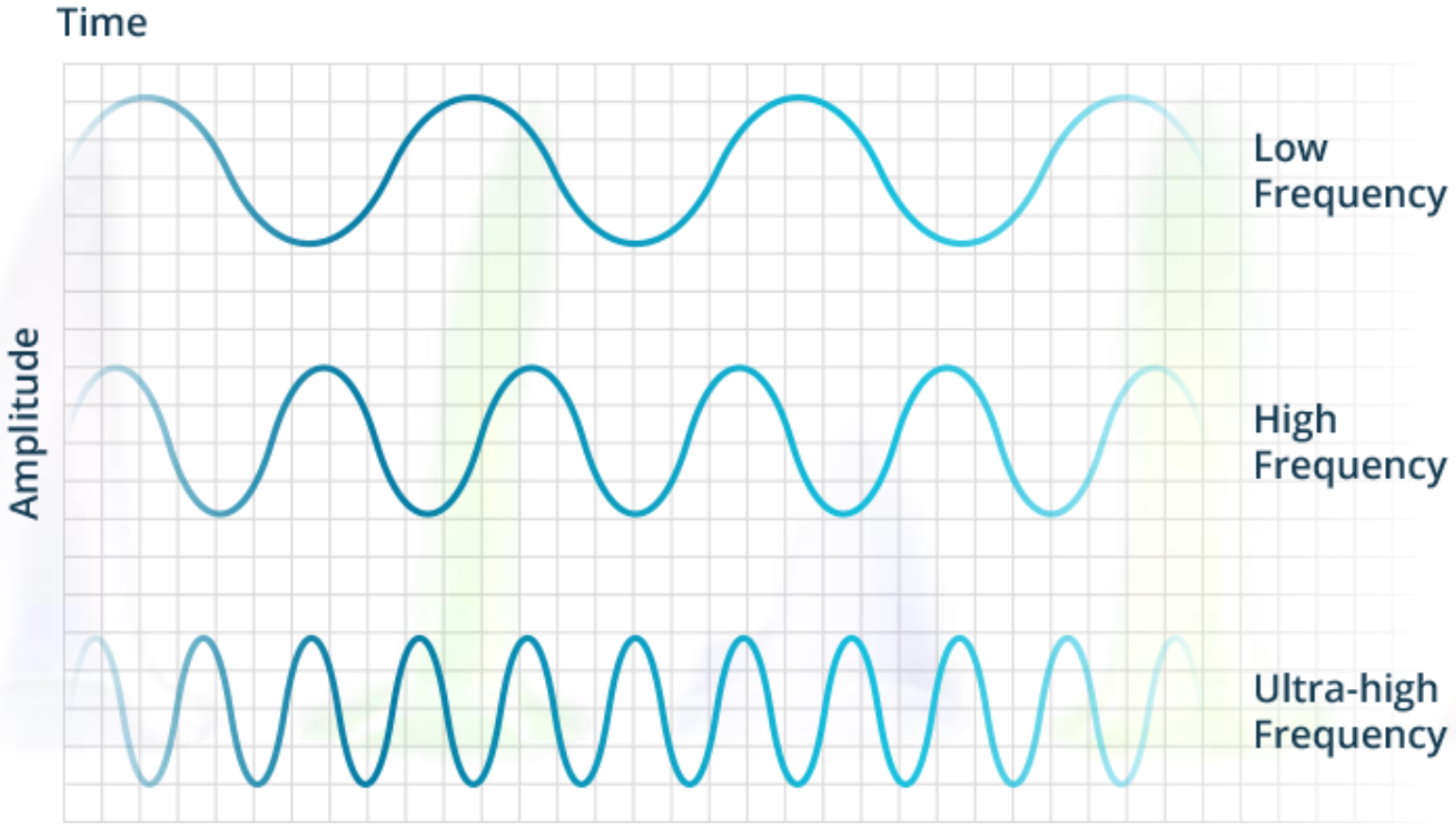


A wave can be characterized by its wavelength and frequency.

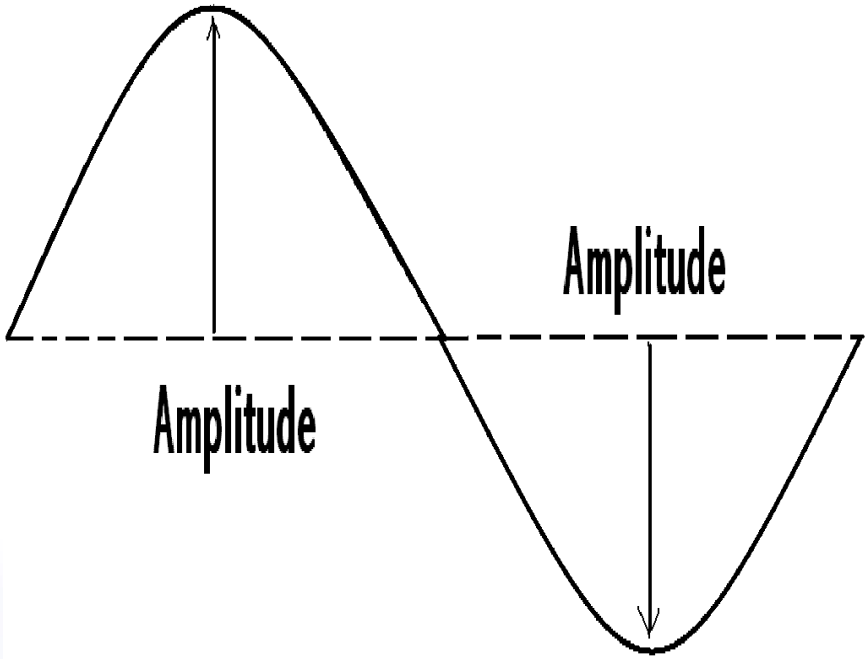
Wavelength, symbolized by the Greek letter lambda, λ, is the **distance between** any two identical points on adjacent waves.



Frequency, symbolized by the Greek letter nu, ν, is the number of wavelengths that pass a fixed point in one unit of time (usually a second). The unit is $^{1}/_{S}$ or s^{-1}, which is also called the Hertz (Hz).

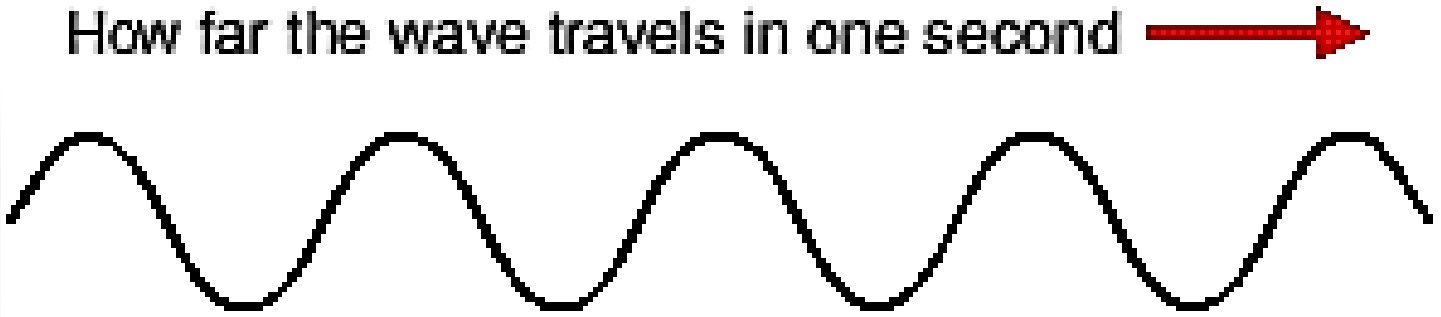


Amplitude, The maximum displacement of the vibrating particle of the given medium from the mean(equilibrium) position is defined as the Amplitude of the wave. Amplitude is directly Proportional to the energy of a wave, a high energy wave has a high amplitude and a low energy wave has a low amplitude.

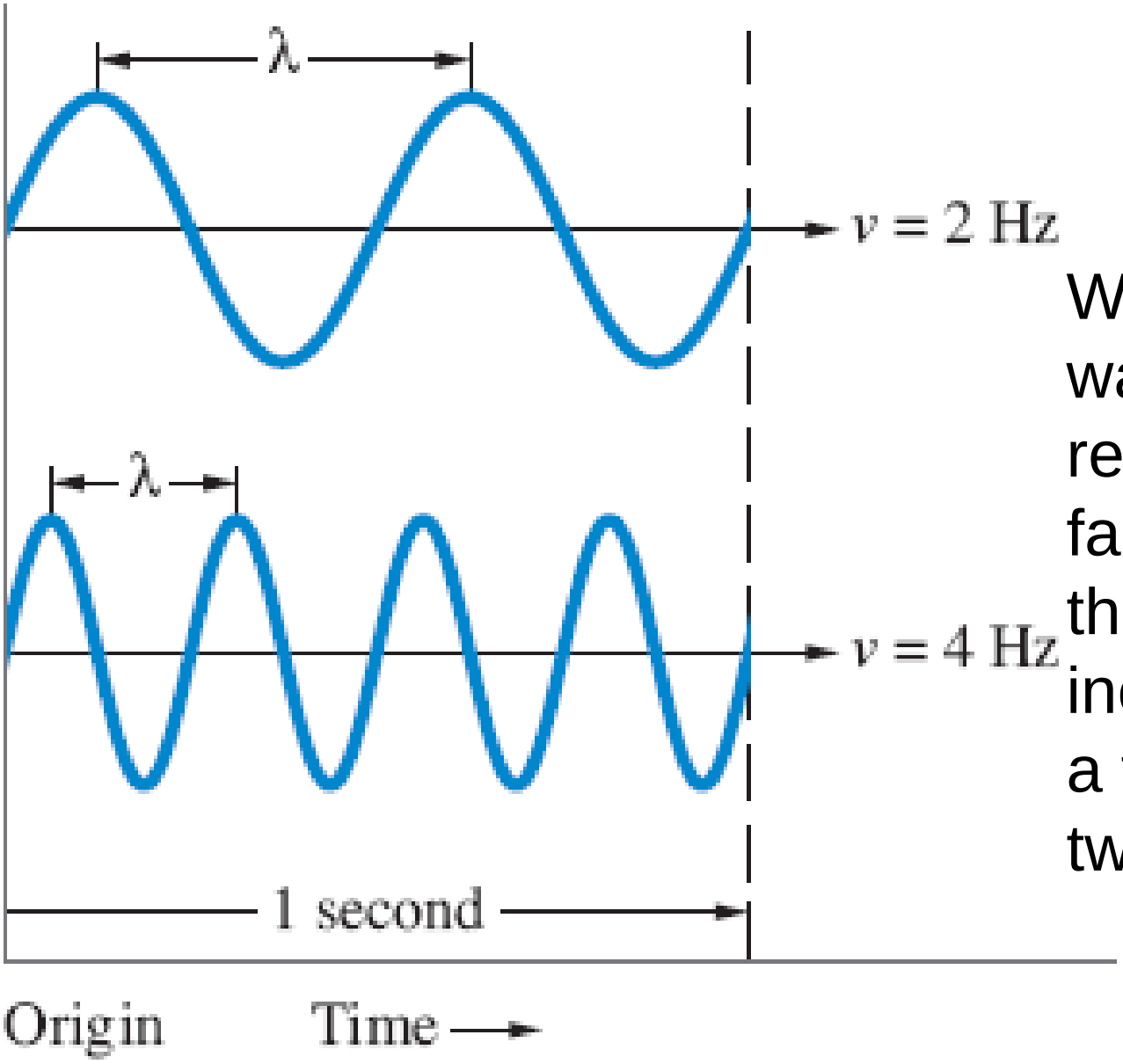


Wavelength and frequency are related by the wave speed, which for light is *c*, the speed of light, 3.00 x 10^8 m/s.

$$c = \nu\lambda$$

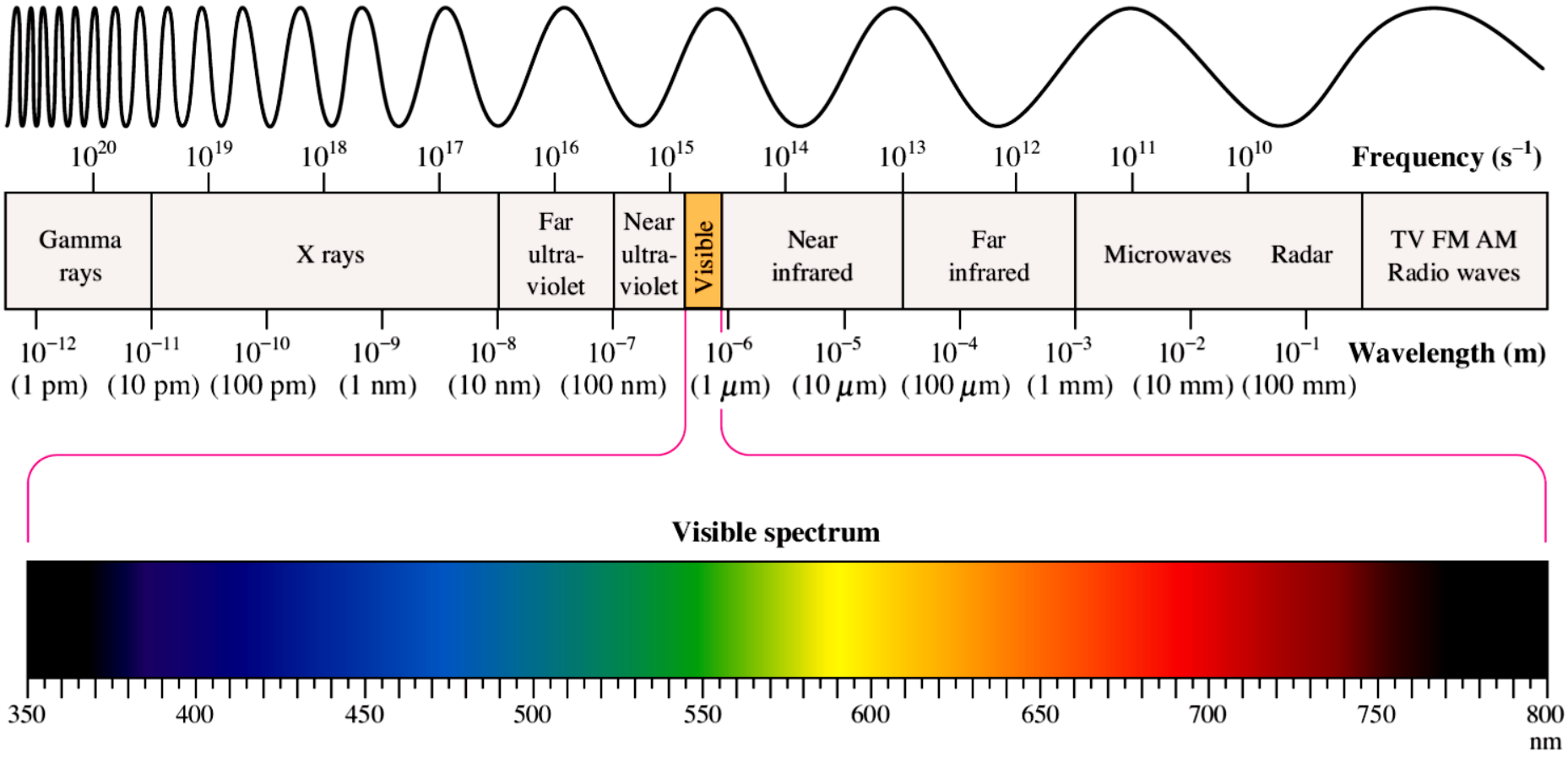


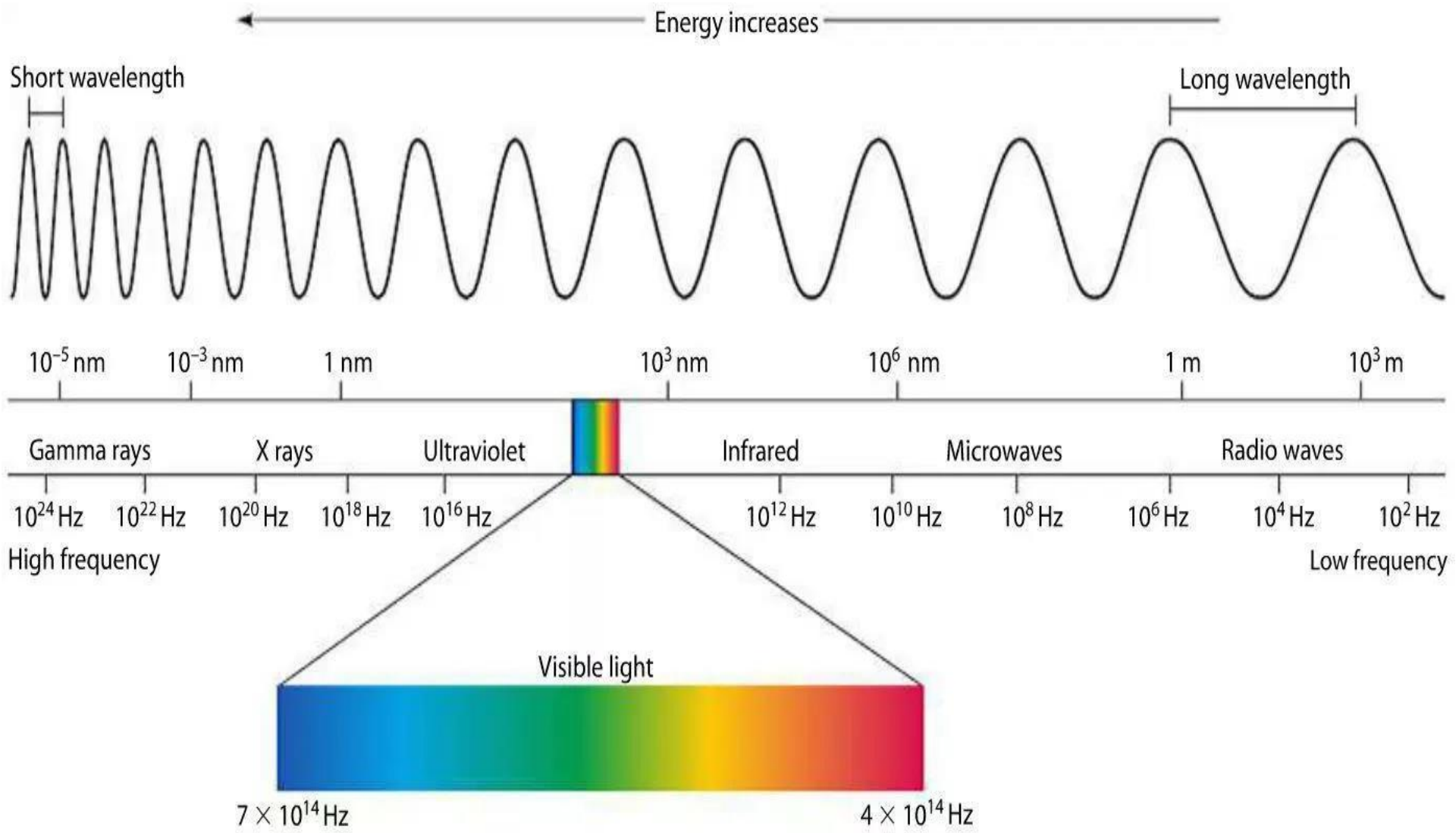
Sound in air	velocity = 340 ms^{-1}
Sound in water	velocity = 1400 ms^{-1}
Light in a vacuum	velocity = 300,000,000 ms^{-1}



When the wavelength is reduced by a factor of two, the frequency increases by a factor of two.

The range of frequencies and wavelengths of electromagnetic radiation is called the electromagnetic spectrum.




Energy increases
Short wavelength
Long wavelength
10^{-5} nm
10^{-3} nm
1 nm
10^{3} nm
10^{6} nm
1 m
10^{3} m
Gamma rays
X rays
Ultraviolet
Infrared
Microwaves
Radio waves
10^{24} Hz
10^{22} Hz
10^{20} Hz
10^{18} Hz
10^{16} Hz
10^{12} Hz
10^{10} Hz
10^{8} Hz
10^{6} Hz
10^{4} Hz
10^{2} Hz
High frequency
Low frequency
Visible light
7×10^{14} Hz
4×10^{14} Hz

Electromagnetic Radiation (4)

Example: Red light has $\lambda = 700$ nm.

Calculate the frequency, ν.

$$\nu = \frac{c}{\lambda} = \frac{3.00 \times 10^{8} \text{ m/s}}{7.00 \times 10^{-7} \text{ m}} = 4.29 \times 10^{14} \text{ Hz}$$

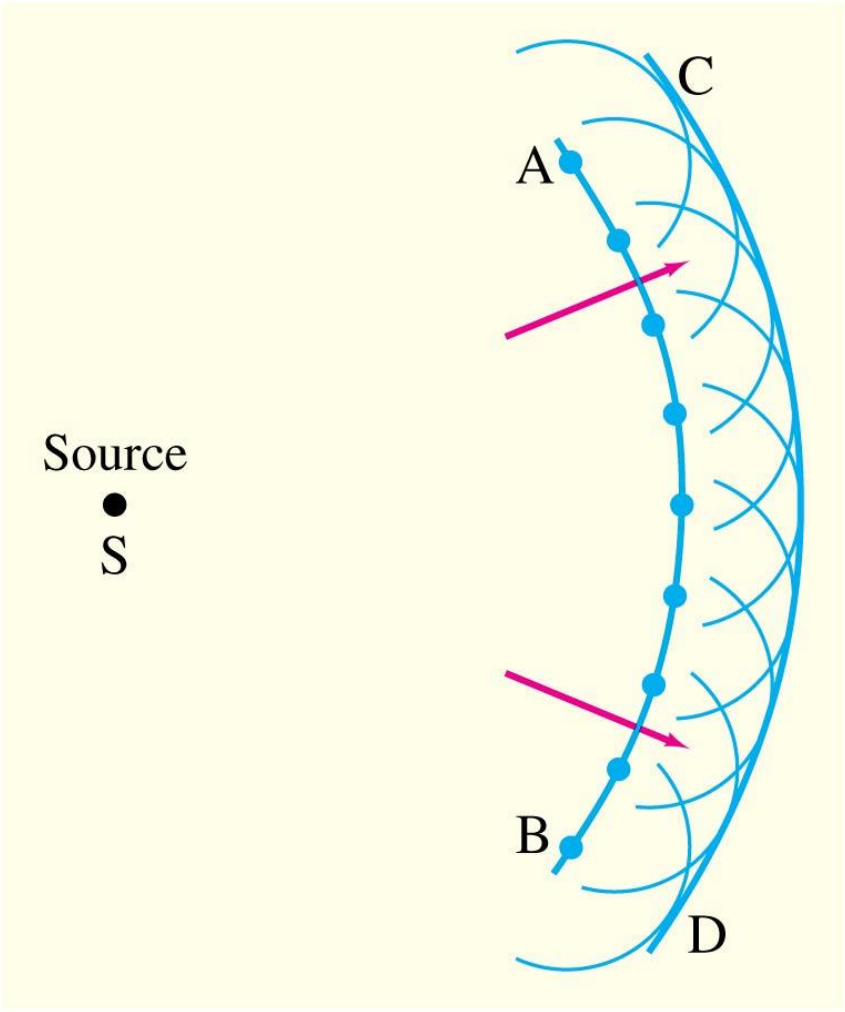
- Wave nature of light is shown by classical wave properties such as
  - *interference*
  - *diffraction*

One property of waves is that they can be diffracted—that is, they spread out when they encounter an obstacle about the size of the wavelength.

In 1801, Thomas Young, a British physicist, showed that **light could be diffracted**. By the early 1900s, the wave theory of light was well established.

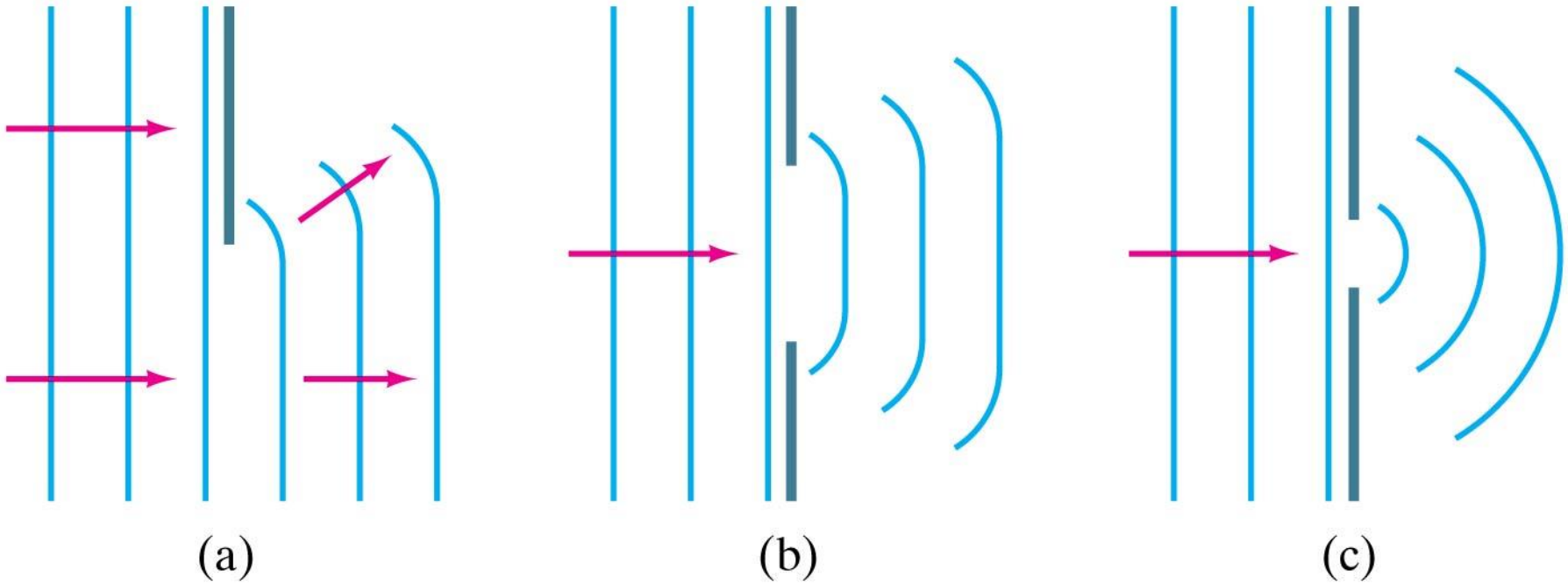
Huygens' Principle and Diffraction

Huygens' principle: Every point on a wave front acts as a point source; the wavefront as it develops is tangent to their envelope



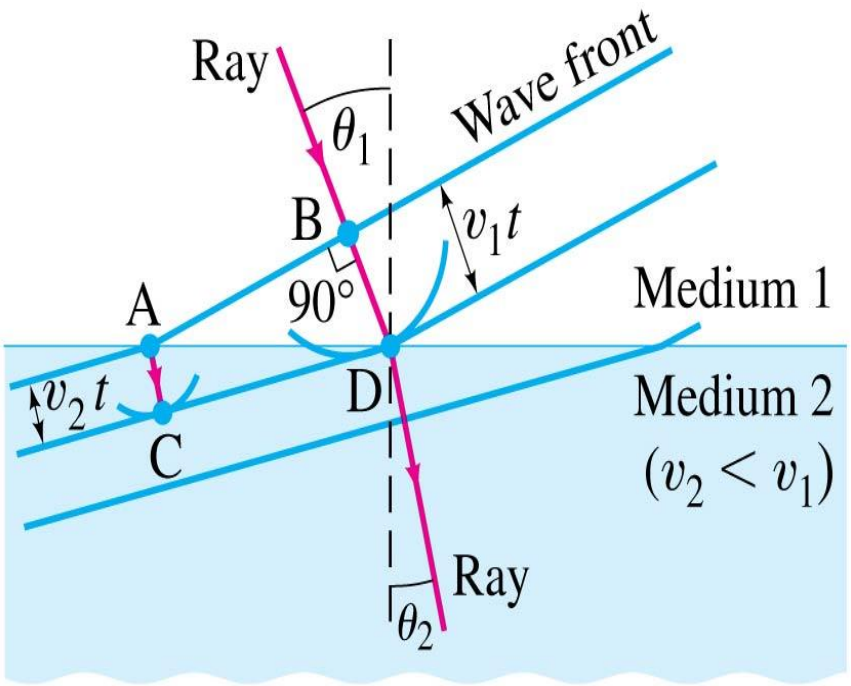
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Huygens' Principle and Diffraction



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Huygens' Principle and the Law of Refraction



As the waves propagate from each point, they propagate more slowly in the medium of higher index of refraction.

This leads to a bend in the wavefront and therefore in the ray.

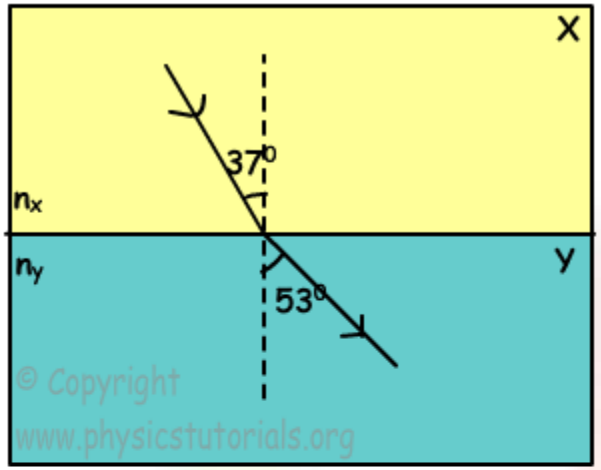
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Huygens' Principle and the Law of Refraction

The frequency of the light does not change, but the wavelength does as it travels into a new medium.

$$\frac{\lambda_2}{\lambda_1} = \frac{v_2 t}{v_1 t} = \frac{v_2}{v_1} = \frac{n_1}{n_2}$$

$$\lambda_n = \frac{\lambda}{n}$$



We use snell's law to solve this example

Snell's Law;

$n_1.\sin\theta_1 = n_2.\sin\theta_2$

$n_x.\sin 37^0 = n_y.\sin 53^0$

$n_x.0,6 = n_y.0,8$

$$\frac{n_x}{n_y} = \frac{4}{3}$$

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A ray of light is incident through glass, with refractive index 1.52, on an interface separating glass and water with refractive index 1.32. What is the angle of refraction if the angle of incidence of the ray in glass is 25 °?

What should be the angle of incidence of a light ray incident through air on the boundary separating air from water so that the angle of refraction is 30 °?(refractive index of air is 1 and that of water is 1.32)

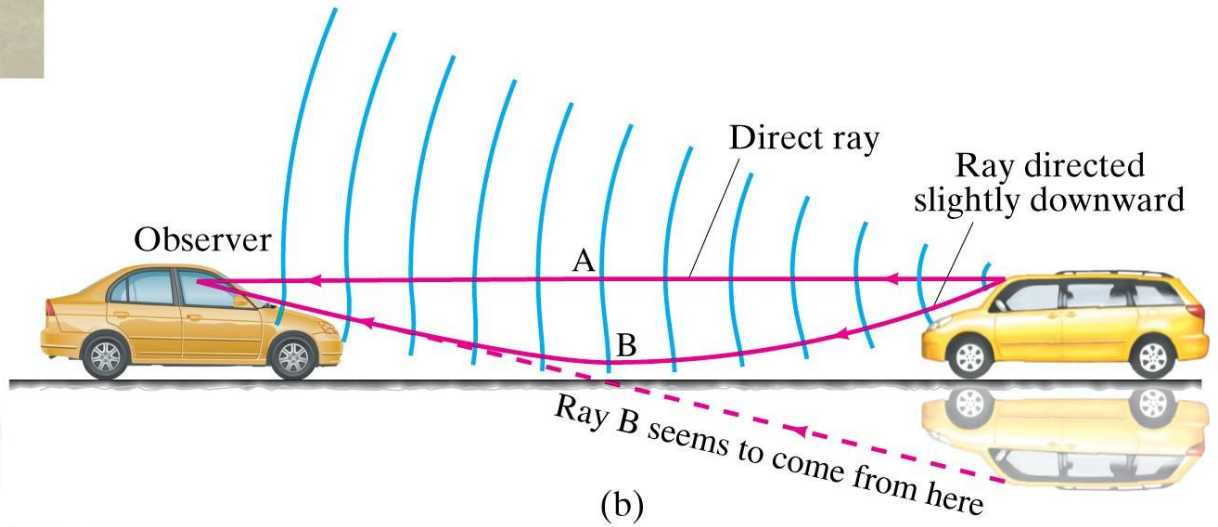
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Huygens' Principle and the Law of Refraction



(a)

Highway mirages are due to a gradually changing index of refraction in heated air.



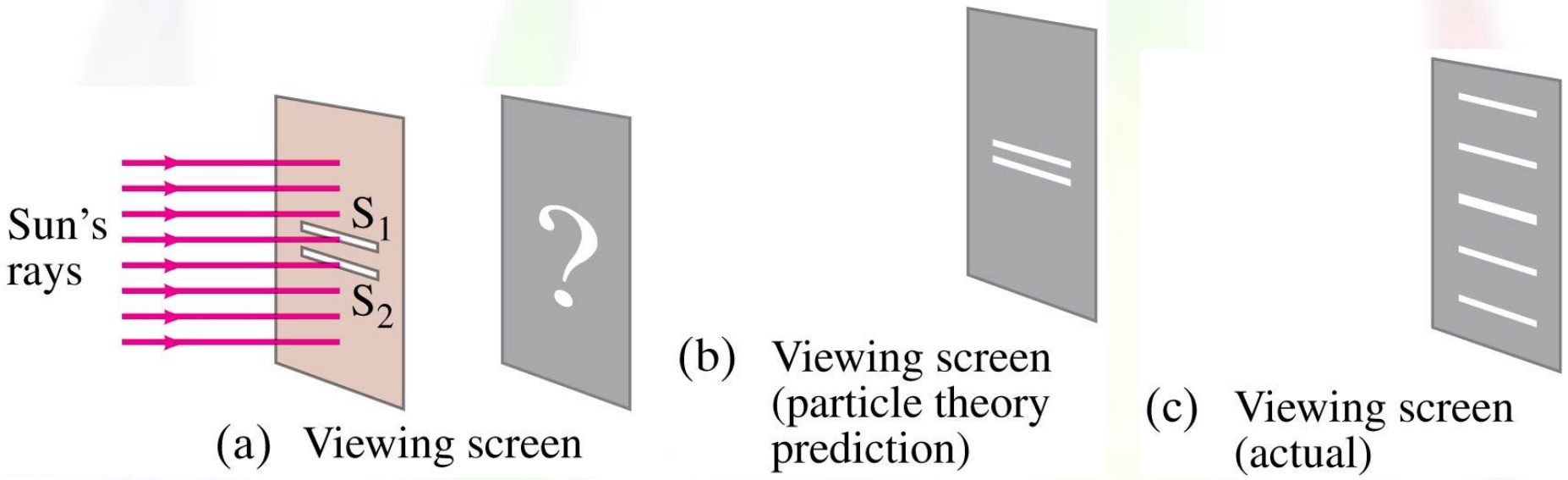
(b)

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Young's Double-Slit Experiment

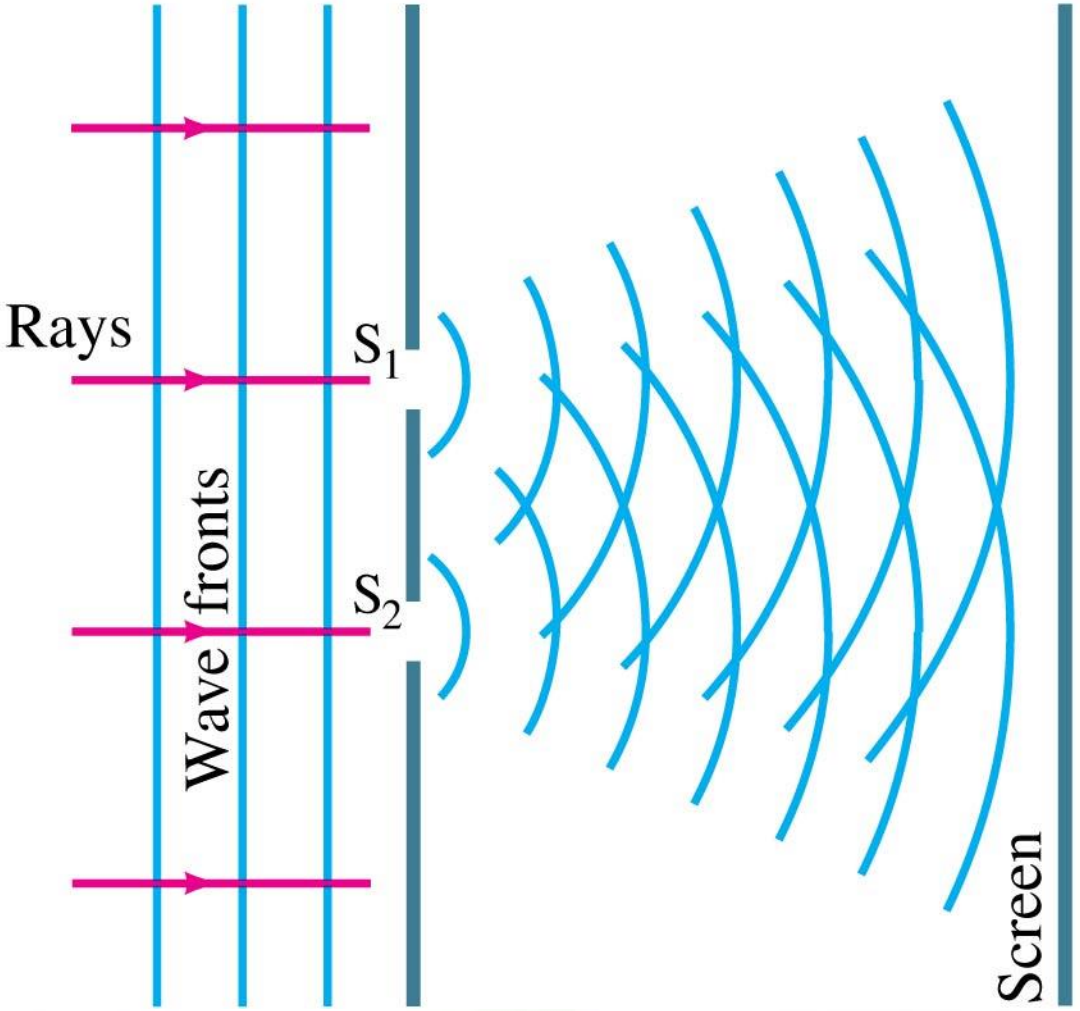
If light is a wave, interference effects will be seen, where one part of wavefront can interact with another part.

One way to study this is to do a double-slit experiment:



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Young's Double-Slit Experiment: interference

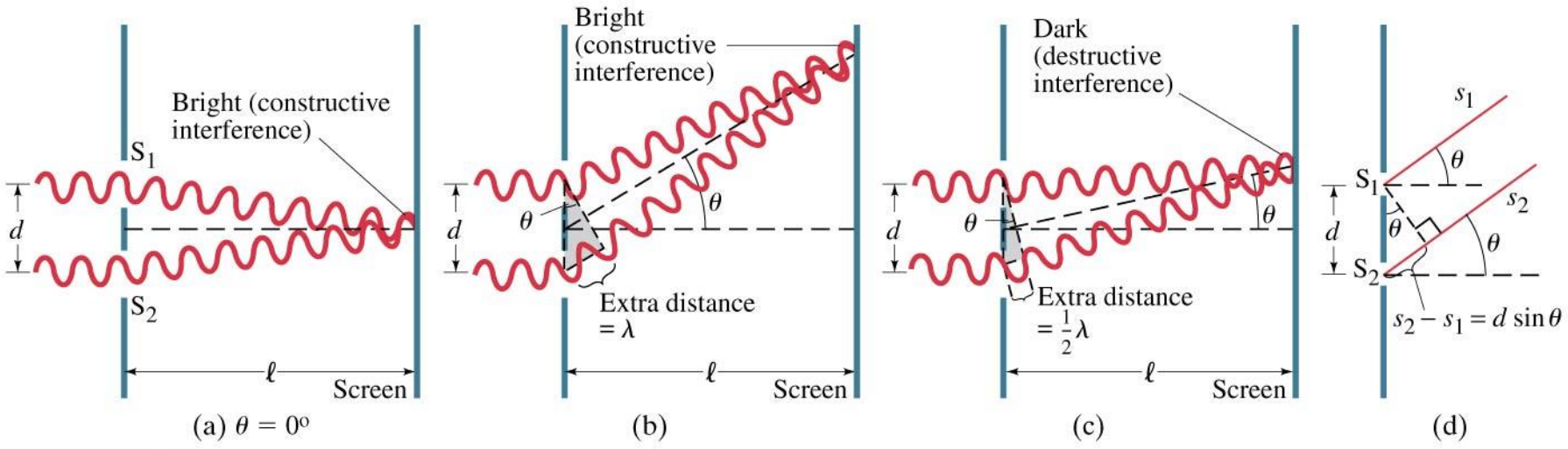


If light is a wave, there should be an interference pattern.

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Young's Double-Slit Experiment: interference

The interference occurs because each point on the screen is not the same distance from both slits. Depending on the path length difference, the wave can interfere constructively (bright spot) or destructively (dark spot).



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Young's Double-Slit Experiment: interference

We can use geometry to find the conditions for constructive and destructive interference:

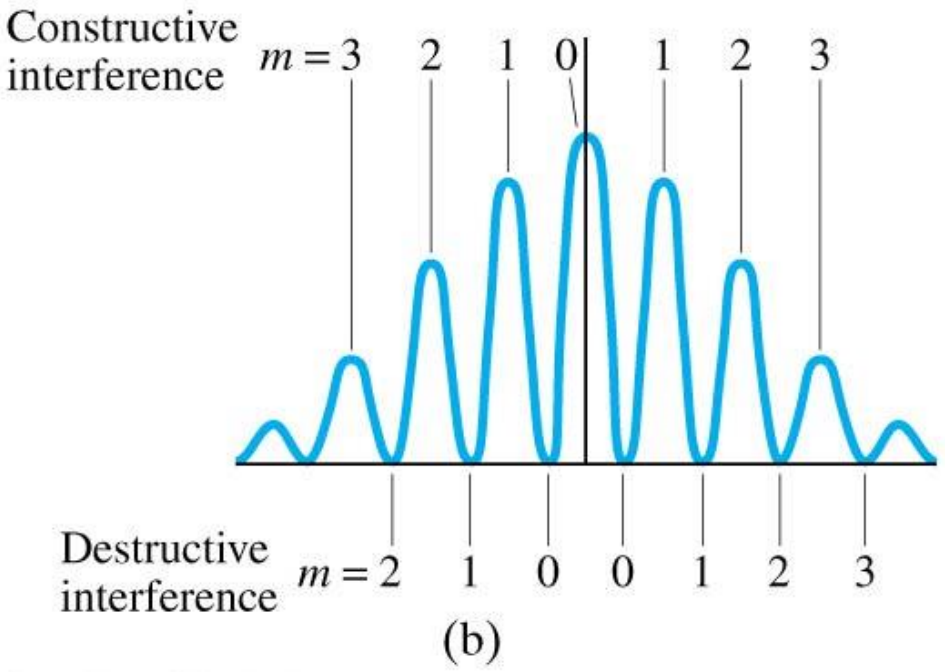
$$d \sin\theta = m\lambda, \quad m = 0, 1, 2, \cdots. \qquad \left[\begin{array}{c}\text{constructive}\\ \text{interference}\\ \text{(bright)}\end{array}\right]$$

$$d \sin\theta = \left(m + \tfrac{1}{2}\right)\lambda, \quad m = 0, 1, 2, \cdots. \qquad \left[\begin{array}{c}\text{destructive}\\ \text{interference}\\ \text{(dark)}\end{array}\right]$$

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Young's Double-Slit Experiment: interference

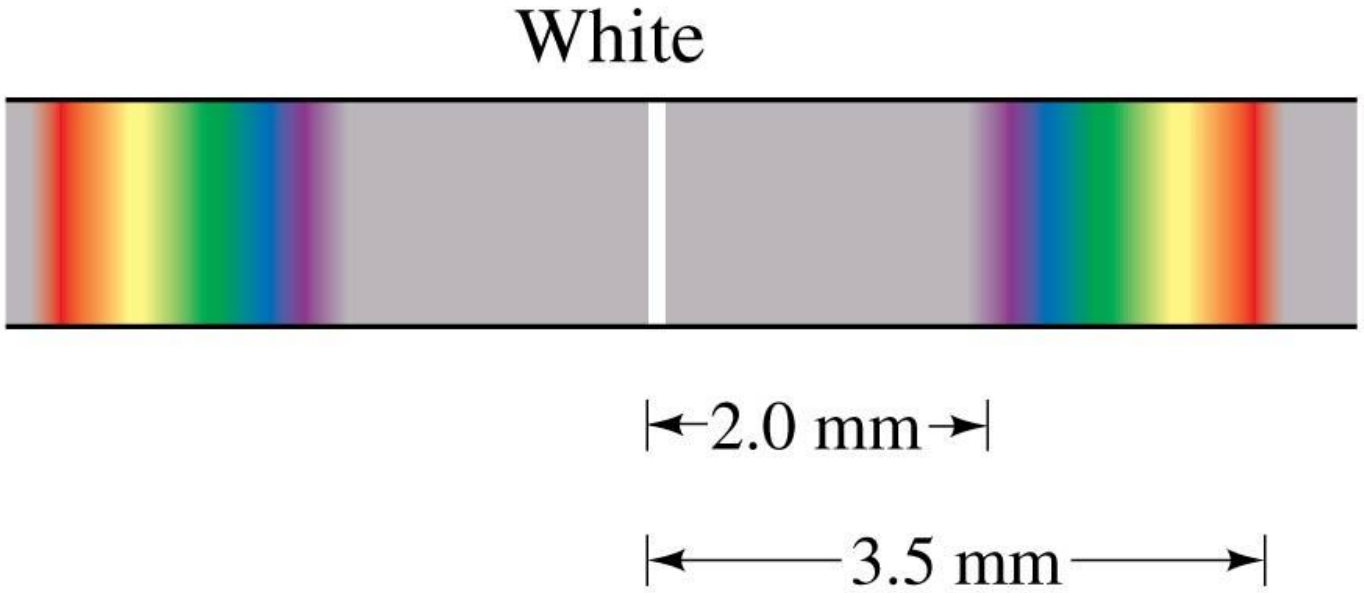
Between the maxima and the minima, the amplitude varies smoothly.



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Young's Double-Slit Experiment: interference

Since the position of the maxima (except the central one) depends on wavelength, the first- and higher-order fringes contain a spectrum of colors.

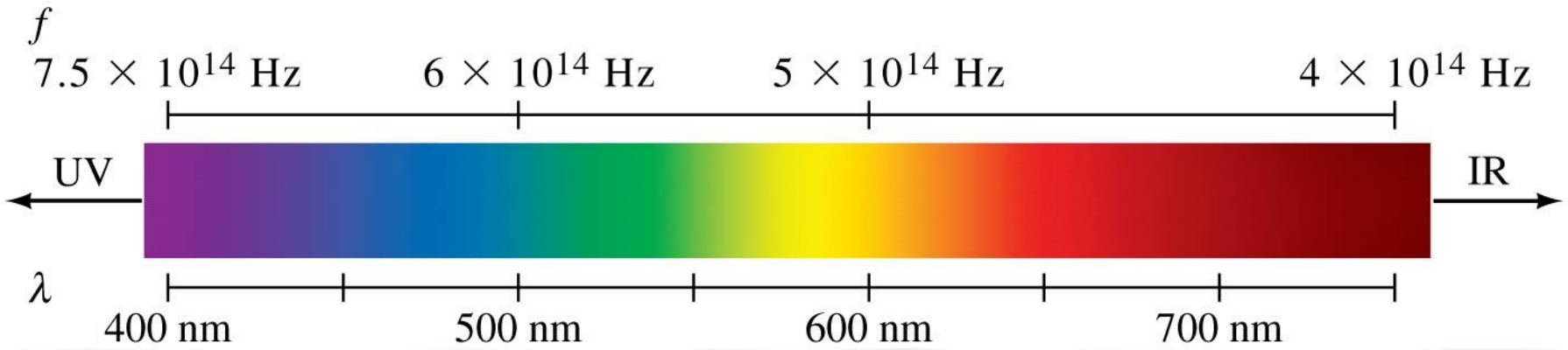


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The Visible Spectrum and Dispersion

Wavelengths of visible light: 400 nm to 750 nm

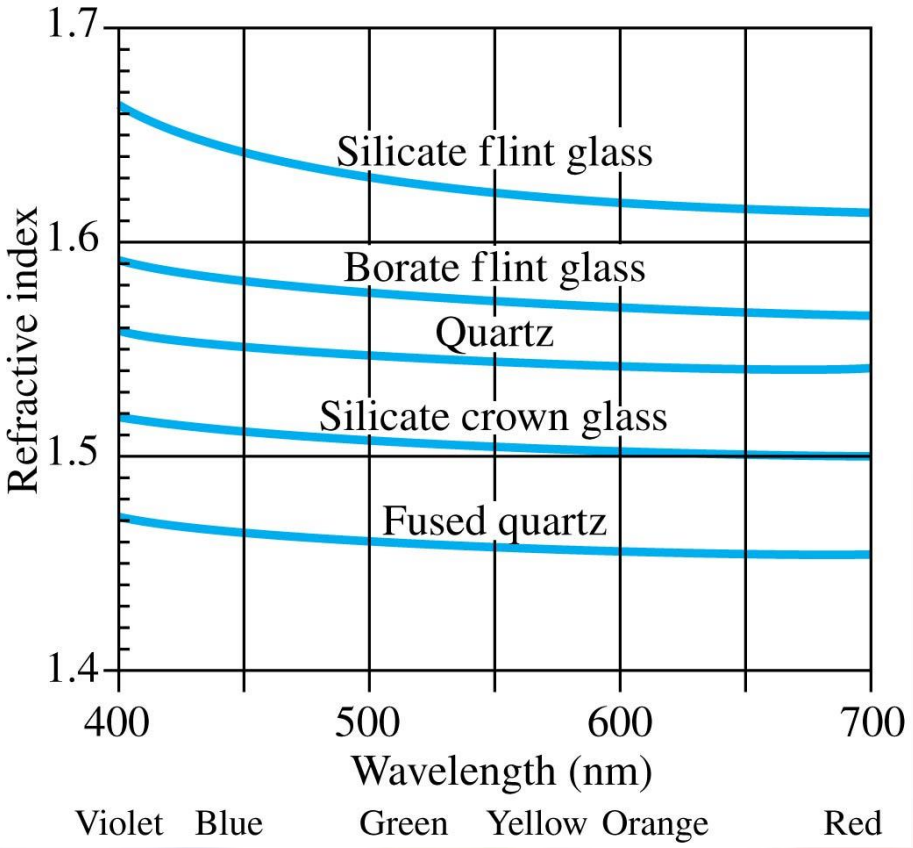
Shorter wavelengths are ultraviolet; longer are infrared



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The Visible Spectrum and Dispersion

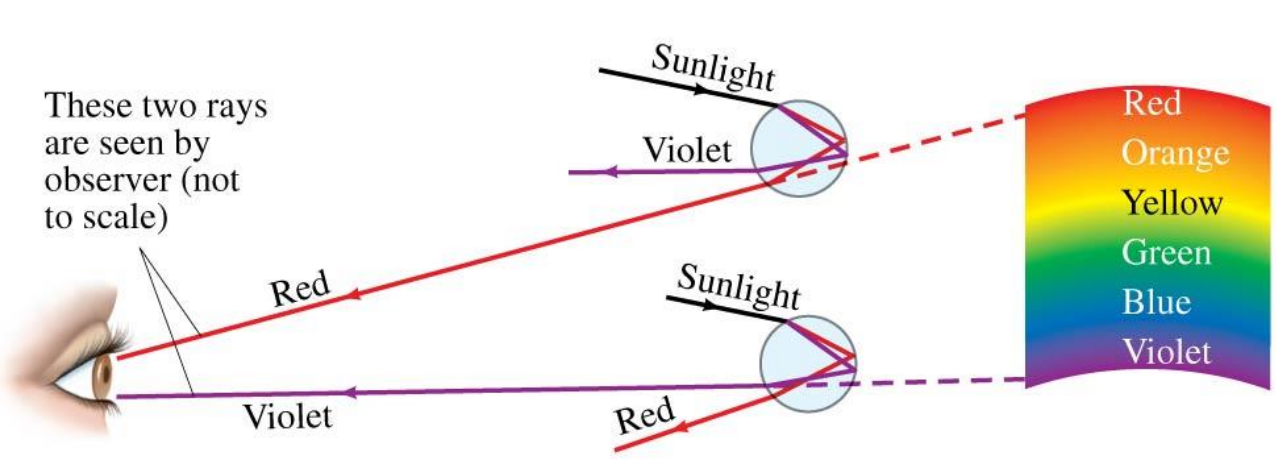
The index of refraction of a material varies somewhat with the wavelength of the light.



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The Visible Spectrum and Dispersion

Atmospheric rainbows are created by dispersion in tiny drops of water.



(a)

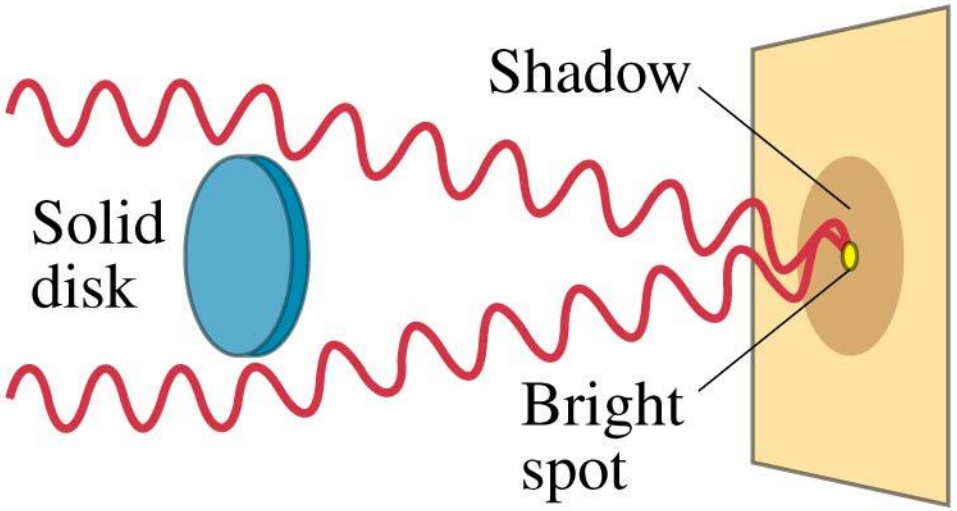


(b)

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24-5 Diffraction by a Single Slit or Disk

Light will al obstacle.

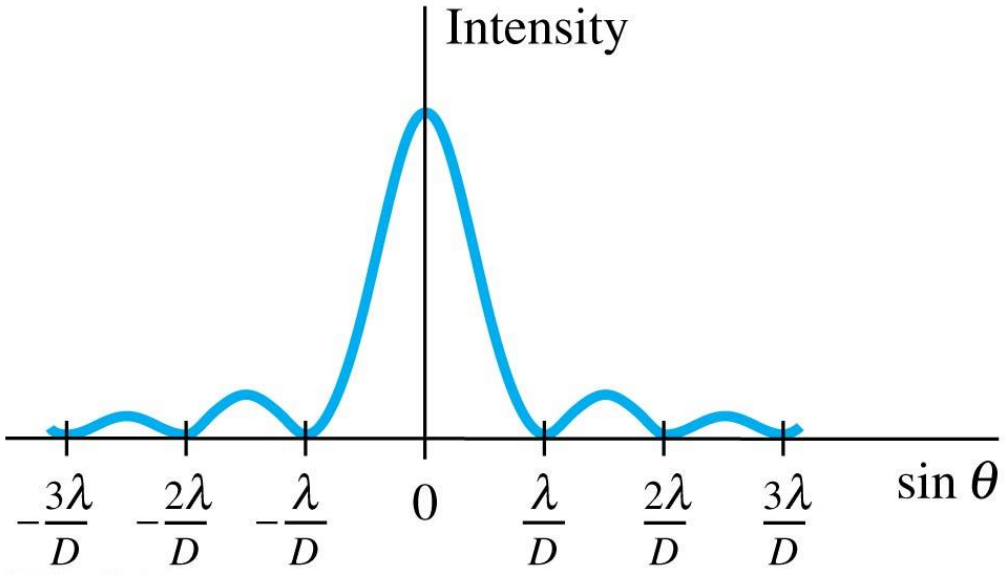


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Diffraction by a Single Slit or Disk

The resulting pattern of light and dark stripes is called a diffraction pattern.

This pattern arises because different points along a slit create wavelets that interfere with each other just as a double slit would.



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Diffraction by a Single Slit or Disk

The minima of the single-slit diffraction pattern occur when

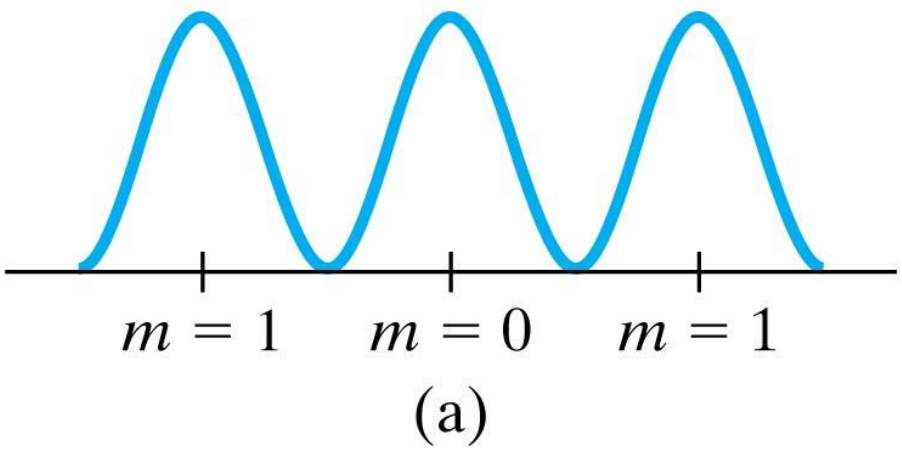
$$D \sin\theta = m\lambda, \qquad m = \pm 1, \pm 2, \pm 3, \cdots,$$

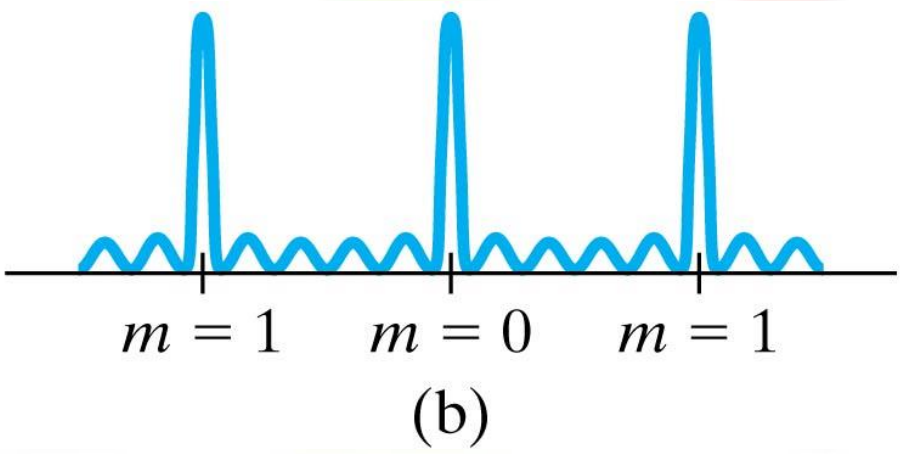
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Diffraction Grating

A diffraction grating consists of a large number of equally spaced narrow slits or lines. A **transmission grating** has slits, while a **reflection grating** has lines that reflect light.

The more lines or slits there are, the narrower the peaks.



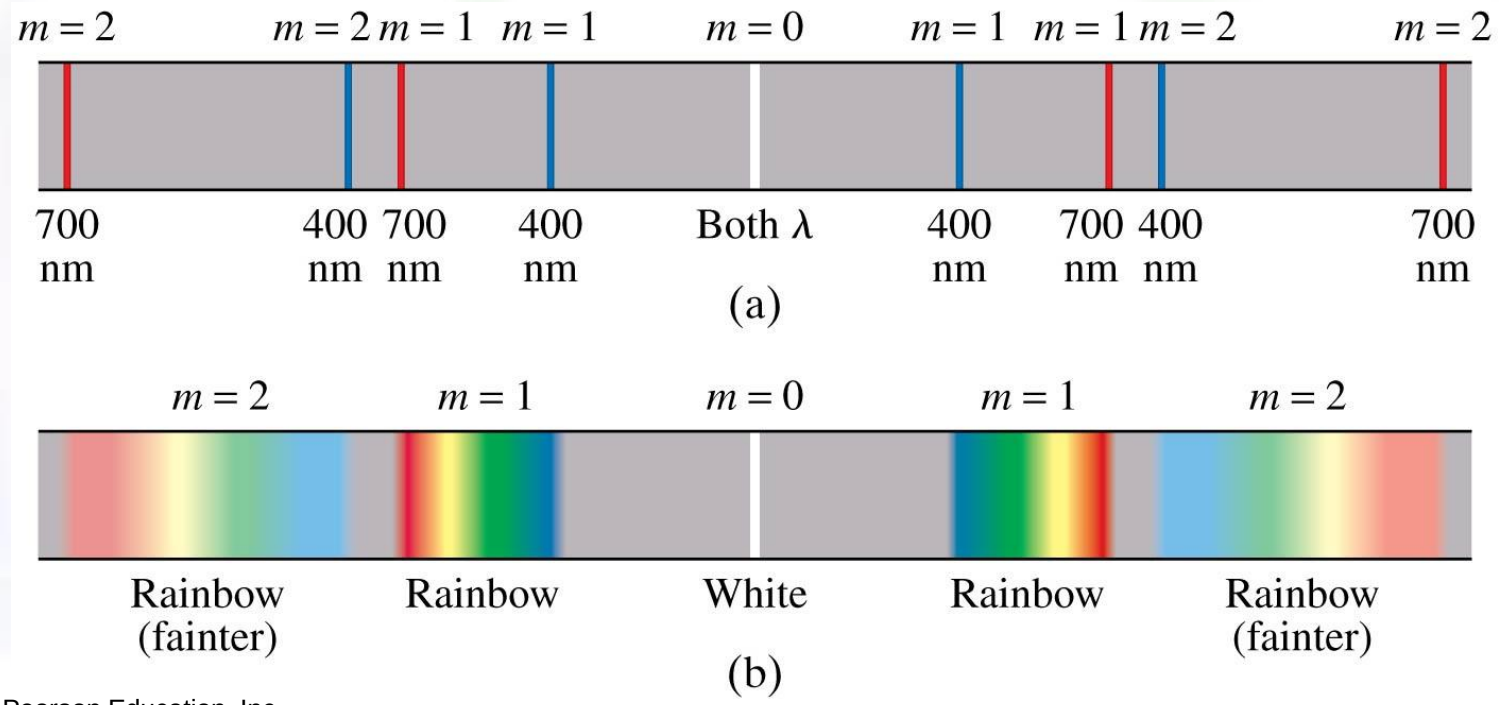


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Diffraction Grating

The maxima of the diffraction pattern are defined by

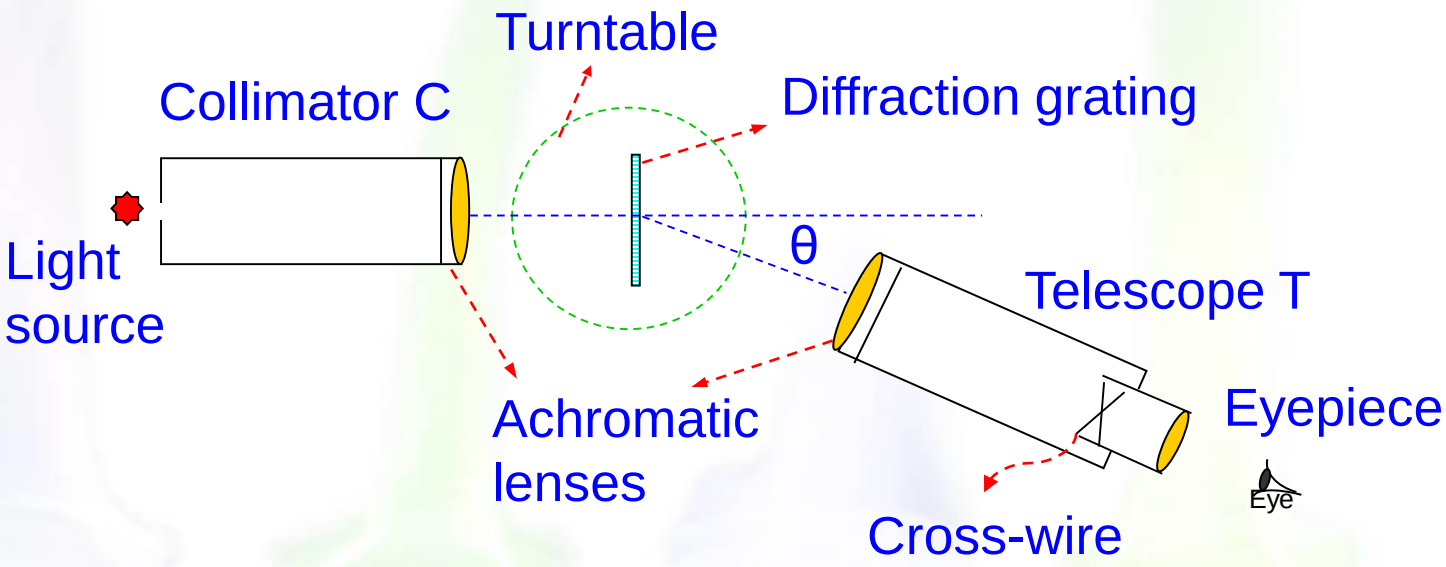
$$\sin\theta = \frac{m\lambda}{d}, \quad m = 0,\ 1,\ 2,\ \cdots$$



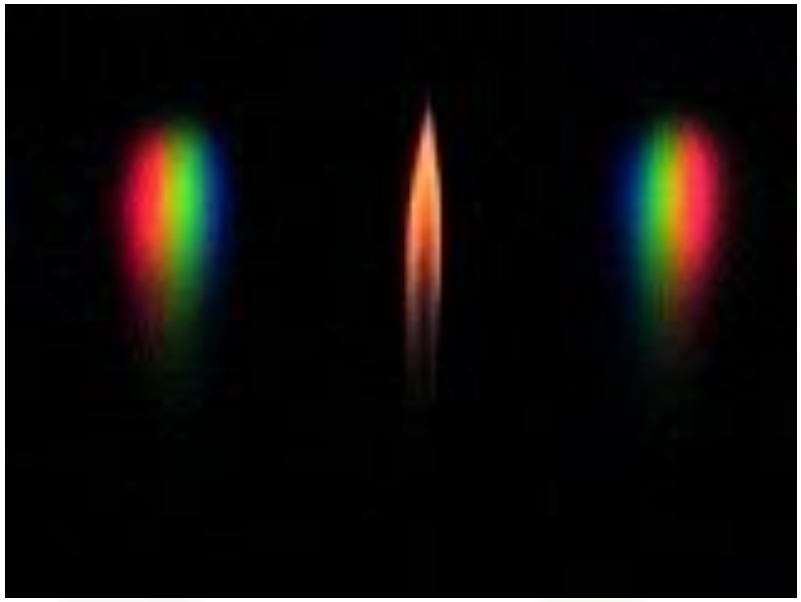
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Using a diffraction grating to measure the wavelength of light

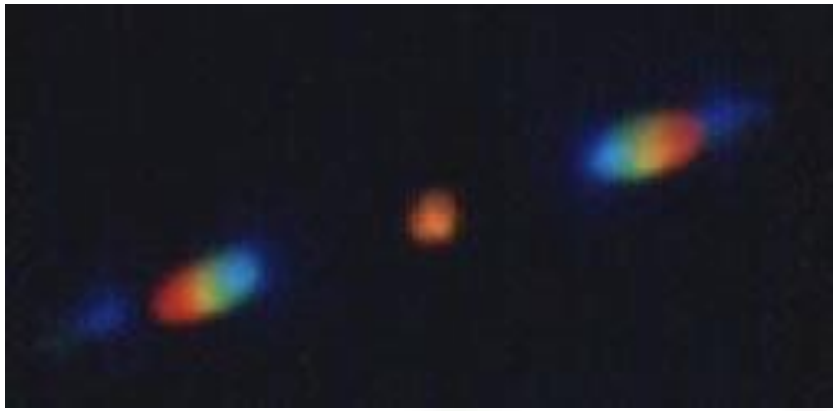
A spectrometer is a device to measure wavelengths of light accurately using diffraction grating to separate.



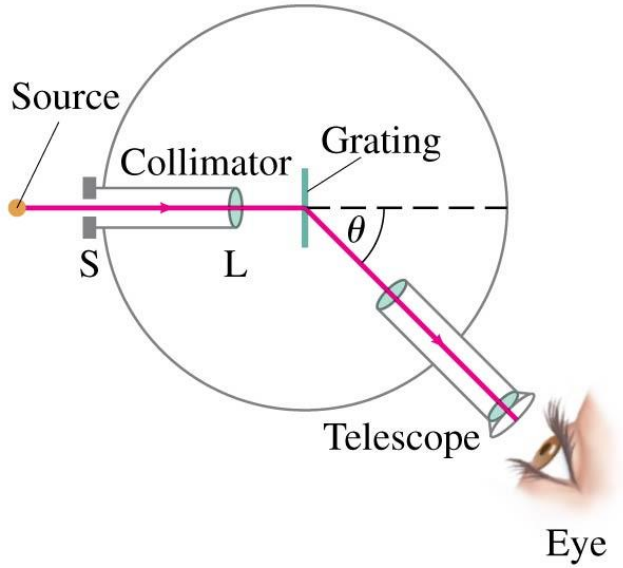
View through Diffraction Grating



Diffraction grating placed in front of a methane air flame

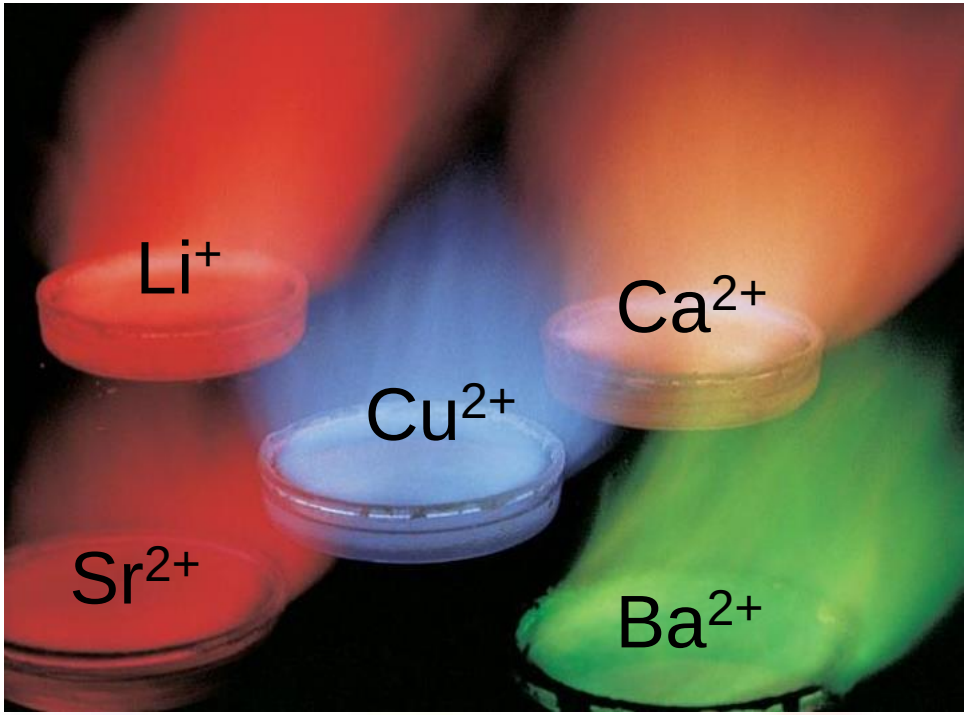


- Spectrum of a star - Procyon



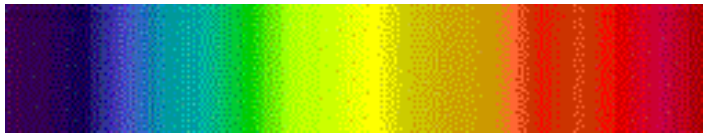
Failures of Classial Physics

- Line spectra of atoms
- Black body radiation
- Heat capacity of solids
- Photoelectric effect



Types of Spectra

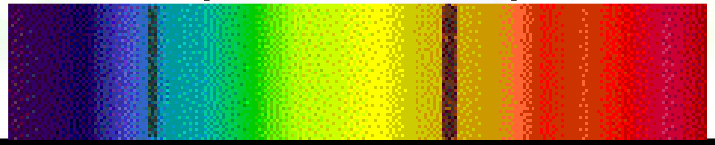
- **Continuous spectrum:** Produced by solids, liquids & dense gases produce - no “gaps” in wavelength of light produced:



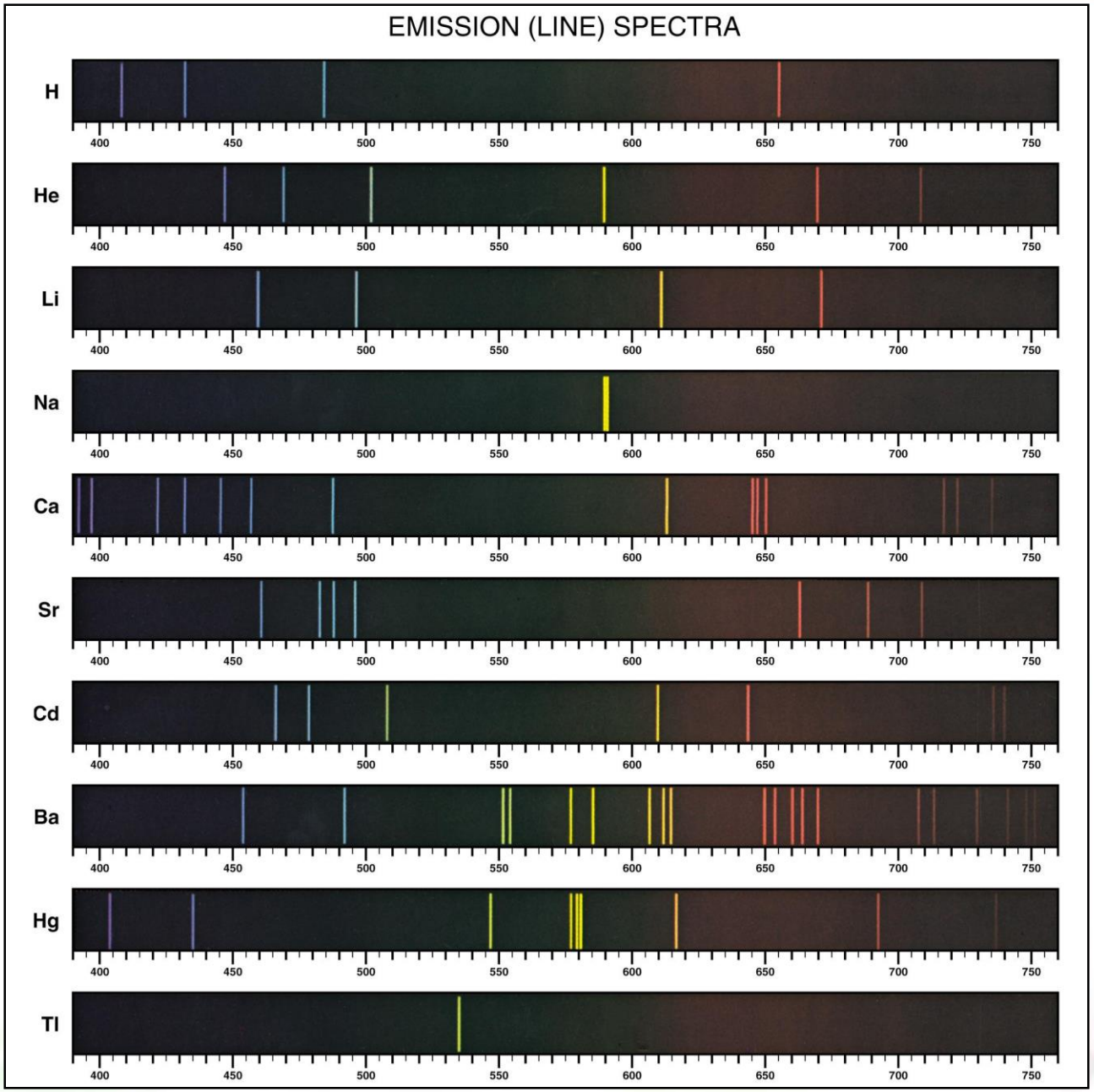
- **Emission spectrum:** Produced by rarefied gases – emission only in narrow wavelength regions:



- **Absorption spectrum:** Gas atoms absorb the same wavelengths as they usually emit and results in an *absorption line spectrum*:



Emission (line) spectra of some elements. Discontinuous spectra



The black body spectrum

Measure the radiated power of the emission from some hot object such as a hot filament at various temperatures and, as Joseph Stephan showed experimentally in 1879 and

Ludwig Boltzmann showed theoretically using thermodynamic arguments, you will find that it depends on the fourth power of the filament's temperature, e.g., $P(T) = \sigma T^4$.

- The Stephan-Boltzmann law: **radiated power is proportional to T^4.**

σ is Stephan Boltzmann constant **5.67×10^{-8} W/m^2 K^4**

In 1894 Wilhelm Wein determined that the wavelength of the maximum black body radiation times the temperature of the black body was a constant, e.g. **$\lambda T = 2898$ μm K**.

Unfortunately, at very long wavelengths (low temperatures) the experimental data disagreed with this result!!!

The Rayleigh-Jeans Law

Rayleigh in 1900 and with Jeans corrections in 1905 formulated the Rayleigh-Jeans Law in which **the energy density of black body radiation per unit wavelength interval is proportional to the temperature divided by the fourth power of the wavelength**.

This worked well in the infrared but when re-written in terms of frequency it suggests that the energy density increases without bound as the frequency increases.

For wavelength

$$B_\lambda(T) = \frac{2cK_BT}{\lambda^4}$$

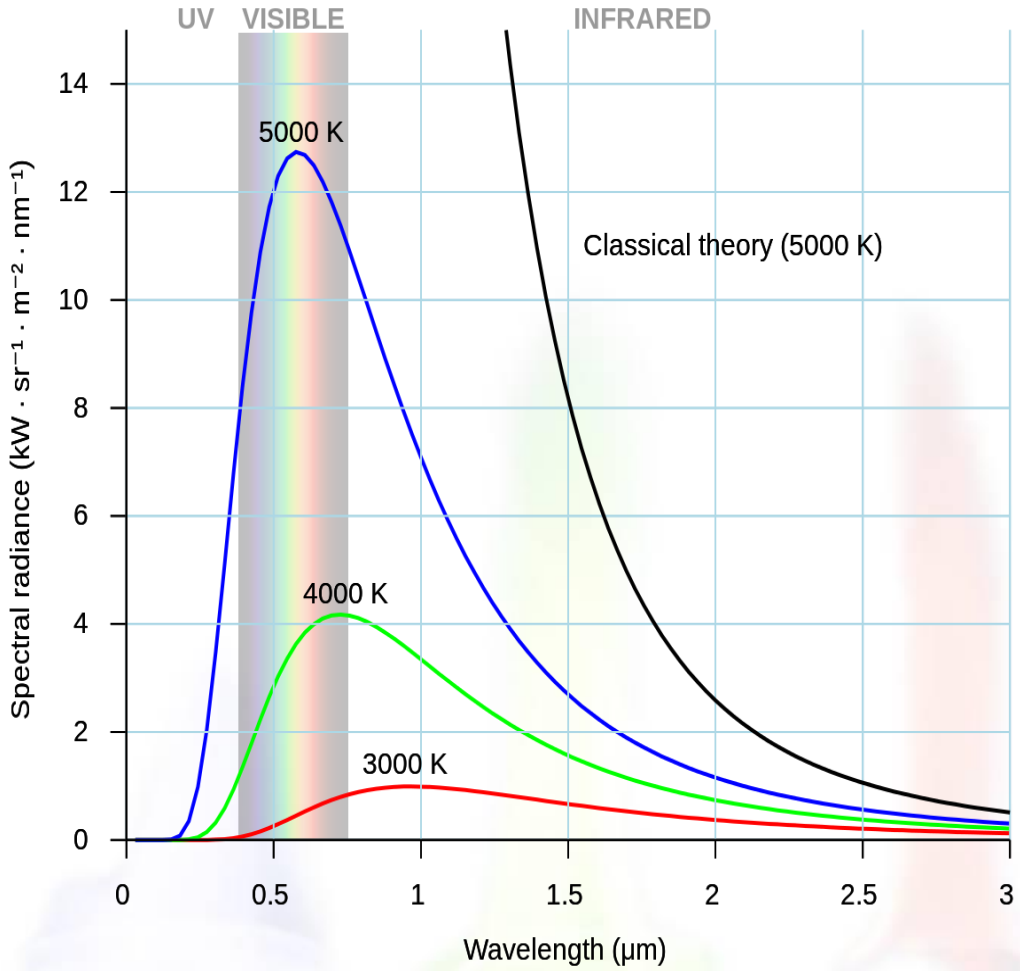
For frequency

$$B_\nu(T) = \frac{2\nu^2K_BT}{c^2}$$

Where: B is the spectral radiance

UV- Catastrophe

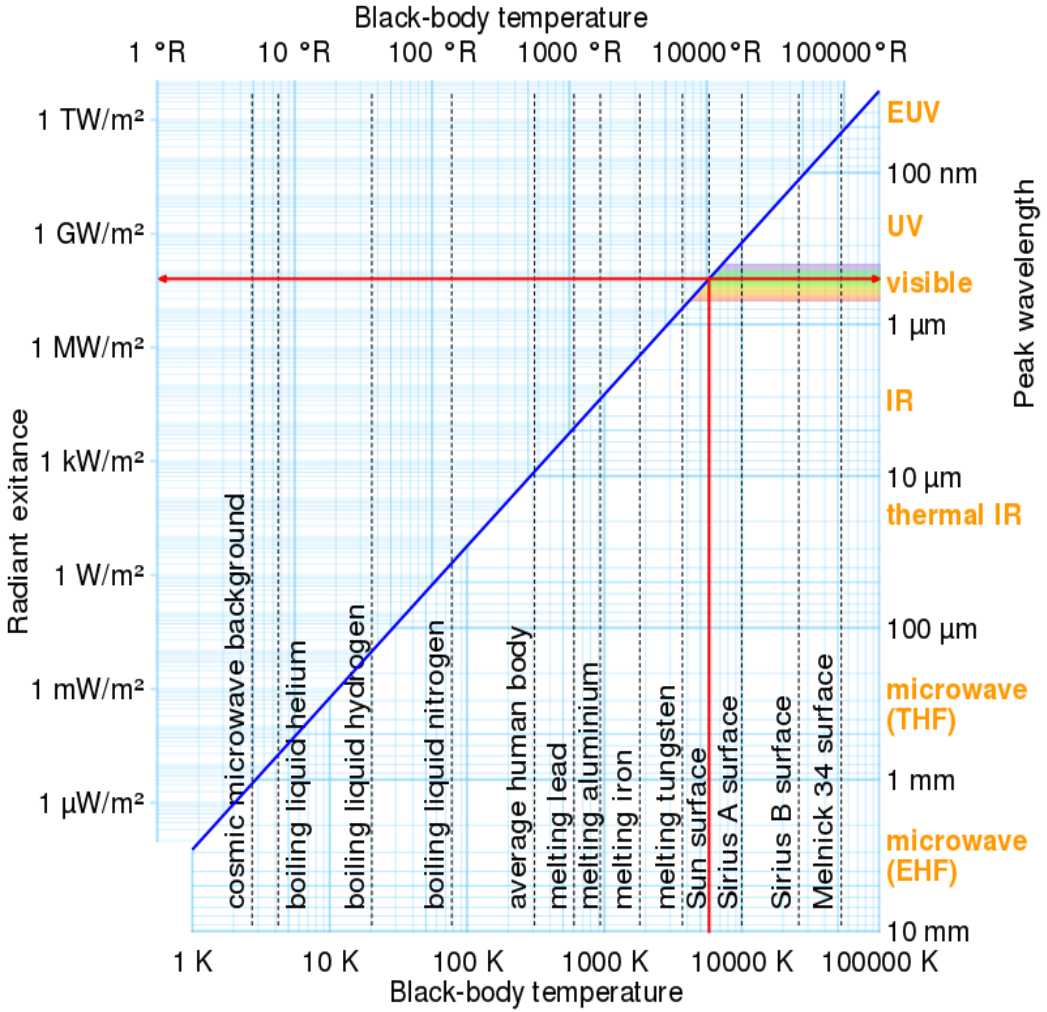
The black bodies do not radiate immense amounts of high frequency light and so faced the **ultraviolet catastrophe** – failure of the model.



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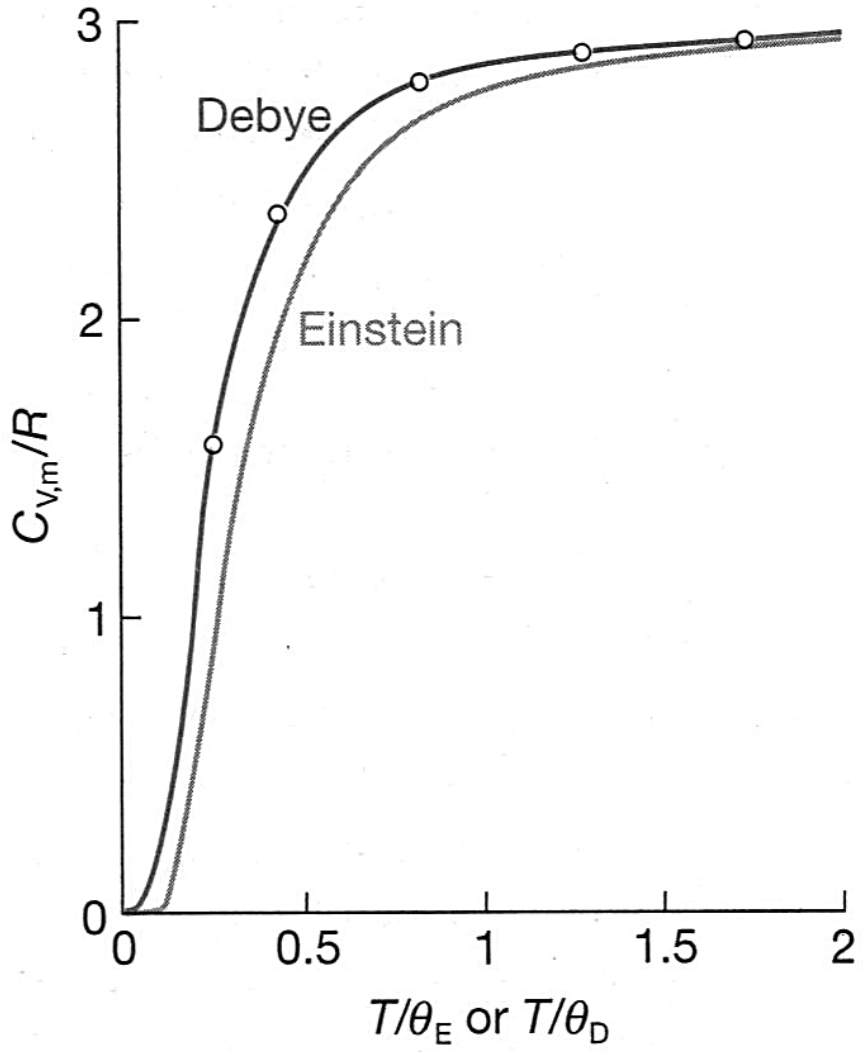
Wien's law, also called **Wien's displacement law**, relationship between the temperature of a blackbody and the wavelength at which it emits the most light.

Wien's law of the shift of the radiative power maximum to higher frequencies as the temperature is raised expresses in a quantitative form commonplace observations. Warm objects emit infrared radiation.



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Heat capacity of metals



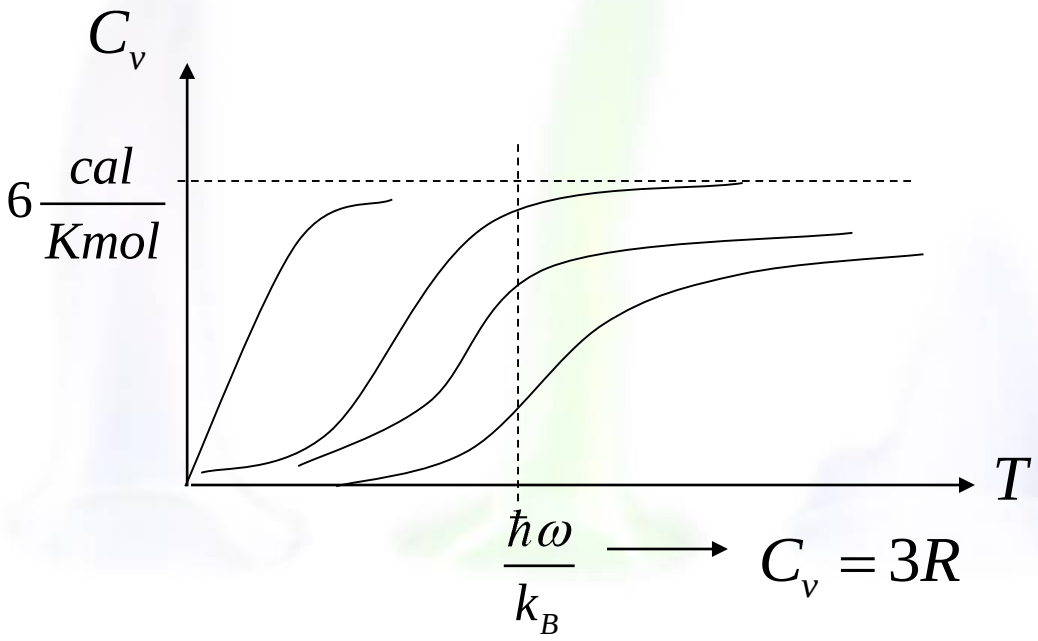
The atoms in a crystal vibrate about their equilibrium positions. This motion produces vibrational waves.

The amplitude of this vibrational motion increases as the temperature increases.

Einstein contribution

• *At high temperatures*, all crystalline solids have a specific heat of 6 cal/K per mole.

•Observations show that ***at room temperatures and below*** the specific heat of crystalline solids is not a universal constant.



In each of these materials (Pb,Al, Si,and Diamond) specific heat approaches constant value asymptotically at high T. But at low T's, the specific heat decreases towards zero which is in a complete contradiction with the above classical result.

Debye Model

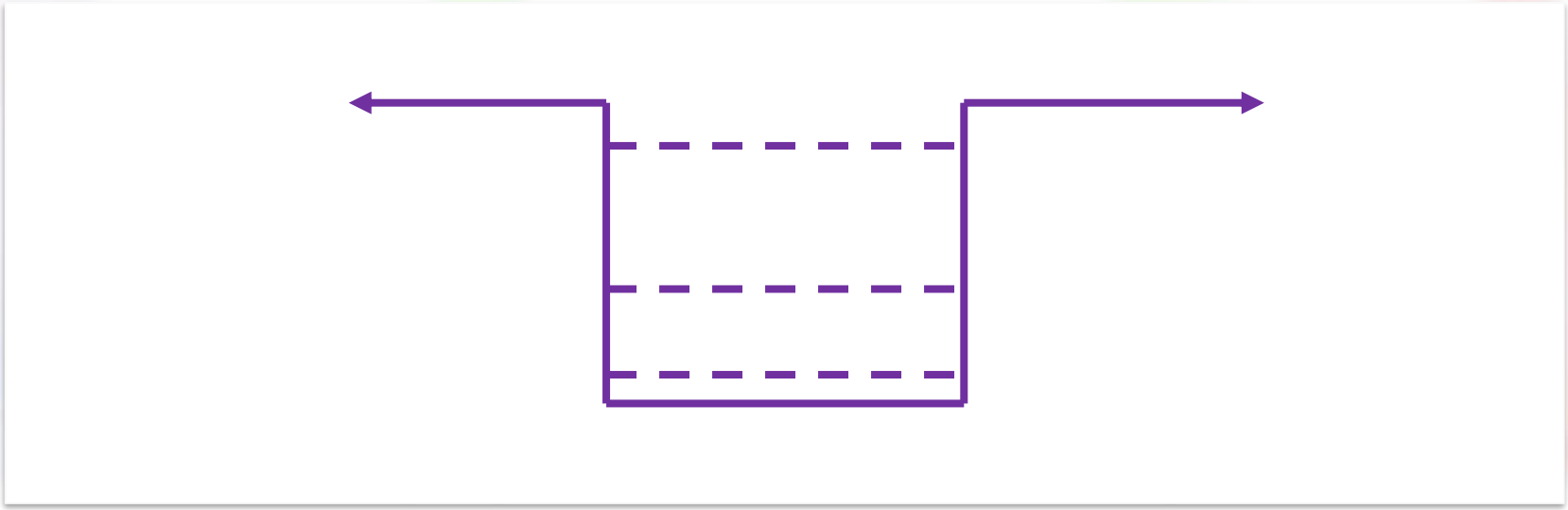
Density of States

According to Quantum Mechanics if a particle is constrained;

the energy of particle can only have special discrete energy values.

it cannot increase infinitely from one value to another.

it has to go up in steps.



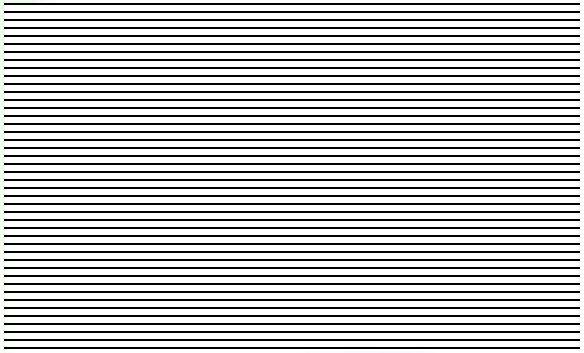
These “**steps**” can be so small depending on the system that the energy can be considered as **continuous**.

This is the case of classical mechanics.

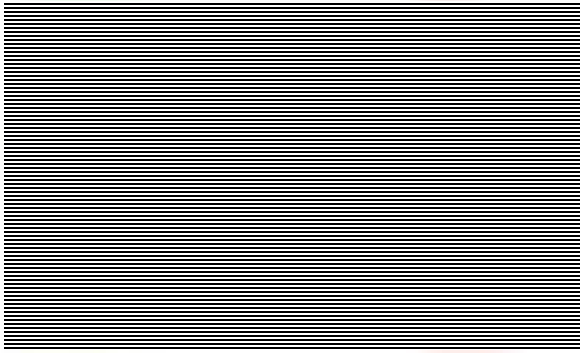
But on atomic scale the energy can only jump by a discrete amount from one value to another.



Definite energy levels



Steps get small



Energy is continuous

In some cases, each particular energy level can be associated with more than one different state (or wavefunction)

This energy level is said to be degenerate.



The density of states $\rho(\varepsilon)$ is the number of discrete states per unit energy interval, and so that the number of states between ε and $\varepsilon + d\varepsilon$ will be $\rho(\varepsilon)d\varepsilon$.

Quantum Effects and Photons

Planck's Quantization of Energy (1900)

- According to Max Planck, the atoms of a solid oscillate with a definite frequency, ν.
- He proposed that an atom could have only certain energies of vibration, E, those allowed by the formula

$$E = h\nu$$

where h (Planck's constant) is assigned a value of 6.63×10^{-34} J· s and n must be an integer.

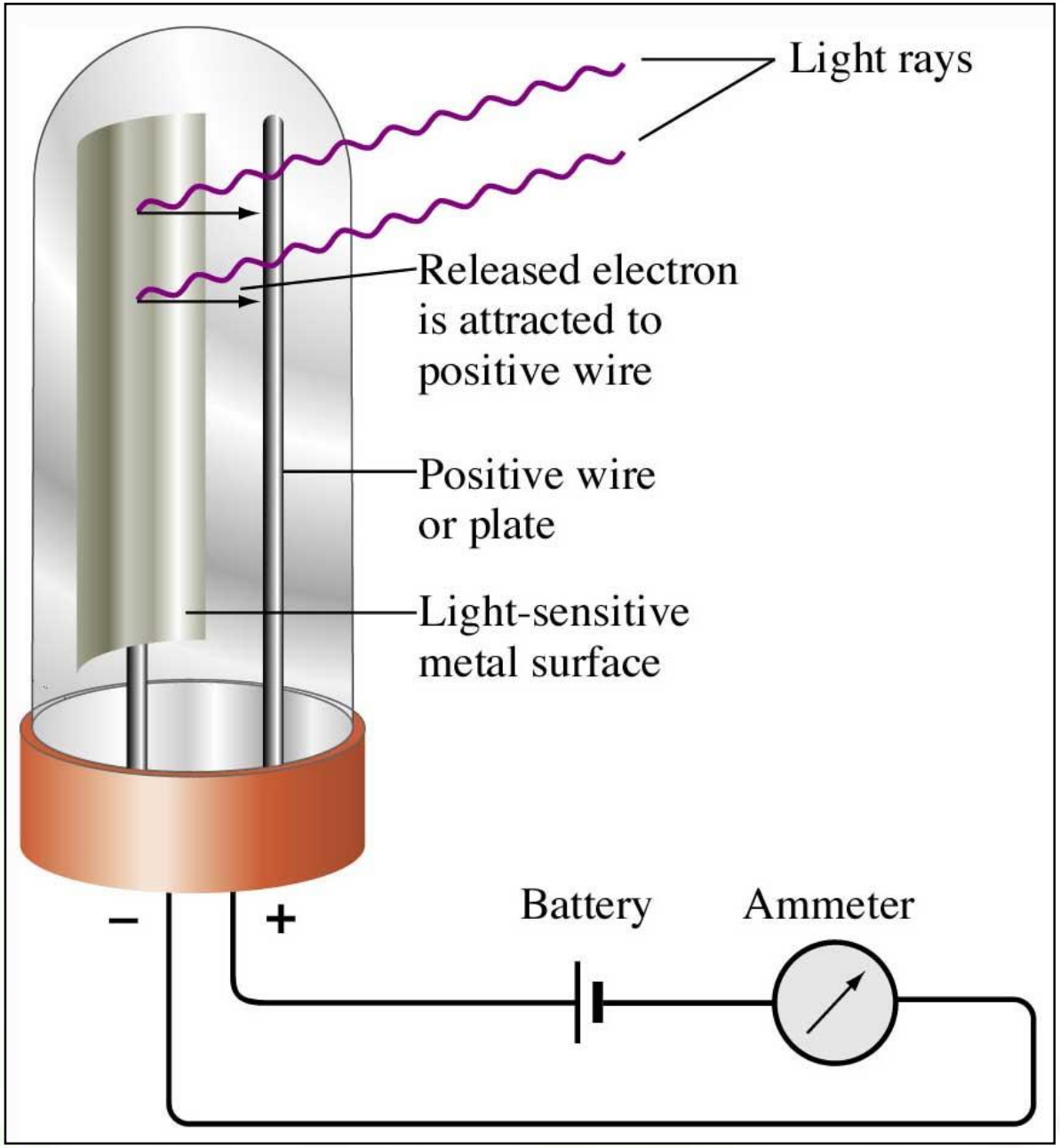
Quantum Effects and Photons

Planck's Quantization of Energy.

- The only energies a vibrating atom can have are $h\nu$, $2h\nu$, $3h\nu$, and so forth.

- The numbers symbolized by n are quantum numbers.
- The vibrational energies of the atoms are said to be quantized.
- Solved the ultraviolet catastrophe in blackbody radiation

The photoelectric effect.



Quantum Effects and Photons

Photoelectric Effect

- The photoelectric effect is the ejection of electrons from the surface of a metal when light shines on it.
- Electrons are ejected only if the light exceeds a certain “threshold” frequency μ_0.
- Violet light, for example, will cause potassium to eject electrons, but no amount of red light (which has a lower frequency) has any effect.

Quantum Effects and Photons

By the early part of twentieth century, the wave theory of light seemed to be well entrenched.

- In 1905, Albert Einstein proposed that light had both wave and particle properties to explain the observations in the photoelectric effect.
- Einstein based this idea on the work of a German physicist, Max Planck.

Quantum Effects and Photons

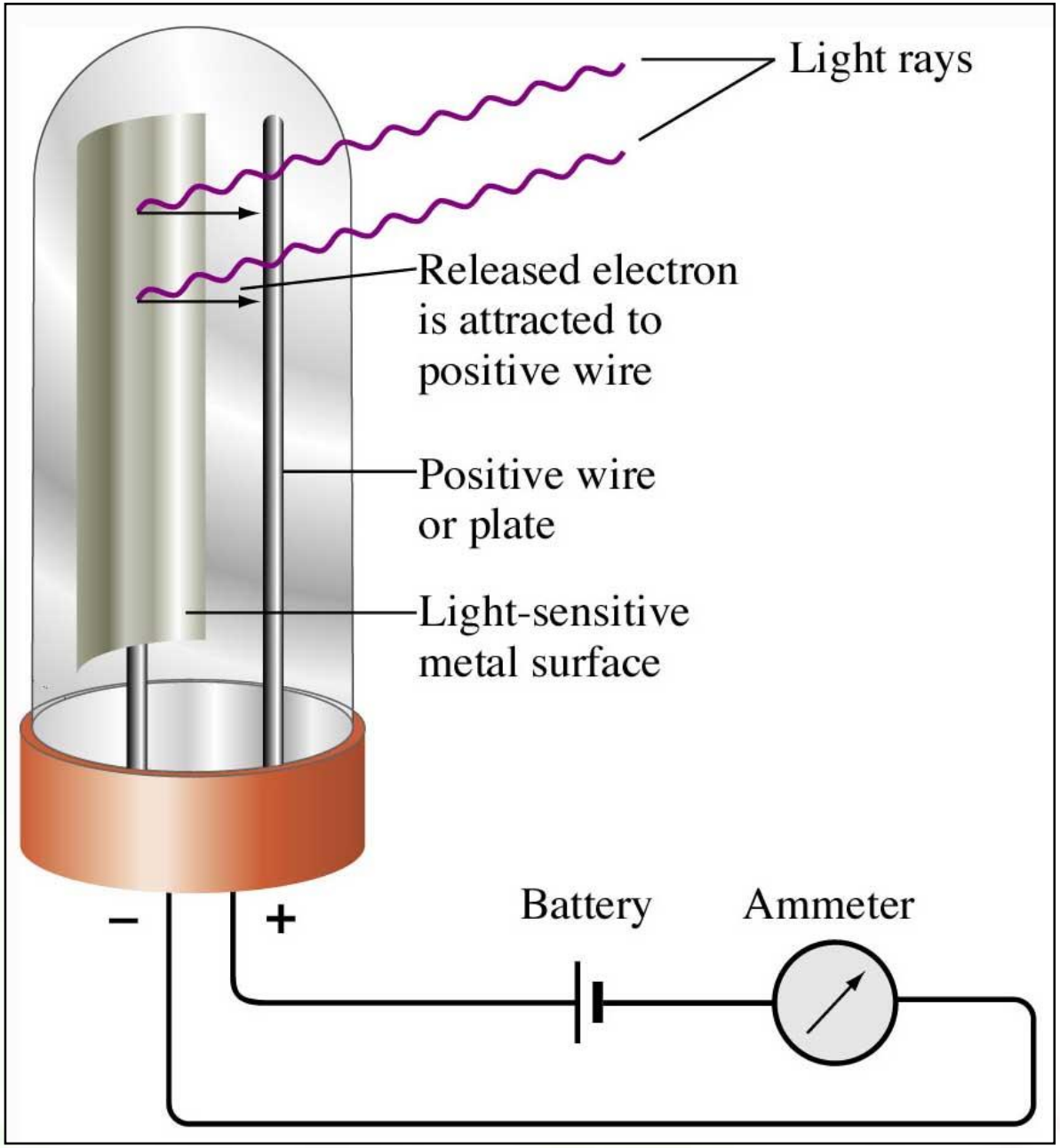
Photoelectric Effect

- The energy of the photons proposed by Einstein would be proportional to the observed frequency, and the proportionality constant would be Planck's constant.

$$E = h\nu$$

- In 1905, Einstein used this concept to explain the "photoelectric effect."

The photoelectric effect.



Quantum Effects and Photons

Photoelectric Effect

- Einstein's assumption that an electron is ejected when struck by a single photon implies that it behaves like a particle.
- When the photon hits the metal, its energy, $h\nu$ is taken up by the electron.
- The photon ceases to exist as a particle; it is said to be "absorbed."

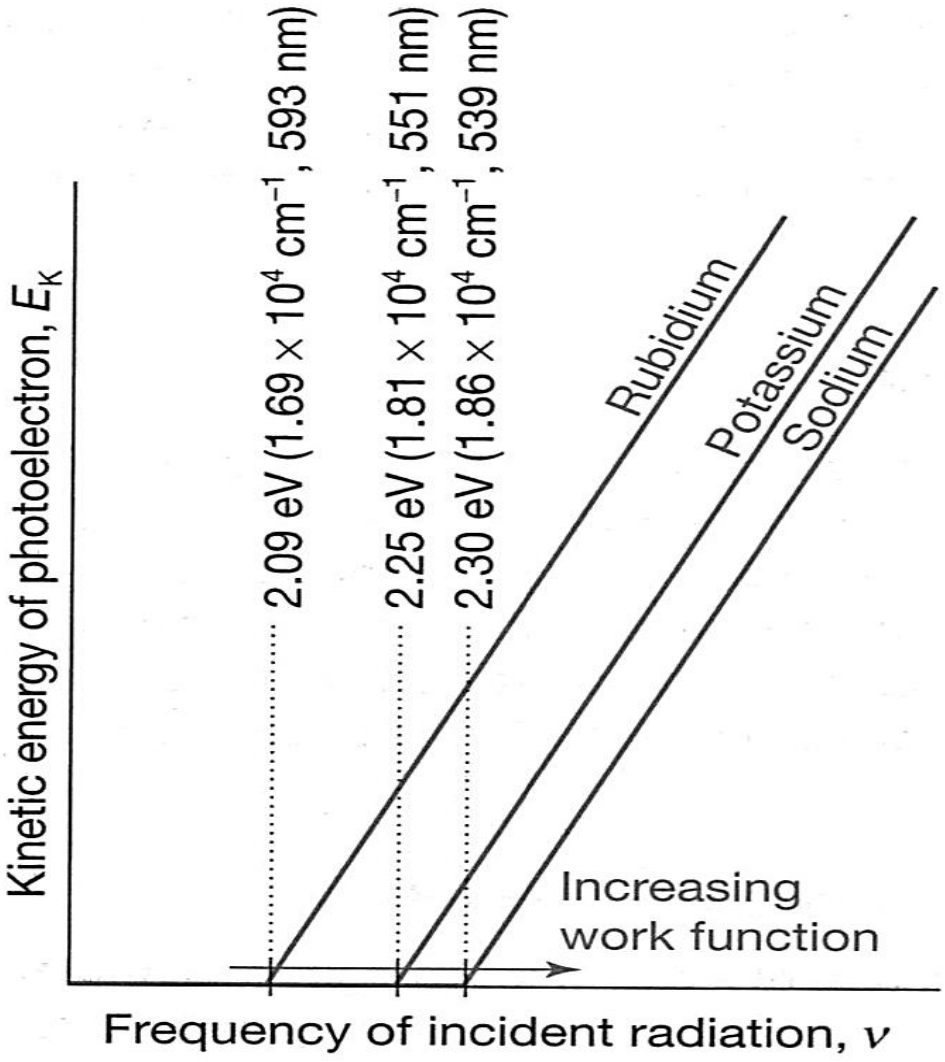
Quantum Effects and Photons

Photoelectric Effect

- The “wave” and “particle” pictures of light should be regarded as complementary views of the same physical entity.
- This is called the wave-particle duality of light.
- The equation $E = h\nu$ displays this duality; E is the energy of the “particle” photon, and ν is the frequency of the associated “wave.”

Photoelectric effect

- For a given metal, a certain amount of energy is needed to eject the electron
- This is called the work function
- Since E=hν, the photons must have a frequency higher than the work function in order to eject electrons



The saturation current is proportional to the beam intensity of light that falls on the cathode.

If V becomes negative, the current does not immediately fall to zero, which suggests that electrons are emitted with some kinetic energy, of so that some reach the other electrode despite the electric field he opposes his movement.

However, for a certain negative value V_0, called braking potential or cut, the photoelectric current is canceled.

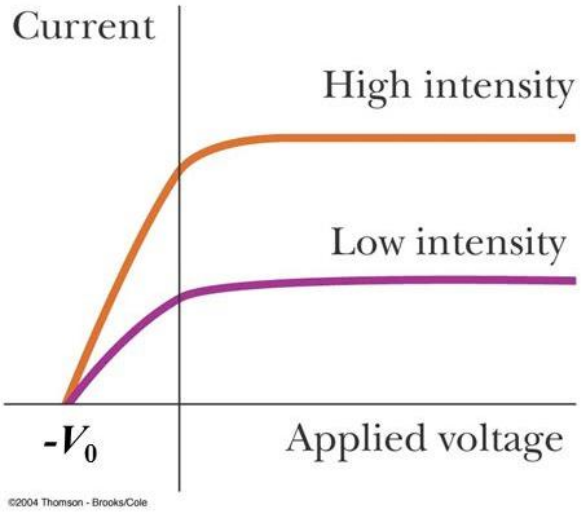
The maximum kinetic energy of the photoelectrons is then:

$$EK_{max} = eV_0$$

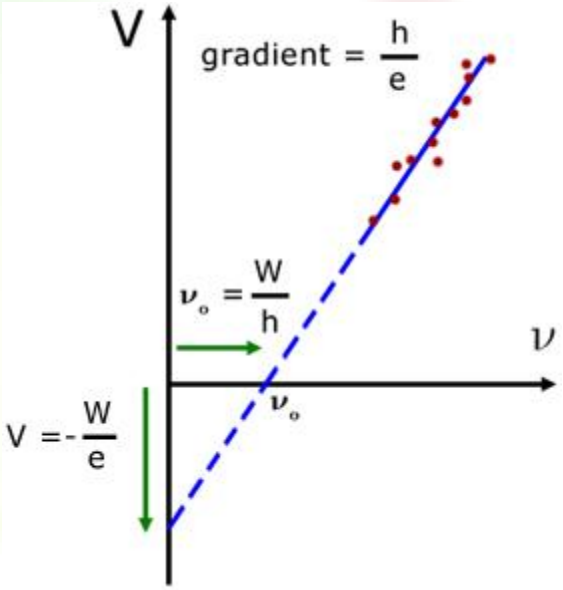
It is independent of the intensity of the light.

Behavior of the braking potential V_0 as function of the frequency μ of the light was studied by Millikan in 1914 and it got a linear graph

- **At large values of *V*, the current reaches a maximum value**
  - **All the electrons emitted at *E* are collected at *C***
- **The maximum current increases as the intensity of the incident light increases**
- **When *V* is negative, the current drops**
- **When *V* is equal to or more negative than V_0, the current is zero**



$K_{max} = eV_0$



METAL	WORKFUNCTION (eV)	METAL	WORKFUNCTION (eV)
Al	4.3	Ru	4.7
Ti	4.33	Rh	4.98
V	4.3	Hf	3.9
Cr	4.5	Ta	4.25
Mn	4.1	W	4.55
Fe	4.7	Re	4.96
Co	5	Os	4.83
Ni	5.15	Ir	5.27
Nb	4.3	Au	5.1
Mo	4.6	TaN/TaSiN	3.9-4.3

$$h\nu = \phi_o + \frac{1}{2} m v^2_{max}$$

$$h\nu = h\nu_o + \frac{1}{2} m v^2_{max}$$

e ν_o = Threshold frequency.

ν = Frequency of radiation

h = Planck's constant.

Bohr's model

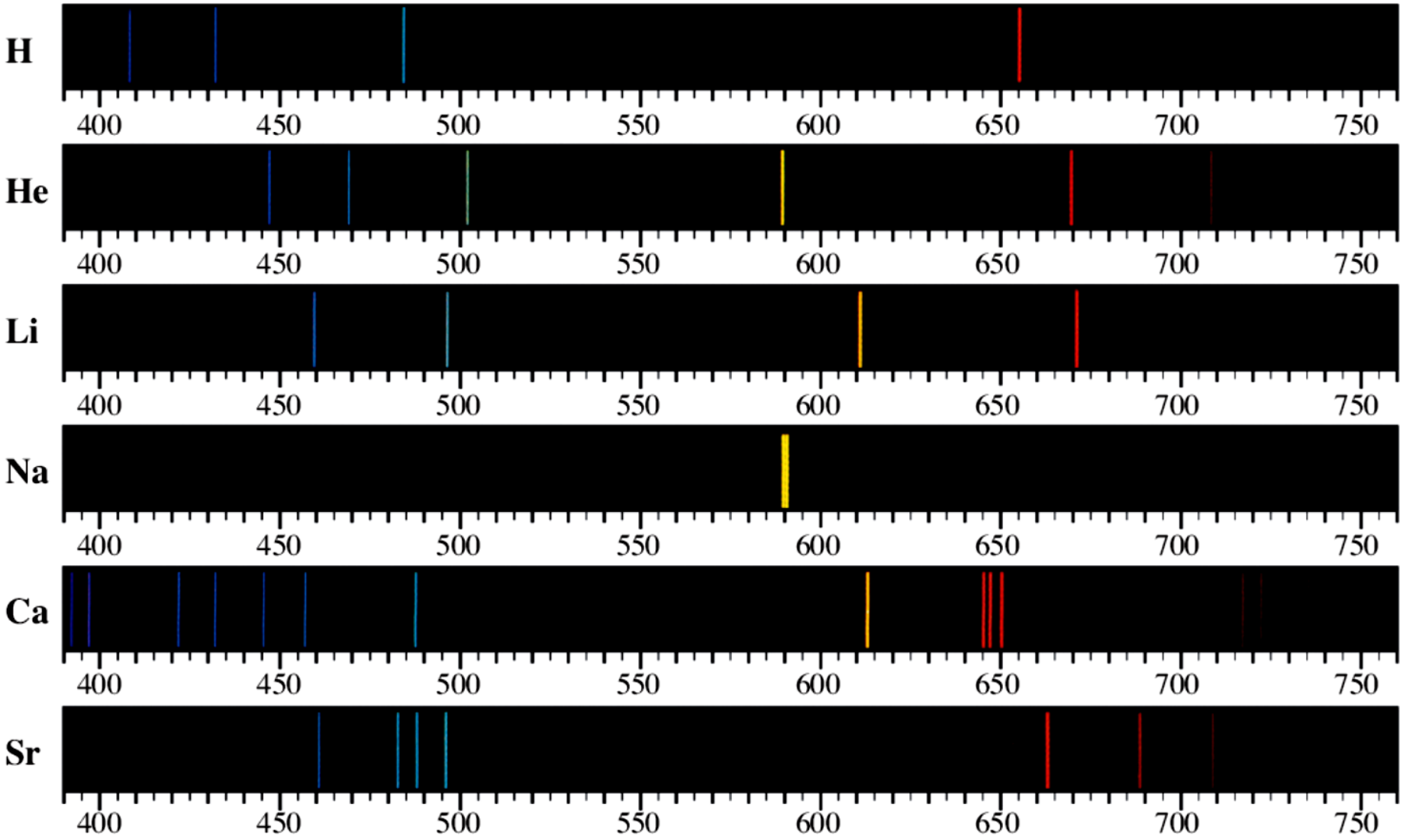
In the early 1900s, the atom was understood to consist of a positive nucleus around which electrons move (Rutherford's model).

This explanation left a theoretical dilemma: According to the physics of the time, an electrically charged particle circling a center would continually lose energy as electromagnetic radiation. But this is not the case—atoms are stable.

In addition, this understanding could not explain the observation of line spectra of atoms.

A **continuous spectrum** contains all wavelengths of light.

A **line spectrum** shows only certain colors or specific wavelengths of light. When atoms are heated, they emit light. This process produces a line spectrum that is specific to that atom. The emission spectra of six elements are shown on the next slide.


H
He
Li
Na
Ca
Sr
400
450
500
550
600
650
700
750

In 1913, Neils Bohr, a Danish scientist, set down postulates to account for

1. The stability of the hydrogen atom
2. The line spectrum of the atom

Bohr postulates

a) An atom is constituted by an electrical charge (nucleus) around which they turn to compensate for that, describing circumferences.

b) Each electron can not move over any orbit, but only in that in sufficient numbers (p) in which its rotational impulse is an integer multiple of $h / 2\pi$.

Bohr postulates

c) When the electron moves on one of its orbits, it does not radiate energy.

d) An electron can spontaneously jump from one orbit to another closer to the nucleus. In doing so its energy decreases in ΔW, and that loss is emitted in the form of light whose frequent the electrons is:

$$\nu = \frac{\Delta W}{h}$$

Energy-Level Postulate

An electron can have only certain energy values, called energy levels. Energy levels are quantized.

For an electron in a hydrogen atom, the energy is given by the following equation:

$$E = -\frac{R_H}{n^2}$$

$R_H = 2.179 \times 10^{-18}$ J

n = principal quantum number

Transitions Between Energy Levels

An electron can change energy levels by absorbing energy to move to a higher energy level or by emitting energy to move to a lower energy level.

For a hydrogen electron the energy change is given by

$$\Delta E = E_f - E_i$$

$$\Delta E = -R_H\left(\frac{1}{n_f^{\,2}} - \frac{1}{n_i^{\,2}}\right)$$

$R_H = 2.179 \times 10^{-18}$ J, Rydberg constant

The energy of the emitted or absorbed photon is related to ΔE:

$$E_{\text{photon}} = \left|\Delta E_{\text{electron}}\right| = h\nu$$

$$h = \text{Planck's constant}$$

We can now combine these two equations:

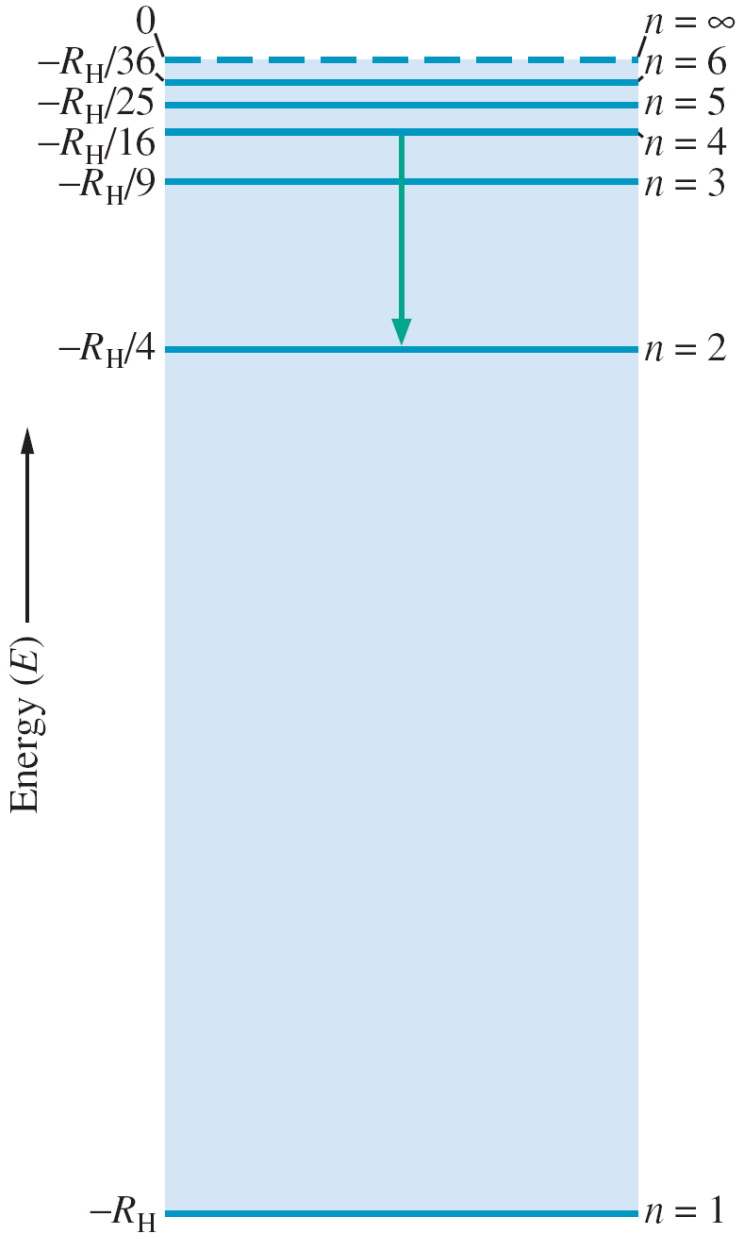
$$h\nu = \left| -R_{\text{H}}\left(\frac{1}{n_{\text{f}}^{\,2}} - \frac{1}{n_{\text{i}}^{\,2}}\right)\right|$$

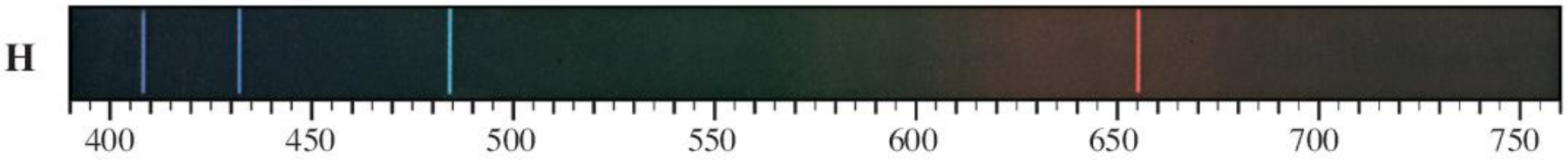
Light is **absorbed** by an atom when the electron transition is from lower *n* to higher *n* ($n_f > n_i$). In this case, ΔE will be positive.

Light is **emitted** from an atom when the electron transition is from higher *n* to lower *n* ($n_f < n_i$). In this case, ΔE will be negative.

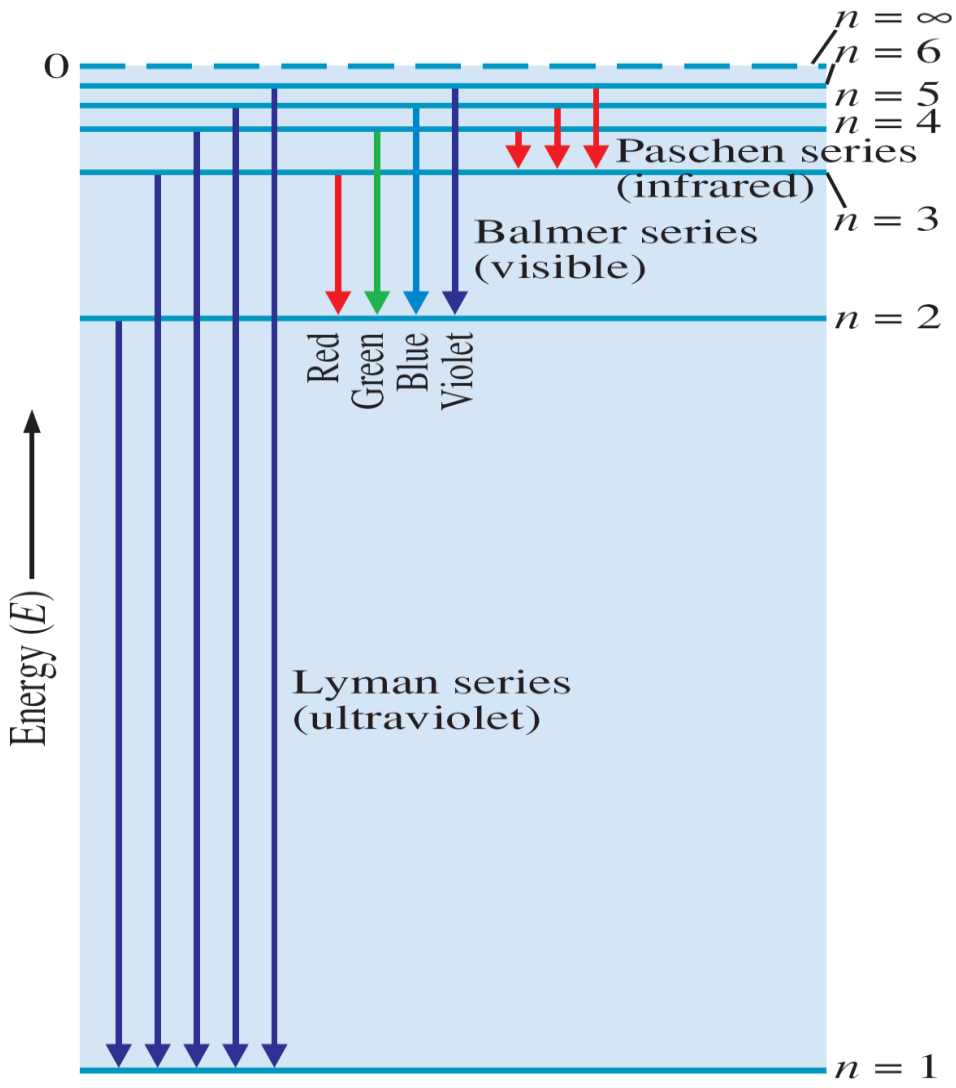
An electron is **ejected** when $n_f = \infty$.

Energy-level diagram for the hydrogen atom.





Electron transitions for an electron in the hydrogen atom.





What is the wavelength of the light emitted when the electron in a hydrogen atom undergoes a transition from $n = 6$ to $n = 3$?

$n_i = 6$

$n_f = 3$

$R_H = 2.179 \times 10^{-18}\ \text{J}$

$$\Delta E = -R_H\left(\frac{1}{n_f^{\,2}} - \frac{1}{n_i^{\,2}}\right)$$

$$|\Delta E| = \frac{hc}{\lambda} \quad \text{so} \quad \lambda = \frac{hc}{|\Delta E|}$$

$$\Delta E = \left(-2.179 \times 10^{-18}\ \text{J}\right)\left(\frac{1}{3^2} - \frac{1}{6^2}\right) = -1.816 \times 10^{-19}\ \text{J}$$

$$\lambda = \frac{\left(6.626 \times 10^{-34}\ \text{J}\bullet\text{s}\right)\left(2.998 \times 10^{8}\ \frac{\text{m}}{\text{s}}\right)}{\left|\left(-1.816 \times 10^{-19}\ \text{J}\right)\right|} = 1.094 \times 10^{-6}\ \text{m}$$

Planck

Vibrating atoms have only certain energies:

$$E = h\nu \text{ or } 2h\nu \text{ or } 3h\nu$$

Einstein

Energy is quantized in particles called photons:

$$E = h\nu$$

Bohr

Electrons in atoms can have only certain values of energy. For hydrogen:

$$E = -\frac{R_H}{n^2}$$

$R_H = 2.179 \times 10^{-18}$ J, n = principal quantum number

Quantum Mechanics

Bohr's theory established the concept of atomic energy levels but did not thoroughly explain the "wave-like" behavior of the electron.

Current ideas about atomic structure depend on the principles of quantum mechanics, a theory that applies to subatomic particles such as electrons.

Quantum Mechanics

The first clue in the development of quantum theory came with the discovery of the **de Broglie relation.**

- In 1923, Louis de Broglie reasoned that if light exhibits particle aspects, perhaps particles of matter show characteristics of waves.
- He postulated that a particle with mass m and a velocity v has an associated wavelength.

$$\lambda = \frac{h}{mv}$$ **de Broglie equation**

de Broglie Relation

For a photon that has both wave and particle characteristics:

$E = h\nu = hc/\lambda$ (recall $c = \nu\lambda$)

$E = mc^2$

$mc^2 = hc/\lambda$ or $\lambda = h/mc$

Since mc is the **momentum of a photon**, can we replace this with the momentum of a particle?

$\lambda = h/mv$

This suggests that **particles have wave-like characteristics!**

Quantum Mechanics

If matter has wave properties, why are they not commonly observed?

- The de Broglie relation shows that a baseball (0.145 kg) moving at about 60 mph (27 m/s) has a wavelength of about 1.7 x 10^{-34} m.

$$\lambda = \frac{6.63 \times 10^{-34} \ \frac{\text{kg}\cdot\text{m}^2}{s}}{(0.145\ kg)(27\ m/s)} = 1.7 \times 10^{-34}\, m$$

- This value is so incredibly small that such waves cannot be detected.

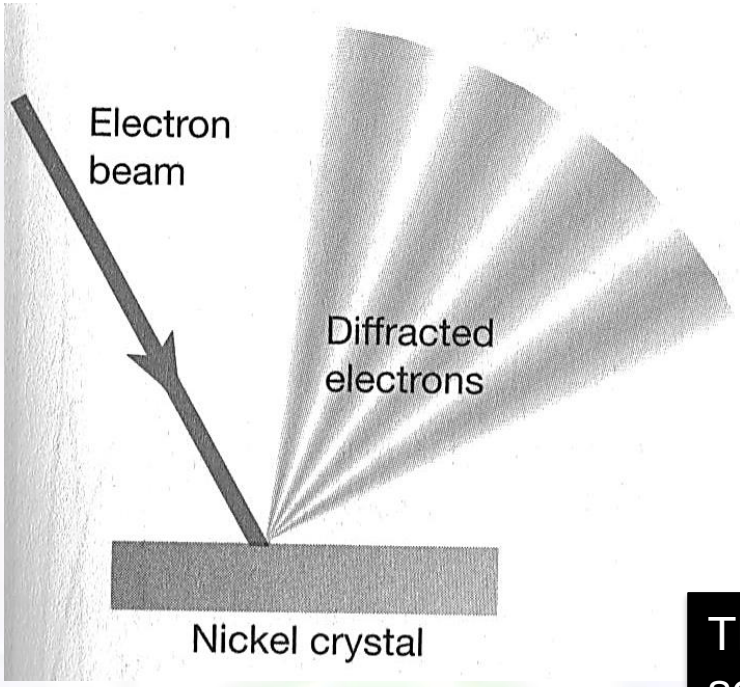
Quantum Mechanics

If matter has wave properties, why are they not commonly observed?

- Electrons have wavelengths on the order of a few picometers (1 pm = 10^{-12} m).
- Under the proper circumstances, the wave character of electrons should be observable.
- Molecules are of the dimension of a few pm, so the wave character of electrons is very important in molecules

Quantum Mechanics

If matter has wave properties, why are they not commonly observed?

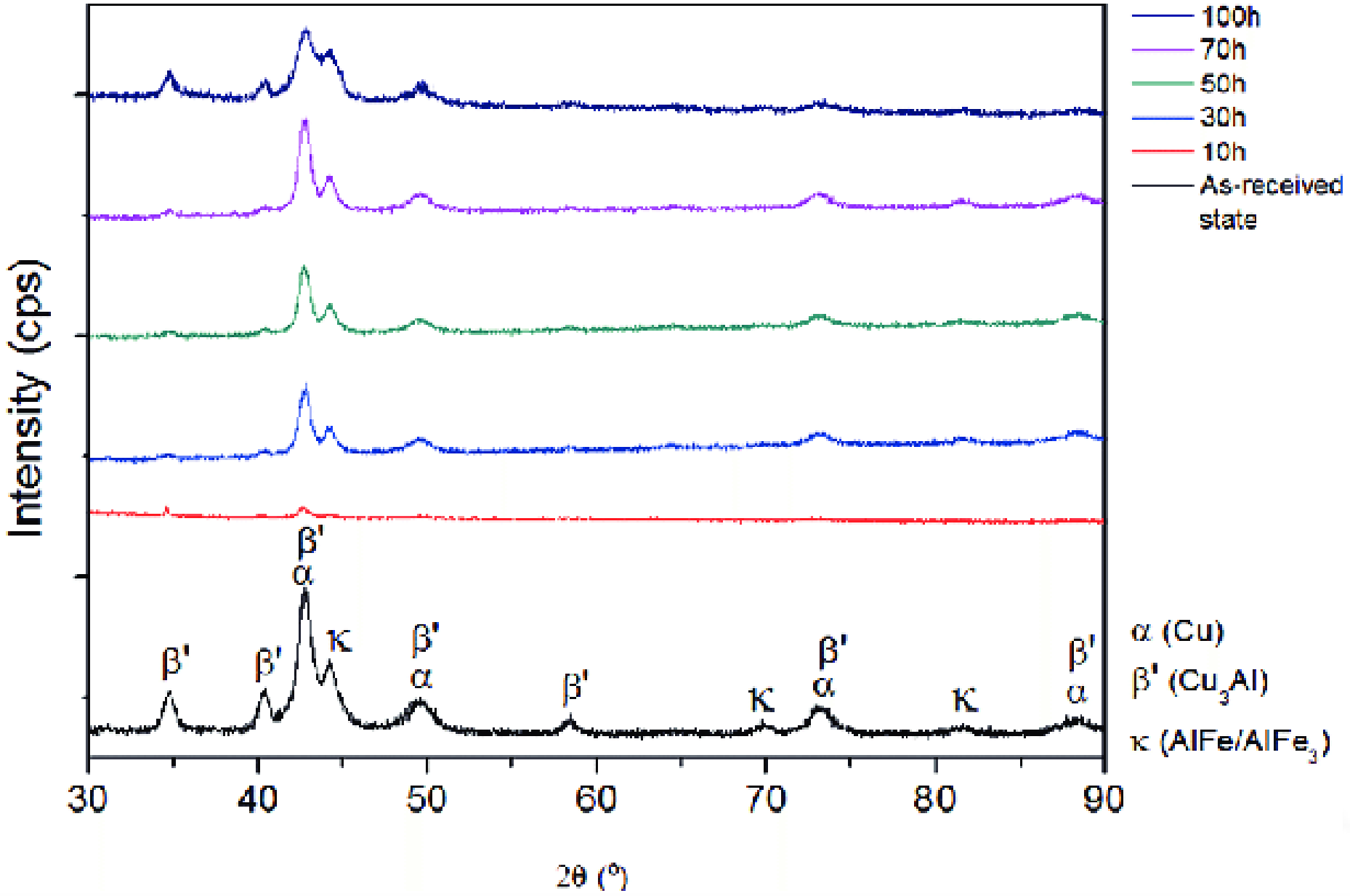


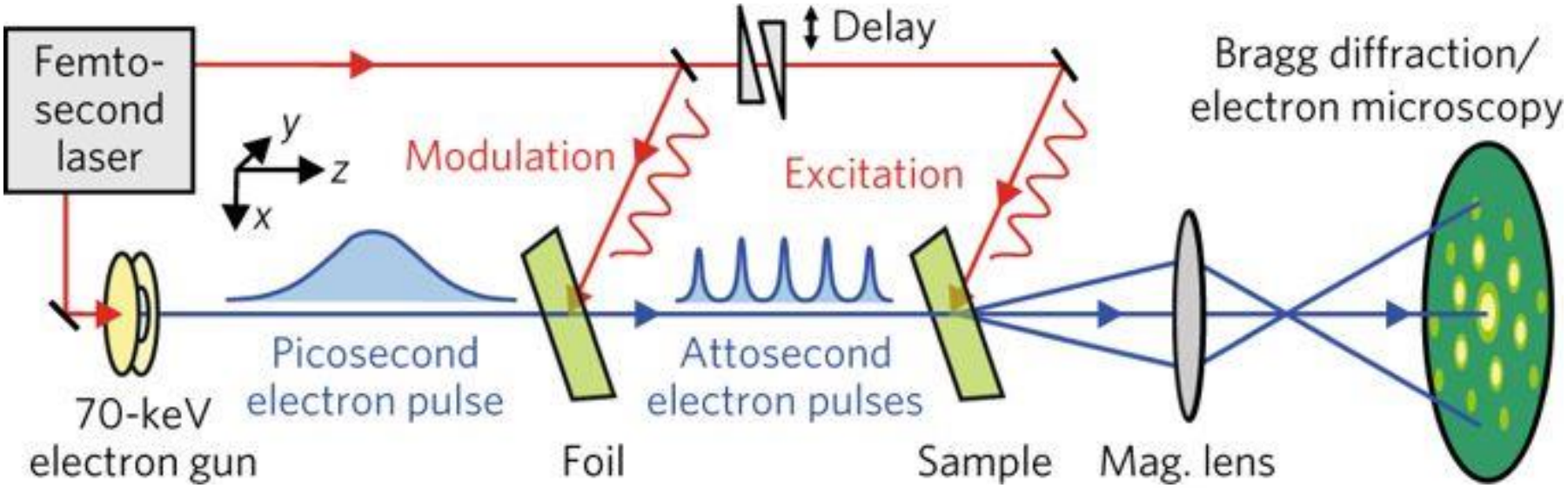
- In 1927, Davisson and Germer was demonstrated that a beam of electrons, just like X rays, could be diffracted by a crystal.

The X-Ray difraction is actually used for solid analysis

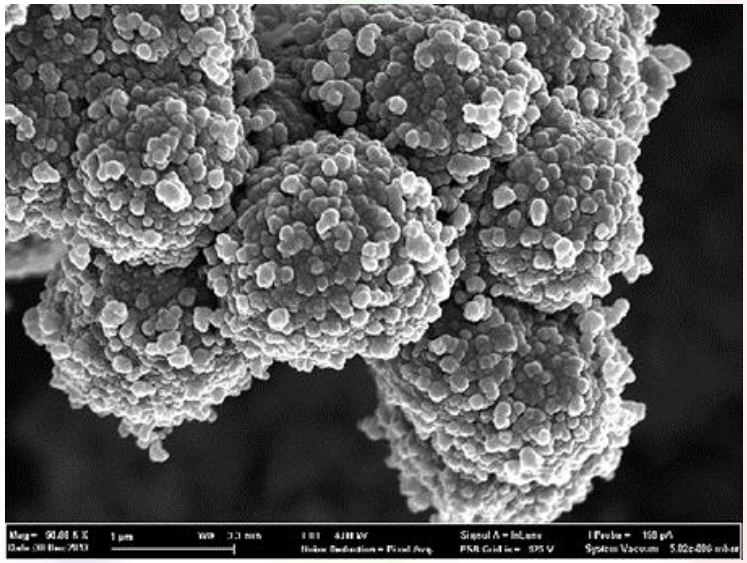




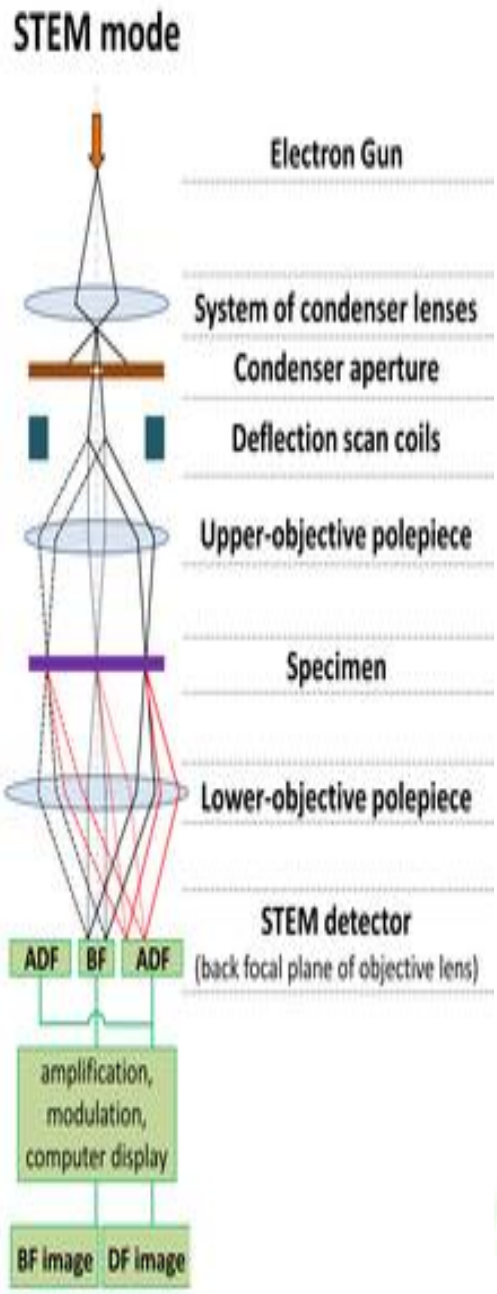

100h
70h
50h
30h
10h
As-received state
Intensity (cps)
2θ (°)
30
40
50
60
70
80
90
β'
α
κ
α (Cu)
β' (Cu3Al)
κ (AlFe/AlFe3)

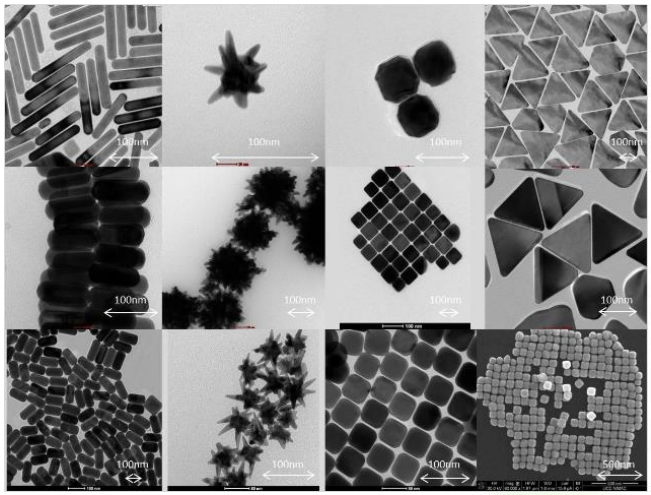


The electron gun at the top of the column produces an electron beam that is focused into a fine spot as small as 1 nm in diameter on the specimen surface. This beam is scanned in a rectangular raster over the specimen and the intensities of various signals created by interactions between the beam electrons and the specimen are measured and stored in computer memory.



The scanning electron microscopy (SEM)





The transmission electron microscopy (TEM) principle, as the name suggests, is to use the transmitted electrons; the electrons which are passing through the sample before they are collected. As a result, TEM offers invaluable information on the inner structure of the sample, such as crystal structure, morphology and stress state information, while SEM provides information on the sample's surface and its composition.

Difference between SEM and TEM

Features	Scanning Electron Microscope	Transmission Electron Microscope
Classification of electrons (e-) used	Scattered (backscattered or secondary) e-	Transmitted e- beam
Image formation process	Image is produced after microscope collects and counts the secondary e-	Internal or beyond e- that directly pass through the sample are the ones illuminated in the image macrom
Focus of analysis	Surface of sample (e.g. fine hairs, eye of a housefly, head of a pin)	Internal or beyond surface (e.g. viruses, organelles, atoms, macromolecules)
Image presentation	3-D	2-D
Special sample preparation	Sample must be "stained" by element that captures secondary e-	Sample must be cut extremely thin

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Quantum Mechanics

Quantum mechanics is the branch of physics that mathematically describes the wave properties of submicroscopic particles.

- We can no longer think of an electron as having a precise orbit in an atom.
- To describe such an orbit would require knowing its exact position and velocity.
- In 1927, Werner Heisenberg showed (from quantum mechanics) that it is impossible to know both simultaneously.

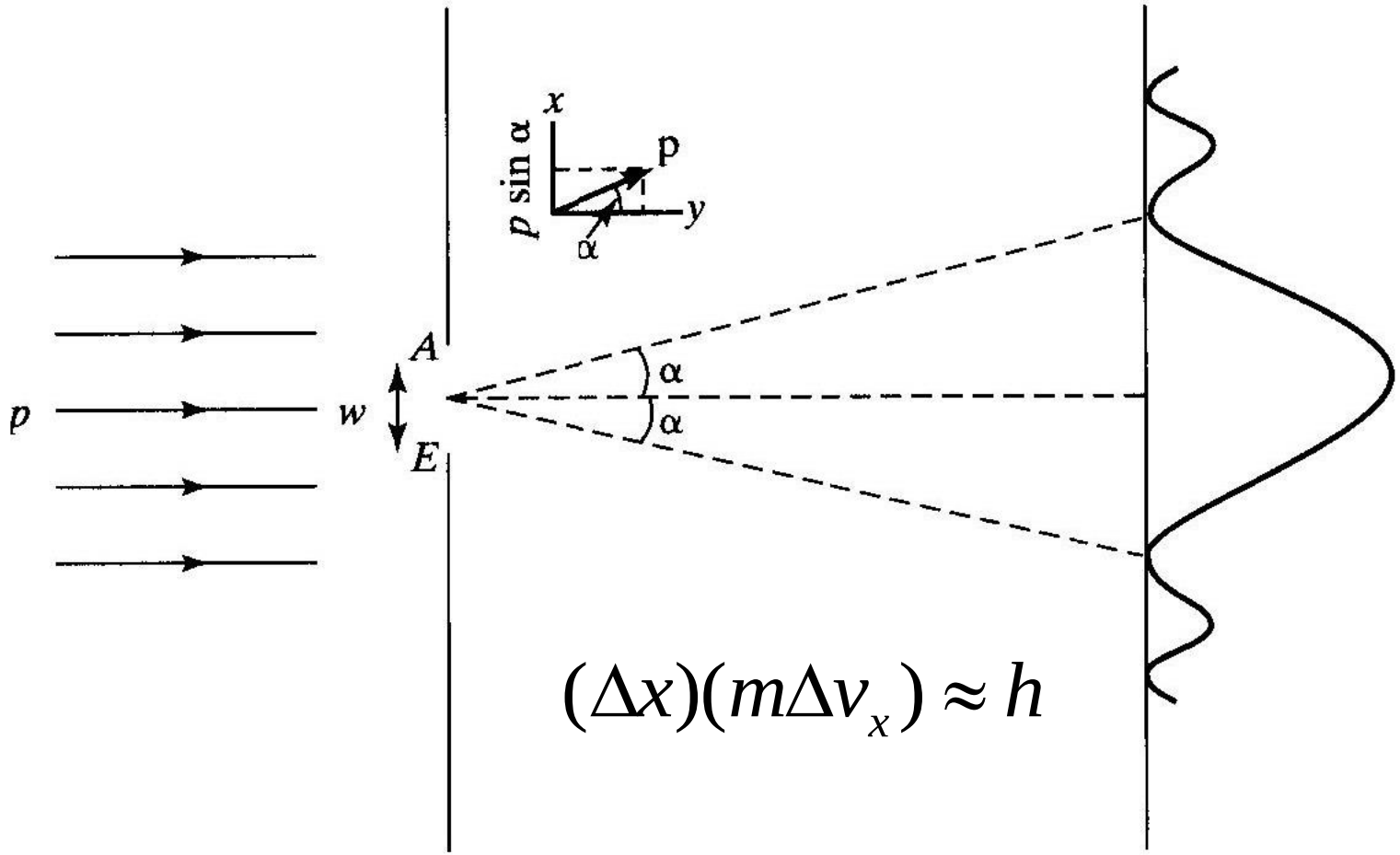
Quantum Mechanics

Heisenberg's uncertainty principle is a relation that states that the product of the uncertainty in position (Δx) and the uncertainty in momentum ($m\Delta v_x$) of a particle can be no larger than $\mathbf{h/4\pi}$.

$$(\Delta x)(m\Delta v_x) \geq \frac{h}{4\pi}$$

- When m is large (for example, a baseball) the uncertainties are small, but for electrons, high uncertainties disallow defining an exact orbit.

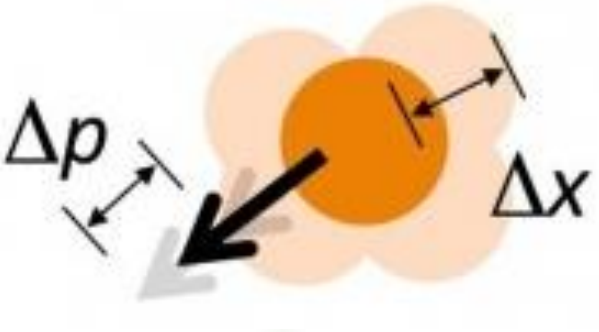
Heisenberg's Uncertainty Principle



$$(\Delta x)(m\Delta v_x) \approx h$$

FIGURE 1.1 Diffraction of electrons by a slit.

Heisenberg's Uncertainty Principle



$$\Delta p \Delta x \geq \frac{\hbar}{2}$$

It is clear that to locate a particle it is necessary to add all the contributions of waves whose wave number varies between zero and infinite and therefore the moment also varies between zero and infinite That is to say that it is completely undetermined..

The uncertainty principle tells us that there is a limit on the precision with which we can determine at the same time the position and momentum of a particle.

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Heisenberg's Uncertainty Principle

A wave packet is constructed by superposition a number infinite harmonic waves of different frequencies.

At a given time, the wave function associated with a packet of waves is given by

$$K = \frac{2\pi}{\lambda} = \frac{2\pi\nu}{c}$$

The momentum of the particle and the number of waves are related as

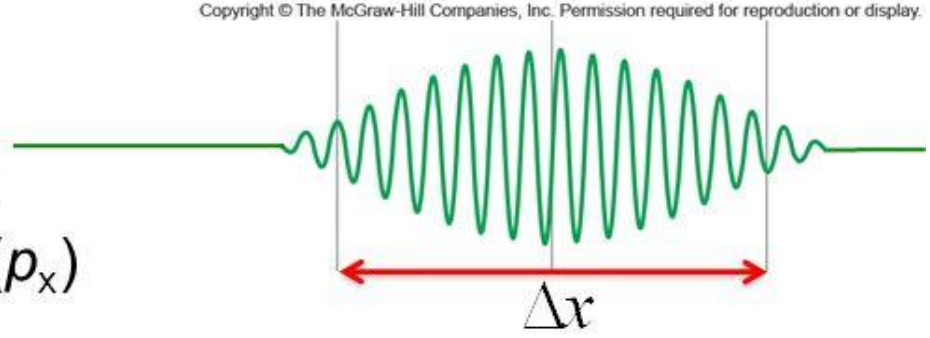
$$P = \frac{h\nu}{c} \qquad K = \frac{2\pi\nu}{c}$$

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§28.4 Heisenberg's Uncertainty Principle

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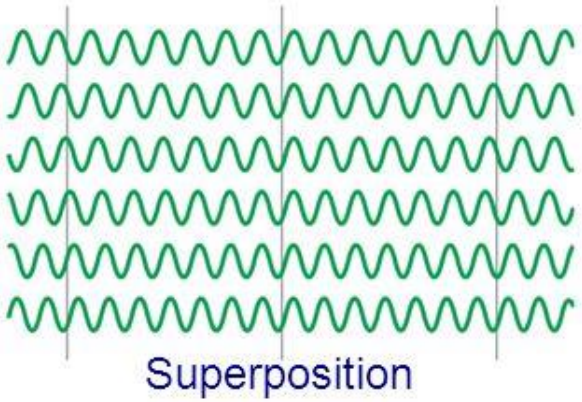
Sets limits on how precise measurements of a particle's position (x) and momentum (p_x) can be:



$$\Delta x \Delta p_x \geq \frac{1}{2}\hbar$$

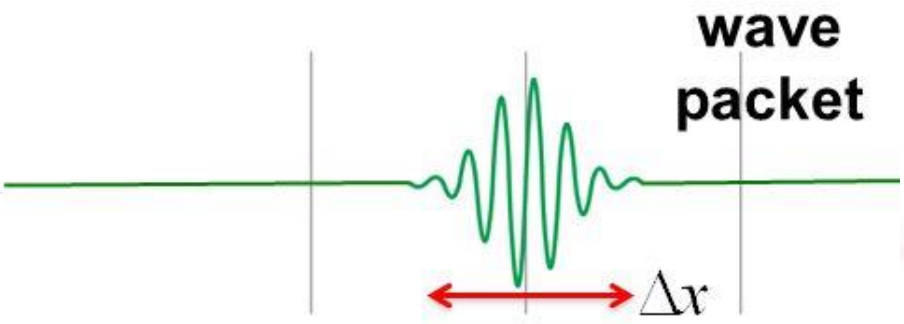
Uncertainty in *position* & *momentum*

where $\hbar = \dfrac{h}{2\pi}$



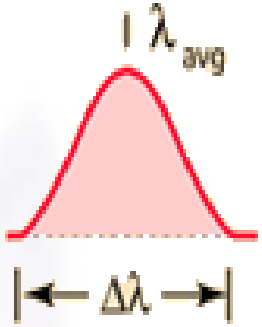
The energy-time uncertainty principle:

$$\Delta E \Delta t \geq \frac{1}{2}\hbar.$$

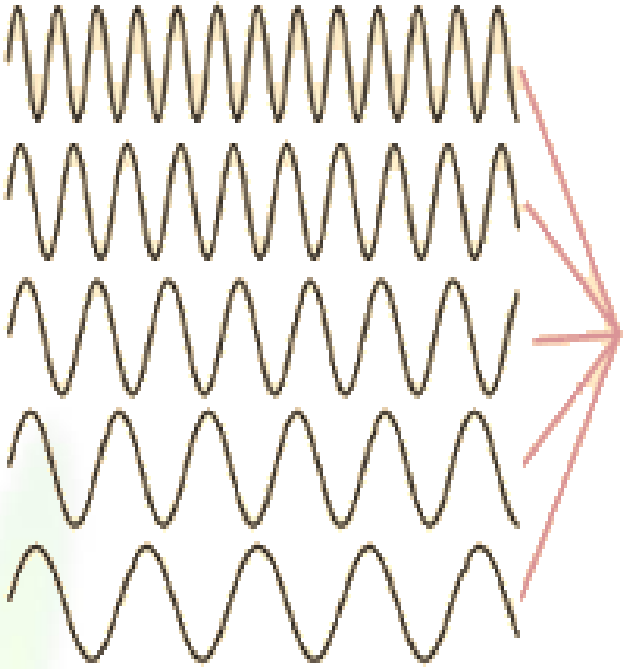


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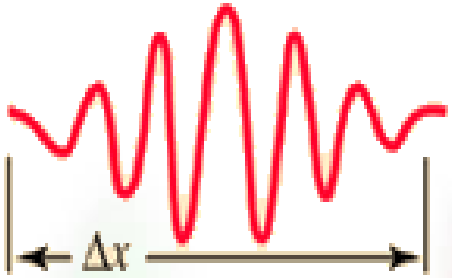
A continuous distribution of wavelengths can produce a localized "wave packet".



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



Each different wavelength represents a different value of momentum according to the DeBroglie relationship.

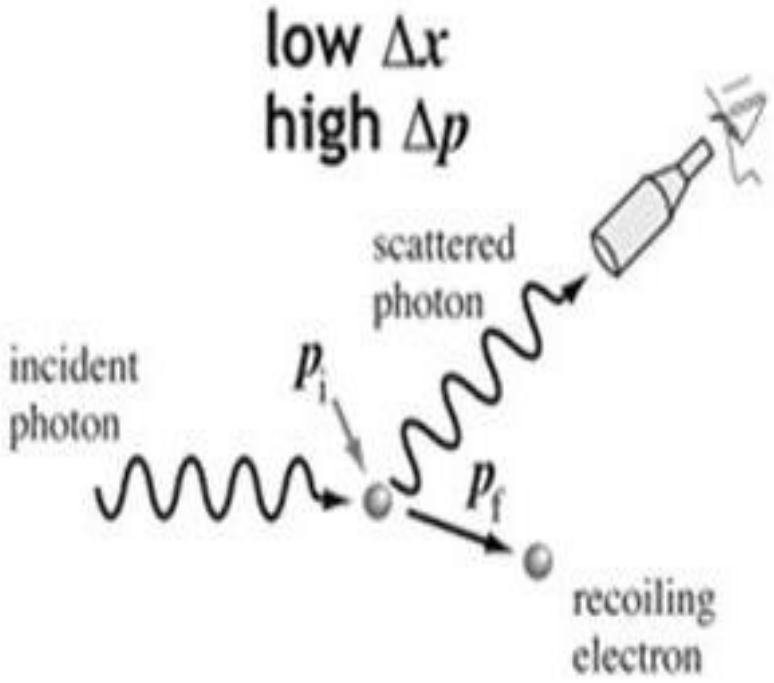


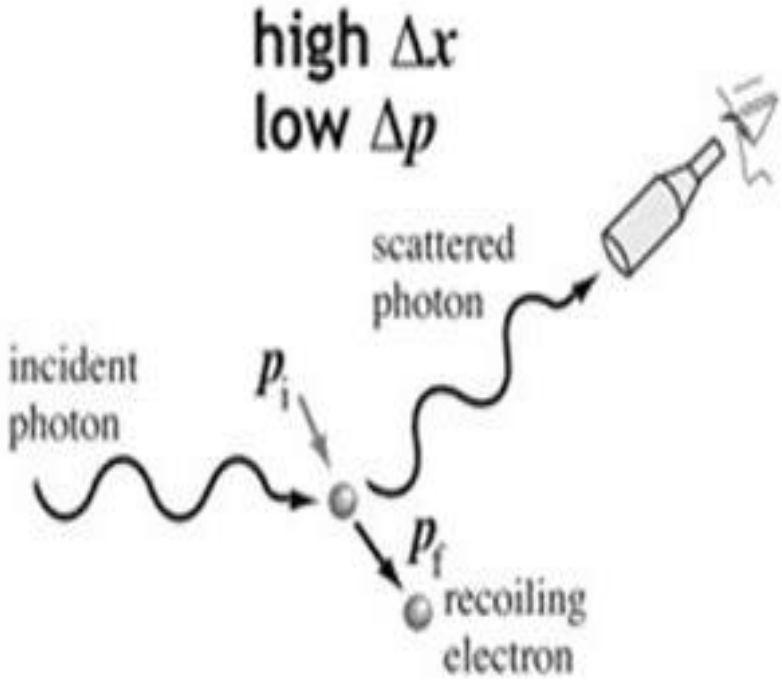
Superposition of different wavelengths is necessary to localize the position. A wider spread of wavelengths contributes to a smaller Δx.

Heisenberg Uncertainty Principle

$$\Delta x \, \Delta p \geq \hbar$$

Δx = uncertainty in position
Δp = uncertainty in momentum
$\hbar$ = $h / 2\pi$





Proposed exercises

The uncertainty in the momentum Δp of a football thrown by Tom Brady during the superbowl traveling at 40m/s is 1×10^{-6} of its momentum. What is its uncertainty in position ΔX ? Mass=0.40kg

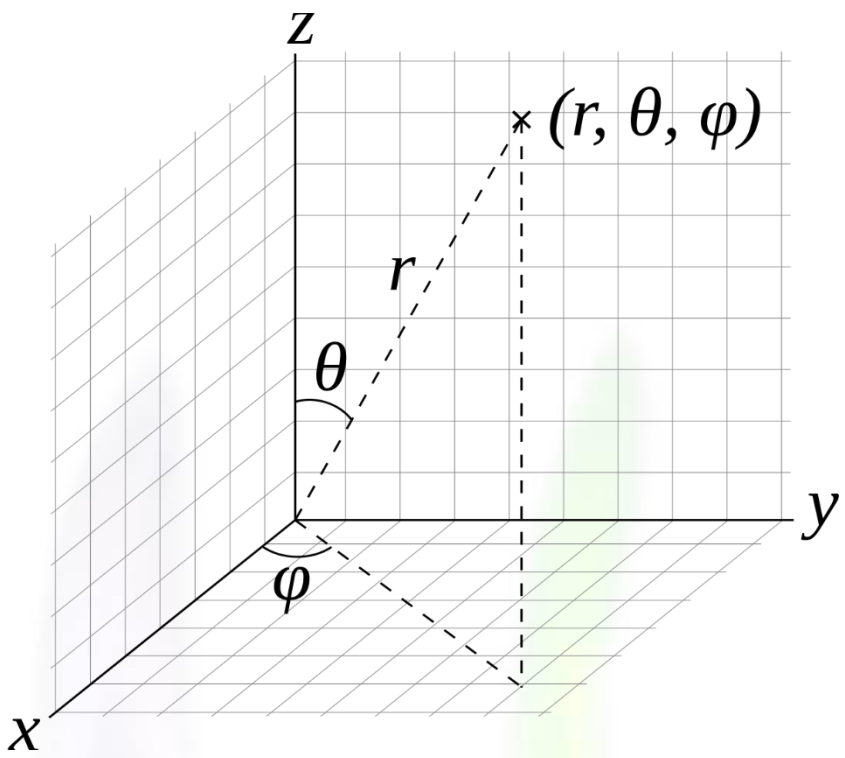
You notice there is 2 mL of water traveling on the football at the same speed and Δp . Calculate its ΔX .

An electron in that molecule of water traveling at the same speed has the same Δp . Calculate its ΔX

Comment on the differences in the uncertainty of momentum between the ball, water, and electron. How does the mass effect this value?

Taking into account all of the information presented above, can you state a situation in which the Heisenberg Uncertainty Principle has little effect on measuring the momentum and position of one object, but dominates for that of another when both objects are part of the same system?

Spherical coordinates



Spherical coordinates (r, θ, φ) as often used in ***mathematics***: radial distance r, azimuthal angle θ, and polar angle φ.

r is the distance of R to 0, r >< 0.

Θ is the same angle used for cilindric coordenates when r> 0.

φ is the angle between positive z axis and the segment OR, 0 > φ < π.

$x = r\,\mathrm{sen}\Theta\cos\varphi$

$y = r\,\mathrm{sen}\Theta\,\mathrm{sen}\,\varphi$

$z = r\cos\varphi$

Quantum Mechanics

Although we cannot precisely define an electron's orbit, we can obtain the ***probability*** of finding an electron at a given point around the nucleus.

- Erwin Schrodinger defined this probability in a mathematical expression called a wave function, denoted ψ (psi).
- The probability of finding a particle in a region of space is defined by ψ^2.

Classical wave equation

$$\frac{1}{\mathrm{v}^2}\frac{\partial^2 u}{\partial t^2} = \frac{\partial^2 u}{\partial x^2} \qquad u(x,t) = \cos(2\pi\nu t)\psi(x)$$

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{4\pi^2\nu^2}{\mathrm{v}^2}\psi(x) = 0$$

since $\mathrm{v} = \nu\lambda$

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{4\pi^2}{\lambda^2}\psi(x) = 0$$

$$\psi(x) = A\cos(2\pi x / \lambda)$$

Schrodinger equation

$E = \frac{m\mathrm{v}^2}{2} + V(x)$, rearrange to give $m\mathrm{v} = \{2\mathrm{m}[\mathrm{E}\text{-}V(x)]\}^{1/2}$

de Broglie relation $\lambda = \frac{h}{m\mathrm{v}} = \frac{h}{\{2\mathrm{m}[\mathrm{E}\text{-}V(x)]\}^{1/2}}$

classical wave eqn. $\frac{\partial^2\psi}{\partial x^2} + \frac{4\pi^2}{\lambda^2}\psi(x) = \frac{\partial^2\psi}{\partial x^2} + \frac{2\mathrm{m}[\mathrm{E}\text{-}V(x)]}{(h/2\pi)^2}\psi(x) = 0$

Schrodinger eqn. $-\frac{(h/2\pi)^2}{2\mathrm{m}}\frac{\partial^2\psi}{\partial x^2} + V(x)\psi(x) = E\psi(x)$



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Postulates of Quantum Mechanics

The state of a quantum mechanical system is completely specified by its wavefunction, $\Psi(x,t)$

To every classical observable there corresponds a linear, Hermitian operator in quantum mechanics

In any measurement associated with an operator, the only values observed are eigenvalues of the operator,

$$A\,\Psi(x,t) = a\,\Psi(x,t)$$

The average values of an observable is given by its expectation value,

$$\langle A \rangle = \int_{-\infty}^{\infty} \Psi^* A \Psi d\tau$$

The wavefunction obeys the time dependent Schrodinger equation,

$$i\frac{h}{2\pi}\frac{\partial \Psi(x,t)}{\partial t} = H\Psi(x,t)$$

The wavefunction

The square of the wavefunction $|\Psi|^2$ is the probability density for finding the particle at that location

The wavefunction must be

- Single valued
- Continuous
- Continuous first derivative
- Quadratically integrable

$$\int_{-\infty}^{\infty} \Psi^* \Psi d\tau \text{ must be finite}$$

The Variational Energy

It can be easily proven that the variational energy is always greater than or equal to the exact energy of the lowest energy state

$$E_{\text{var}} = \frac{\int_{-\infty}^{\infty} \Psi^* H \Psi d\tau}{\int_{-\infty}^{\infty} \Psi^* \Psi d\tau} \geq E_{exact}$$

If we start with an approximate wavefunction and vary it so as to minimize the energy, we obtain a better wavefunction and energy

With enough flexibility in the wavefunction, we can get very close to the exact energy

Particle in a 1-Dimensional Box

Schrodinger equation

$$H\psi = E\psi,$$

$$H = -\frac{(h/2\pi)^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)$$

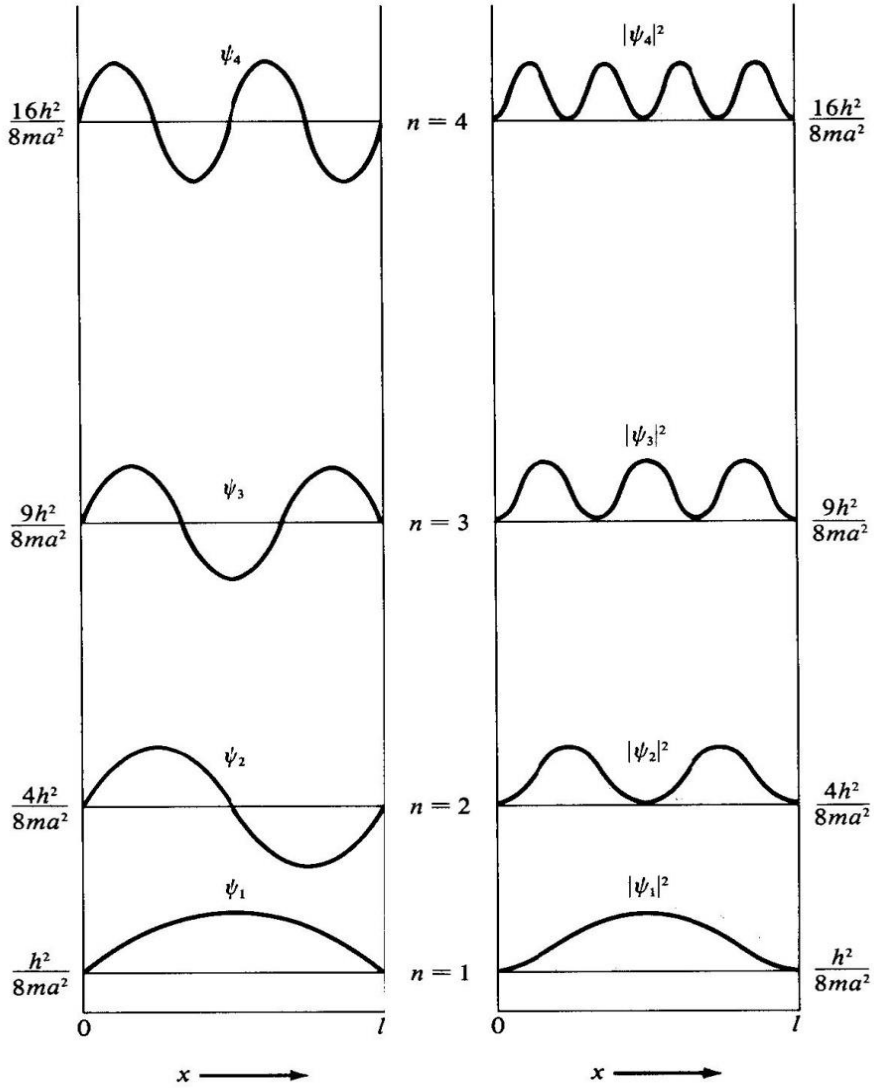
outside the box $V(x) = \infty,$

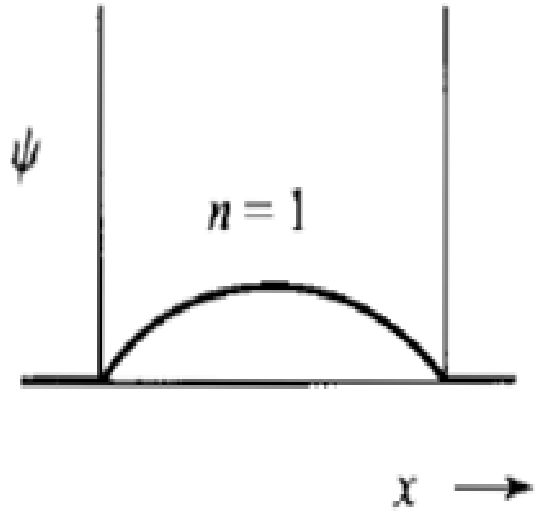
$$\psi(x) = 0$$

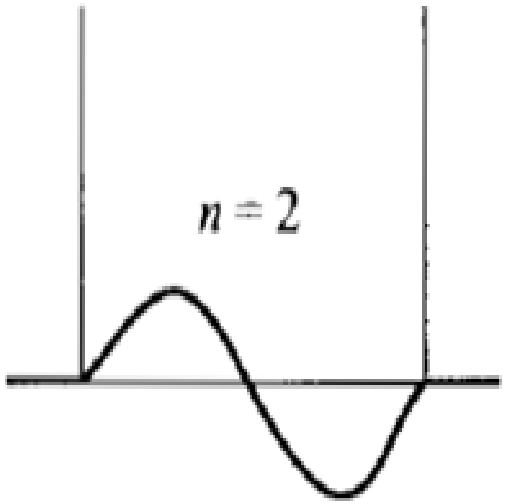
inside the box $V(x) = 0,$

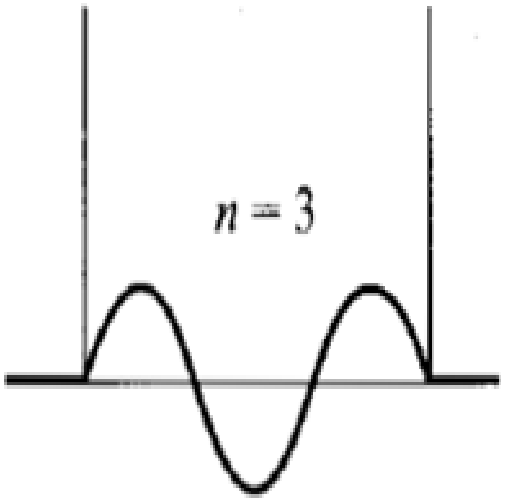
$$\psi(x) = \left(\frac{2}{l}\right)^{1/2} \sin\left(\frac{n\pi x}{l}\right)$$

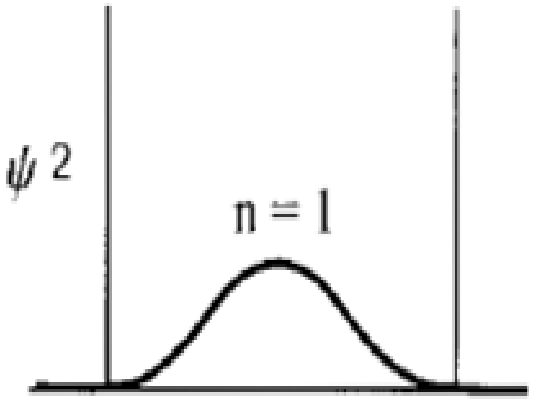
$$E = \frac{n^2 h^2}{8ml^2}, \quad n = 1, 2, \ldots$$

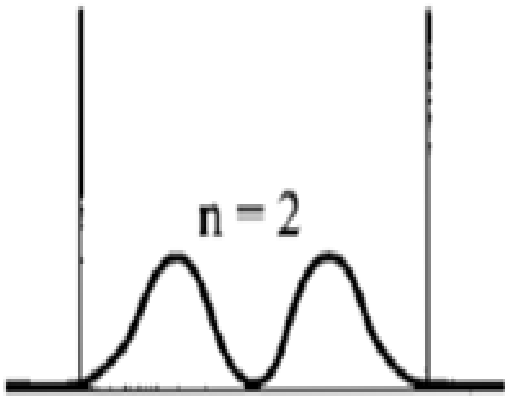


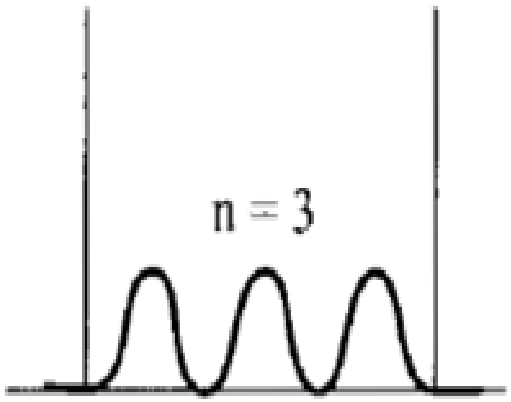












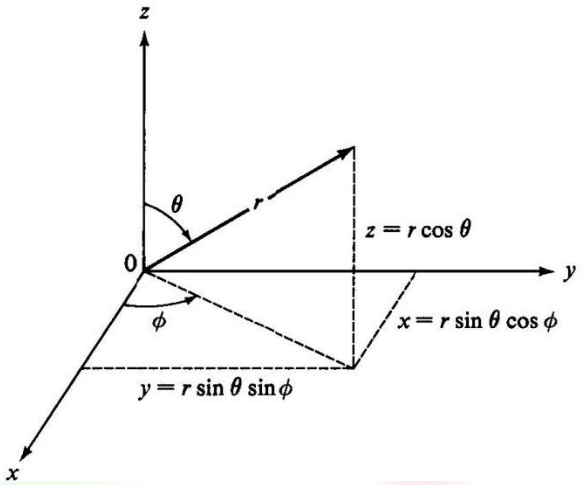
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Hydrogen-like Atom

Nucleus with charge Ze at origin,

Electron with charge -e at (x,y,z) or (r,θ,ϕ)

Schrodinger equation for hydrogen-like atom



$$H\psi = E\psi,$$

$$H = -\frac{(h/2\pi)^2}{2m}\left[\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right]-\frac{Ze^2}{4\pi\varepsilon_0 r}$$

$$H = -\frac{(h/2\pi)^2}{2m}\left[\frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r}\right]+\frac{1}{2mr^2}L^2-\frac{Ze^2}{4\pi\varepsilon_0 r}$$

$$L^2 = -(h/2\pi)^2\left[\frac{\partial^2}{\partial\theta^2}+\cot\theta\frac{\partial}{\partial\theta}+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]$$

$$-\frac{h^2}{8\pi^2 m_e}\left(\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}\right)-Z\frac{e^2}{r}\psi=E\psi$$

$$\hat{H}\Psi=E\Psi$$

$$\nabla^2\psi\equiv\left(\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}\right)$$

Hamiltonian

$$\nabla^2\psi+\frac{8\pi^2 m_e}{h^2}(E-V)\psi=0$$

Wave function Ψ: "describes the wave properties of the particle (electron)

"" is simply a function math

- It is not observable. (Doesn´t have physical meaning)

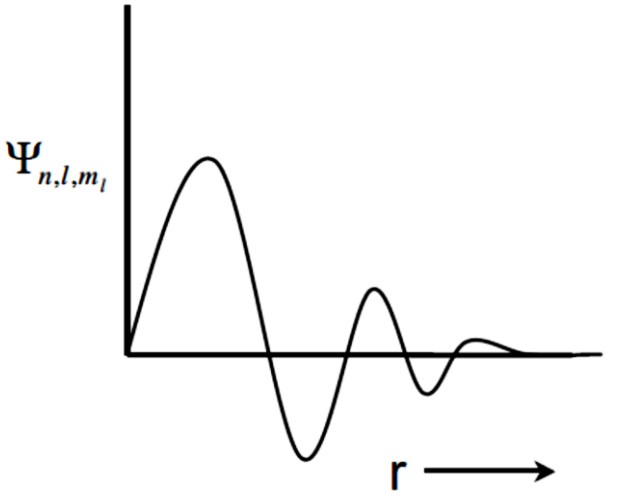
"" can be real or imaginary (in the sense mathematical).

- if it is real corresponds to the amplitude of the wave (can be + or -)

Probability density Ψ^2: is the probability of finding the electron in a small volume element dV

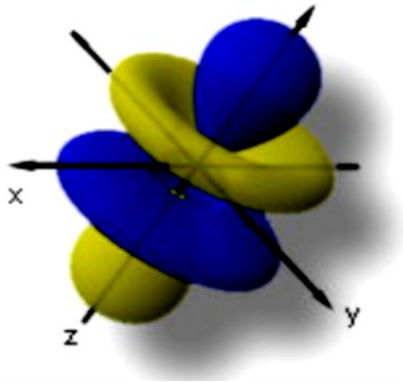
Ψ_{n,l,m_l}

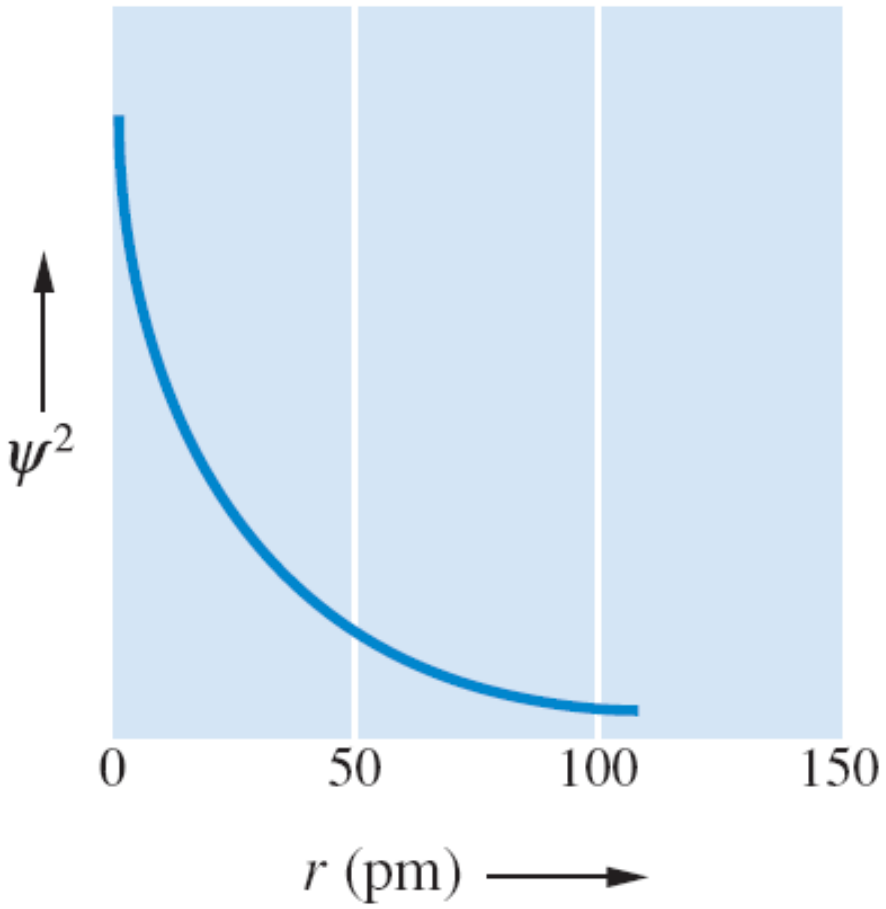
'function'



$\left|\Psi_{n,l,m_l}\right|^2$

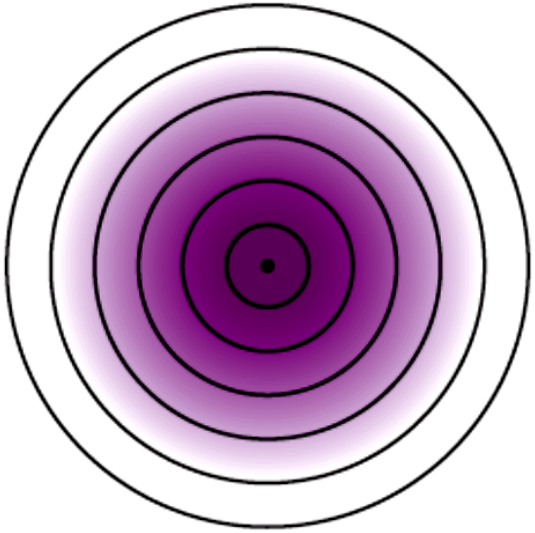
'probability'



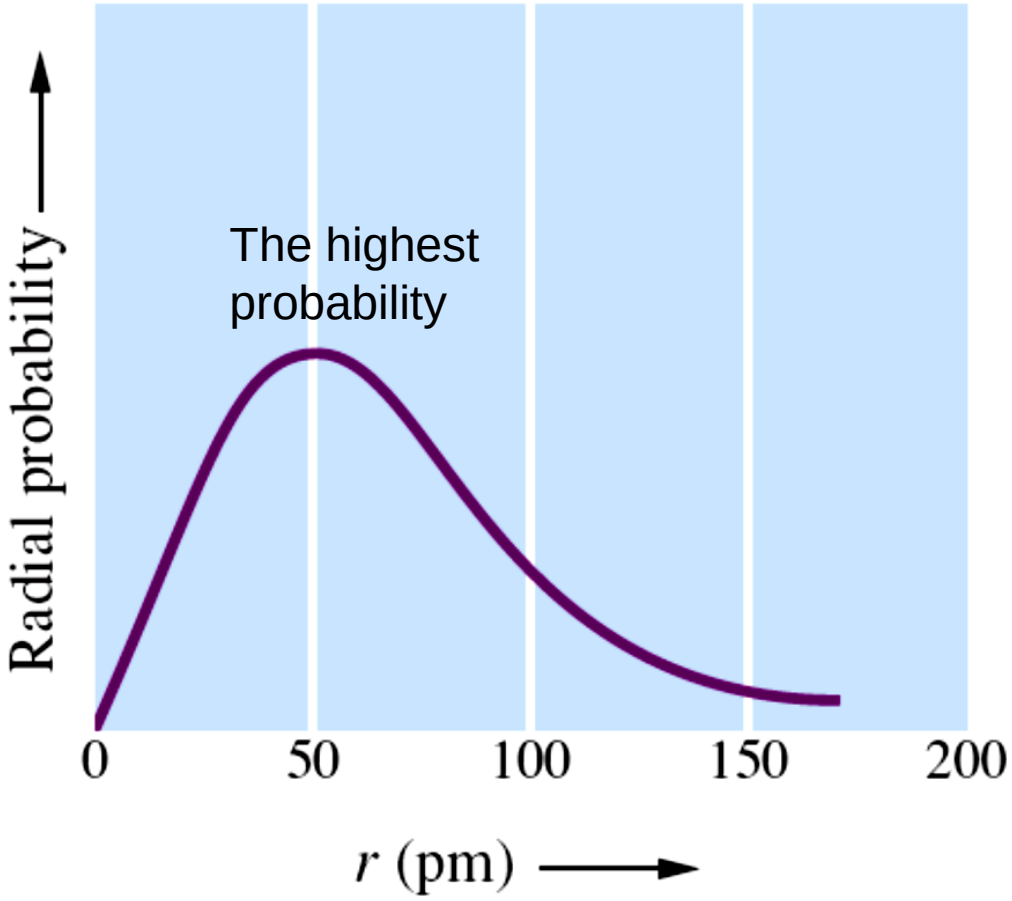


The wave function for the lowest level of the hydrogen atom is shown to the left.

Note that its value is greatest nearest the nucleus, but rapidly decreases thereafter. Note also that it never goes to zero, only to a very small value.



Probability density for an electron in hydrogen



Probability of finding the electron at various distances from the nucleus.

Conditions of Ψ "to be an acceptable solution:

PRECISE (one value at each point)

CONTINUOS (the probability can not change abruptly)

- in any point can be equal to 1
- Should be 0 for r = infinity

NORMALIZED $\int \Psi^2 dV = 1$

Quantization of energy E comes determined by the boundary conditions imposed on Ψ

ORBITAL: each one of the functions of monelectronic waves that describe the behavior of the electron. They are the solutions of the Schrödinger equation

Wavefunctions for Hydrogen-like Atoms

The Complete Hydrogenlike Atomic Wave Functions for $n = 1$, 2, and 3. The Quantity Z Is the Atomic Number of the Nucleus, and $\sigma = Zr/a_0$, Where a_0 is the Bohr Radius.

$n = 1; l = 0, m = 0$	$\psi_{100} = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-\sigma}$
$n = 2; l = 0, m = 0$	$\psi_{200} = \frac{1}{\sqrt{32\pi}}\left(\frac{Z}{a_0}\right)^{3/2} (2 - \sigma)e^{-\sigma/2}$
$l = 1, m = 0$	$\psi_{210} = \frac{1}{\sqrt{32\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \sigma e^{-\sigma/2} \cos\theta$
$l = 1, m = \pm 1$	$\psi_{21\pm 1} = \frac{1}{\sqrt{64\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \sigma e^{-\sigma/2} \sin\theta e^{\pm i\phi}$

TABLE 7.1 Some Hydrogen Atom Wave Functions

n	l	m_l	$R(r)$	$\Theta(\theta)$	$\Phi(\phi)$
1	0	0	$\frac{2}{a_0^{3/2}} e^{-r/a_0}$	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2\pi}}$
2	0	0	$\frac{1}{(2a_0)^{3/2}} \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}$	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2\pi}}$
2	1	0	$\frac{1}{\sqrt{3}(2a_0)^{3/2}} \frac{r}{a_0} e^{-r/2a_0}$	$\sqrt{\frac{3}{2}} \cos\theta$	$\frac{1}{\sqrt{2\pi}}$
2	1	± 1	$\frac{1}{\sqrt{3}(2a_0)^{3/2}} \frac{r}{a_0} e^{-r/2a_0}$	$\mp \frac{\sqrt{3}}{2} \sin\theta$	$\frac{1}{\sqrt{2\pi}} e^{\pm i\phi}$
3	0	0	$\frac{2}{(3a_0)^{3/2}} \left(1 - \frac{2r}{3a_0} + \frac{2r^2}{27a_0^2}\right) e^{-r/3a_0}$	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2\pi}}$
3	1	0	$\frac{8}{9\sqrt{2}(3a_0)^{3/2}} \left(\frac{r}{a_0} - \frac{r^2}{6a_0^2}\right) e^{-r/3a_0}$	$\sqrt{\frac{3}{2}} \cos\theta$	$\frac{1}{\sqrt{2\pi}}$
3	1	± 1	$\frac{8}{9\sqrt{2}(3a_0)^{3/2}} \left(\frac{r}{a_0} - \frac{r^2}{6a_0^2}\right) e^{-r/3a_0}$	$\mp \frac{\sqrt{3}}{2} \sin\theta$	$\frac{1}{\sqrt{2\pi}} e^{\pm i\phi}$
3	2	0	$\frac{4}{27\sqrt{10}(3a_0)^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0}$	$\sqrt{\frac{5}{8}}(3\cos^2\theta - 1)$	$\frac{1}{\sqrt{2\pi}}$
3	2	± 1	$\frac{4}{27\sqrt{10}(3a_0)^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0}$	$\mp \sqrt{\frac{15}{4}} \sin\theta \cos\theta$	$\frac{1}{\sqrt{2\pi}} e^{\pm i\phi}$
3	2	± 2	$\frac{4}{27\sqrt{10}(3a_0)^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0}$	$\frac{\sqrt{15}}{4} \sin^2\theta$	$\frac{1}{\sqrt{2\pi}} e^{\pm 2i\phi}$

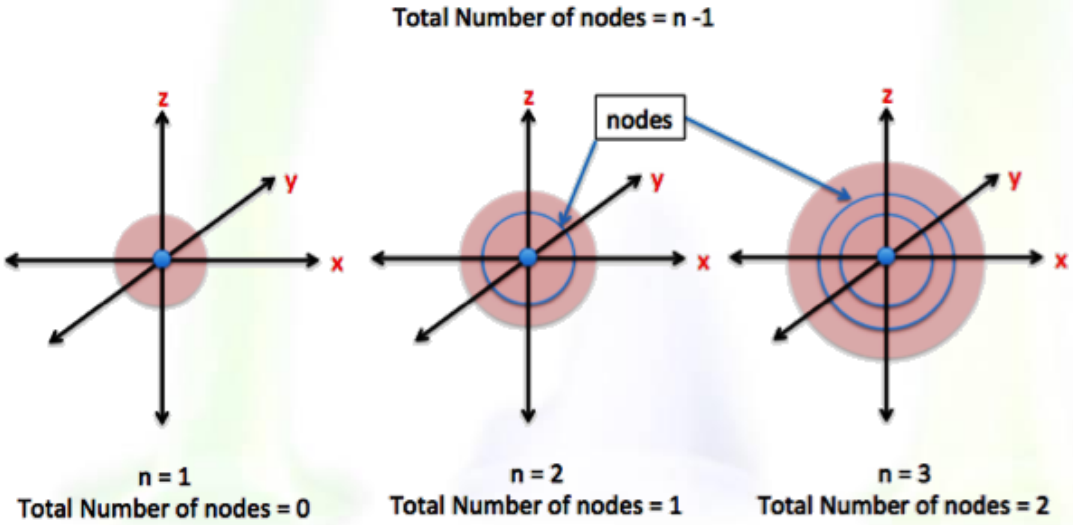
The resolution of the wave equation requires introducing certain parameters that are **quantum numbers**:

1. Principal quantum number (n)
2. Angular momentum quantum number (l)
3. Magnetic quantum number (m_l)

The Principal Quantum Number (n)

Because n describes the most probable distance of the electrons from the nucleus, the larger the number n is, the farther the electron is from the nucleus.

n can be any positive integer starting at 1, as n=1 designates the first principal shell.



Principal Quantum Number and Nodes

The Orbital Angular Momentum Quantum Number (l)

The orbital angular momentum quantum number l determines the shape of an orbital, and therefore the angular distribution.

The number of angular nodes is equal to the value of the angular momentum quantum number l

Each value of l indicates a specific s, p, d, f subshell

Subshells are sometimes designated by lowercase letters:

l	0	1	2	3	. . .
Letter	*s*	*p*	*d*	*f*	
n ≥	1	2	3	4	

Not every subshell type exists in every shell. The minimum value of *n* for each type of subshell is shown above.

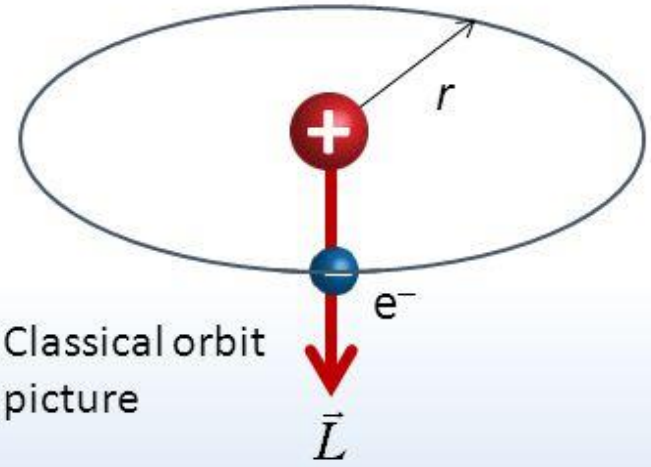
Magnetic Quantum Number, m_l

This quantum number distinguishes orbitals of a given n and l—that is, of a given energy and shape but having different orientations.

The magnetic quantum number depends on the value of l and can have any integer value from $-l$ to 0 to $+l$. Each different value represents a different orbital. For a given subshell, there will be $(2l + 1)$ values and therefore $(2l + 1)$ orbitals.

Angular momentum

What do the quantum numbers ℓ and m_ℓ represent?



Classical orbit picture

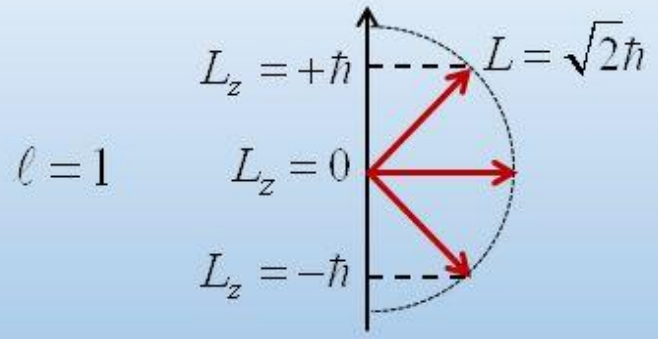
Magnitude of angular momentum vector quantized

$$|\vec{L}| = L = \sqrt{\ell(\ell+1)}\hbar \qquad \ell = 0, 1, 2 \cdots n-1$$

Only *one* component of *L* quantized

$$L_z = m_\ell \hbar \qquad m_\ell = -\ell, \cdots -1, 0, 1, \cdots \ell$$

Other components L_x, L_y are not quantized



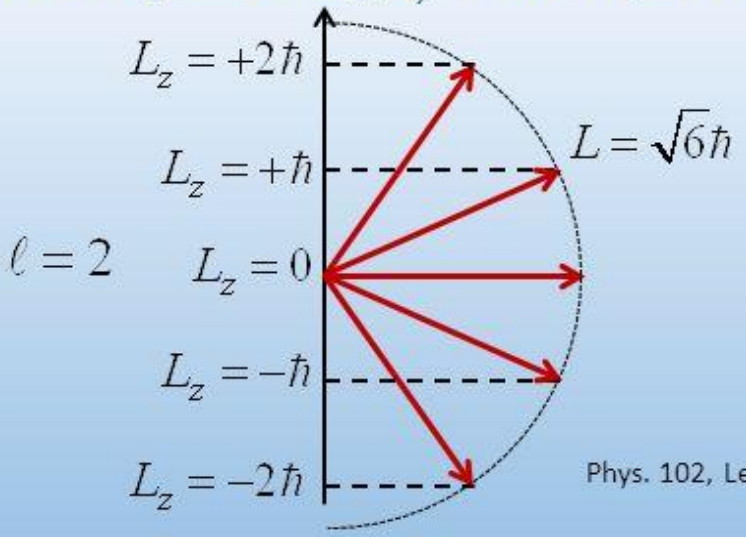
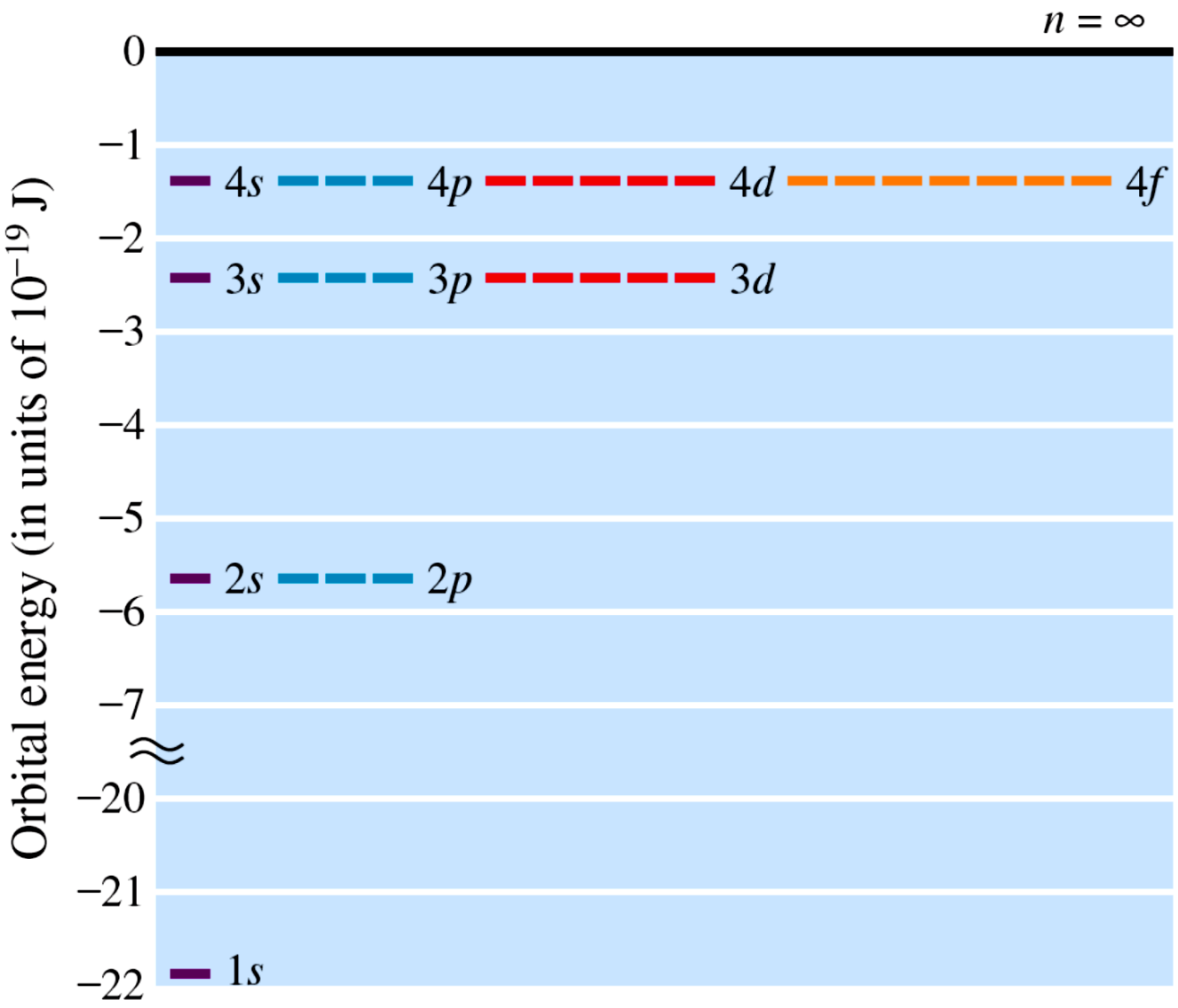


TABLE 7.1 Permissible Values of Quantum Numbers for Atomic Orbitals

n	l	m_l*	Subshell Notation	Number of Orbitals in the Subshell
1	0	0	1*s*	1
2	0	0	2*s*	1
2	1	−1, 0, +1	2*p*	3
3	0	0	3*s*	1
3	1	−1, 0, +1	3*p*	3
3	2	−2, −1, 0, +1, +2	3*d*	5
4	0	0	4*s*	1
4	1	−1, 0, +1	4*p*	3
4	2	−2, −1, 0, +1, +2	4*d*	5
4	3	−3, −2, −1, 0, +1, +2, +3	4*f*	7

*Any one of the m_l quantum numbers may be associated with the n and l quantum numbers on the same line.



The figure shows relative energies for the hydrogen atom shells and subshells; each orbital is indicated by a dashed-line.

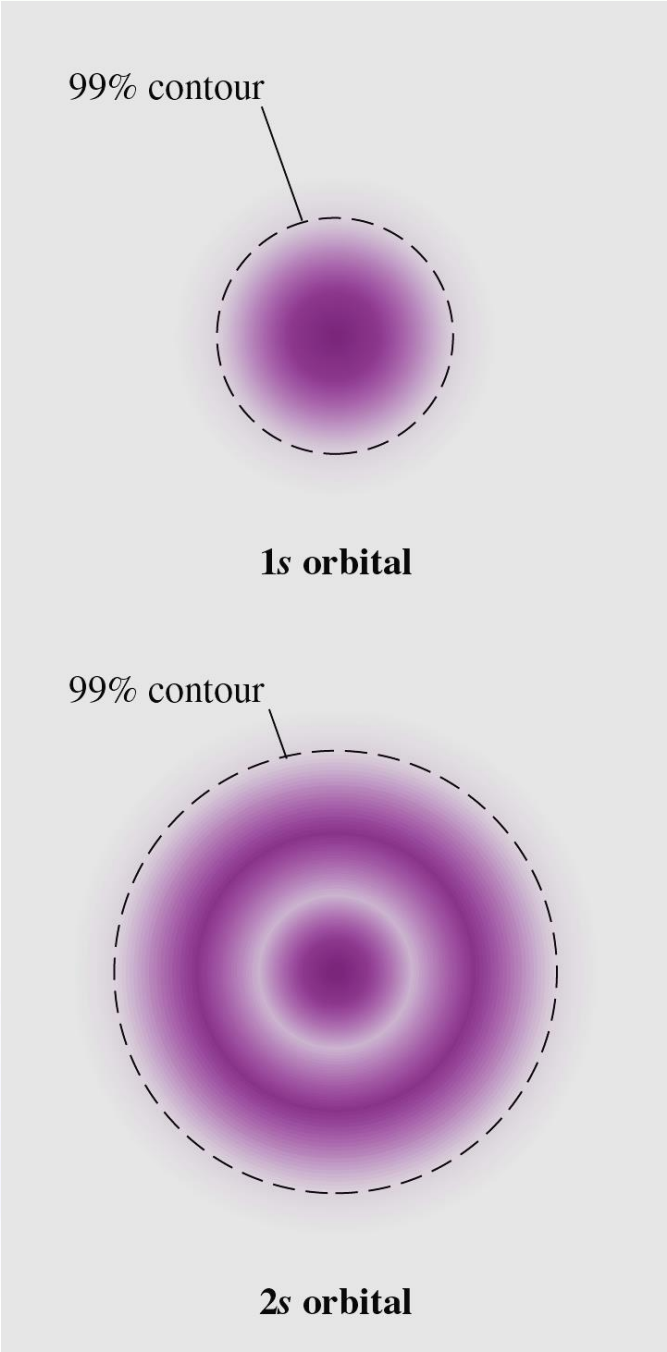
Atomic Orbital Shapes

An *s* orbital is spherical.

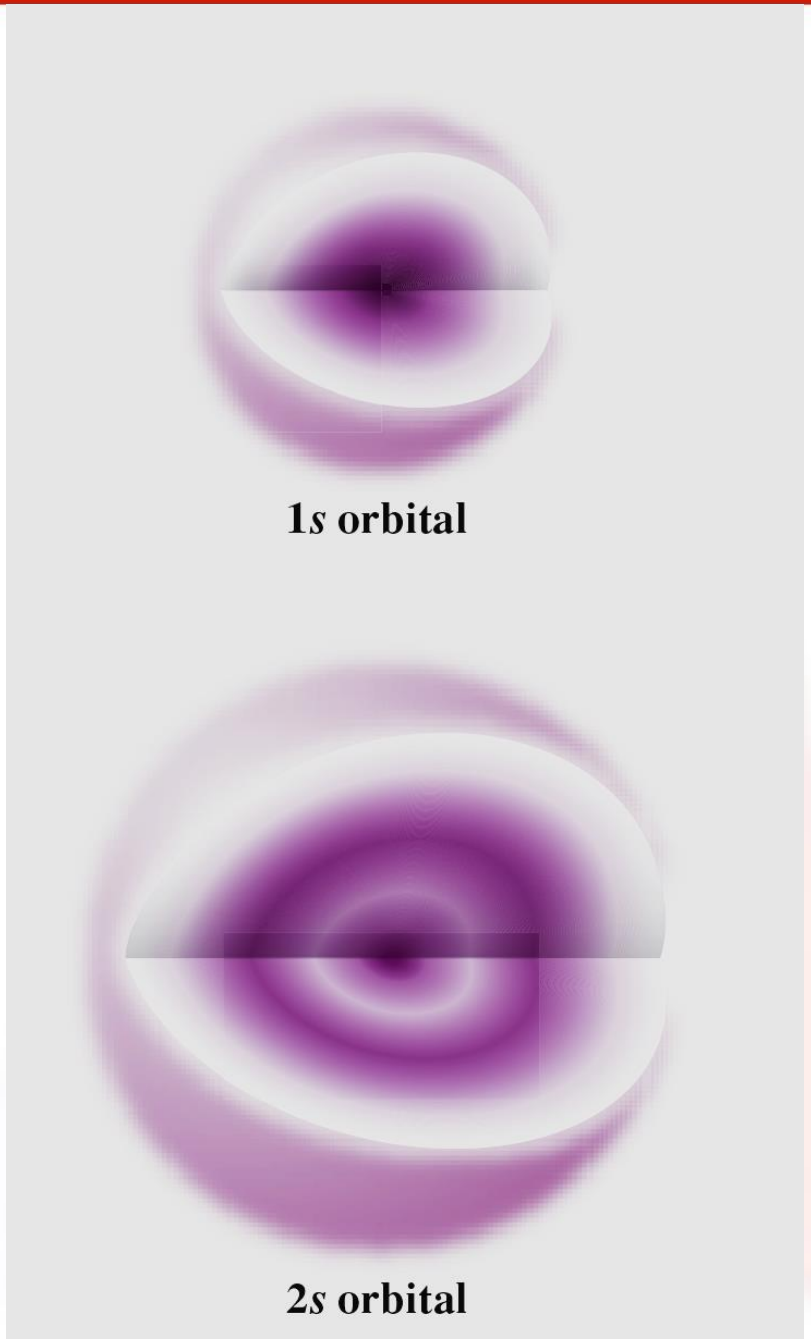
A *p* orbital has two lobes along a straight line through the nucleus, with one lobe on either side.

A *d* orbital has a more complicated shape.

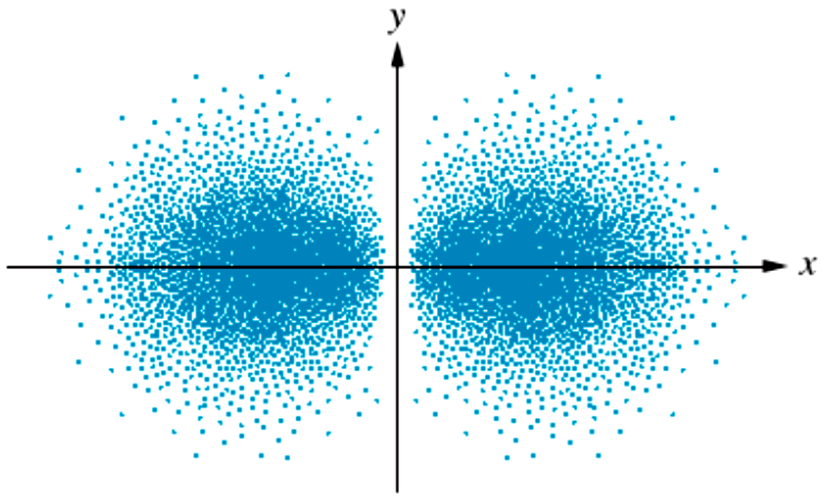
The cross-sectional view of a 1*s* orbital and a 2*s* orbital highlights the difference in the two orbitals' sizes.



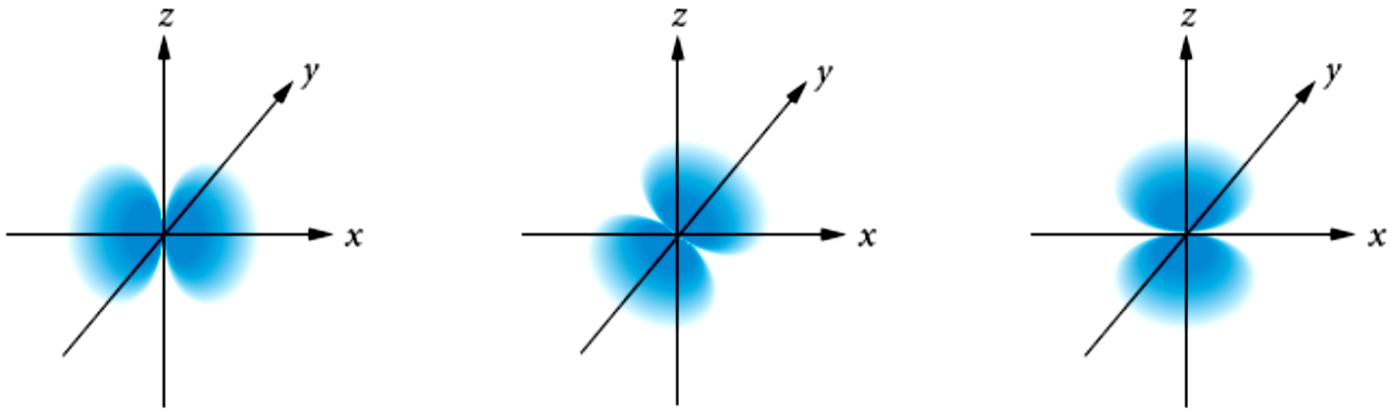
The cutaway diagrams of the 1*s* and 2*s* orbitals give a better sense of them in three dimensions.



Shape of the three *p* orbitals



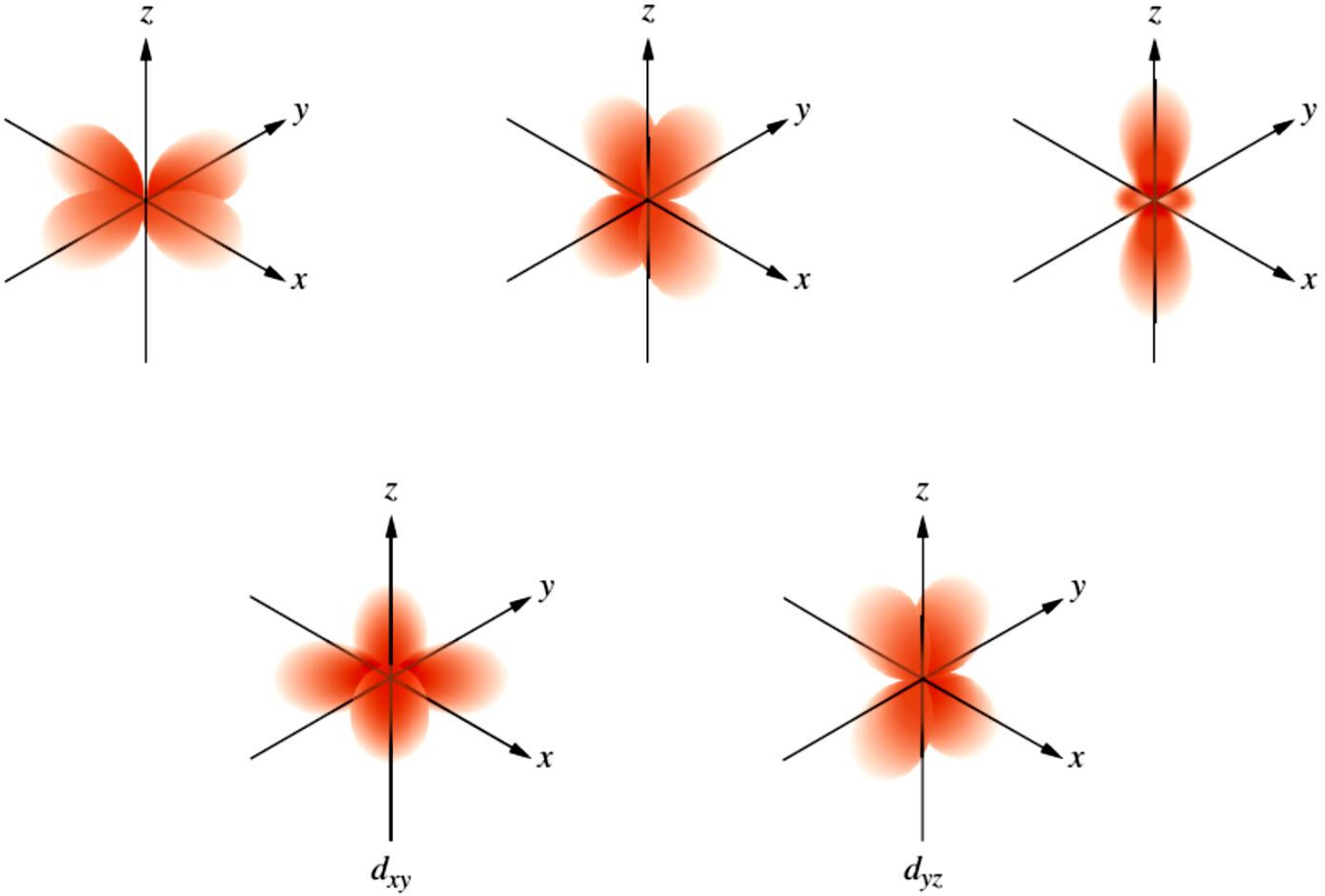
A



$2p_x$ orbital $2p_y$ orbital $2p_z$ orbital

B

Shape of the five *d* orbitals

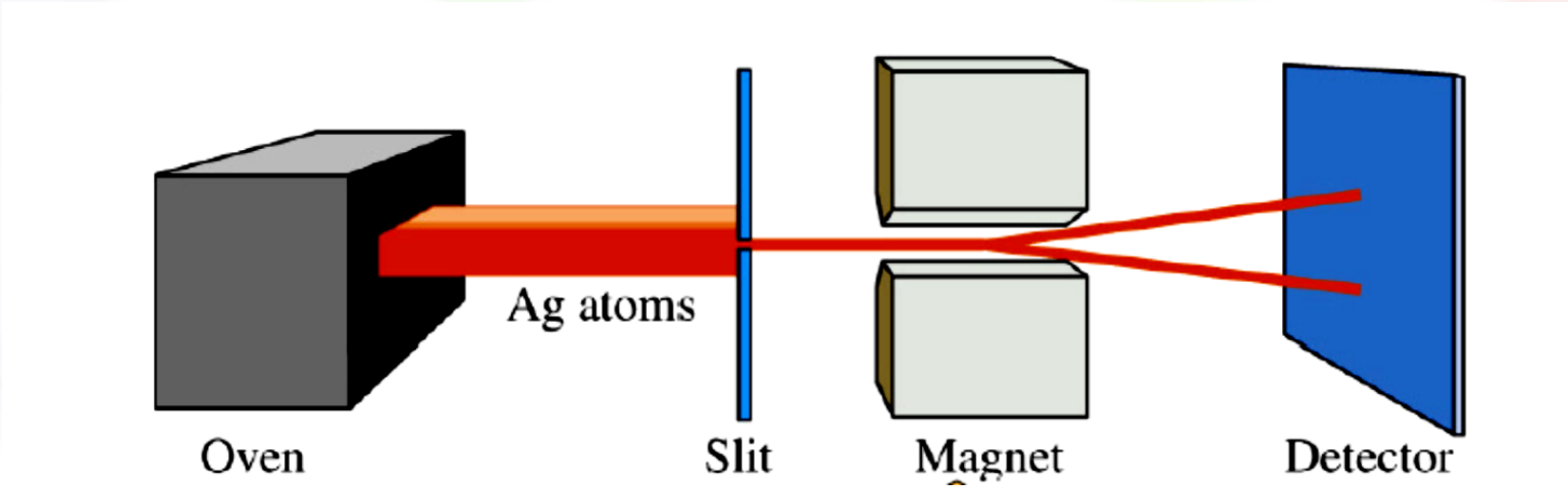


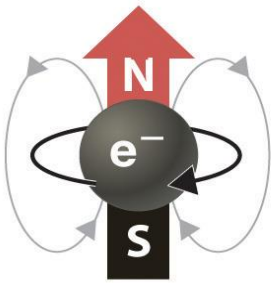
Electron Spin Quantum Number (ms)

This means that when ms is positive the electron has an upward spin, which can be referred to as "spin up."

When it is negative, the electron has a downward spin, so it is "spin down."

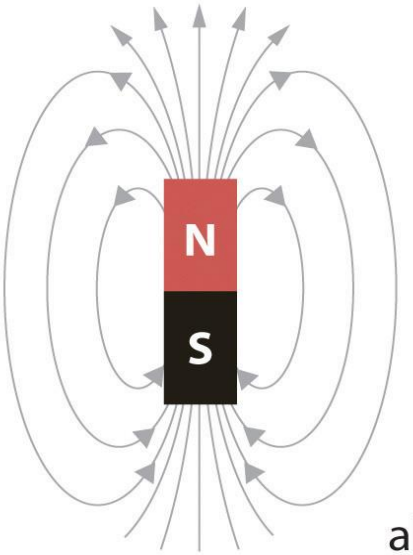
The significance of the electron spin quantum number is its determination of an atom's ability to generate a magnetic field or not.

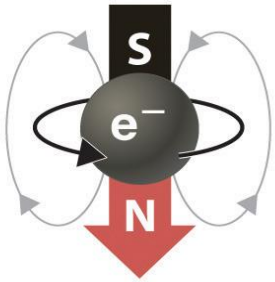




Electron aligned with magnetic field:

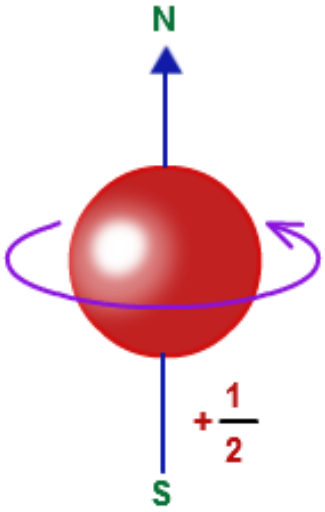
$m_s = +\frac{1}{2}$

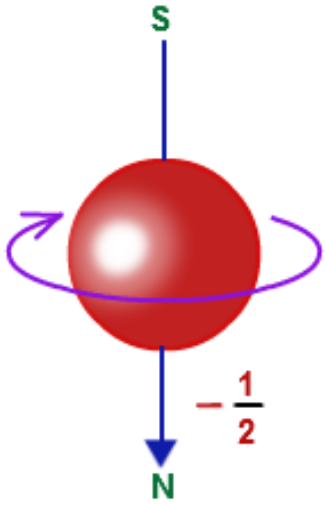


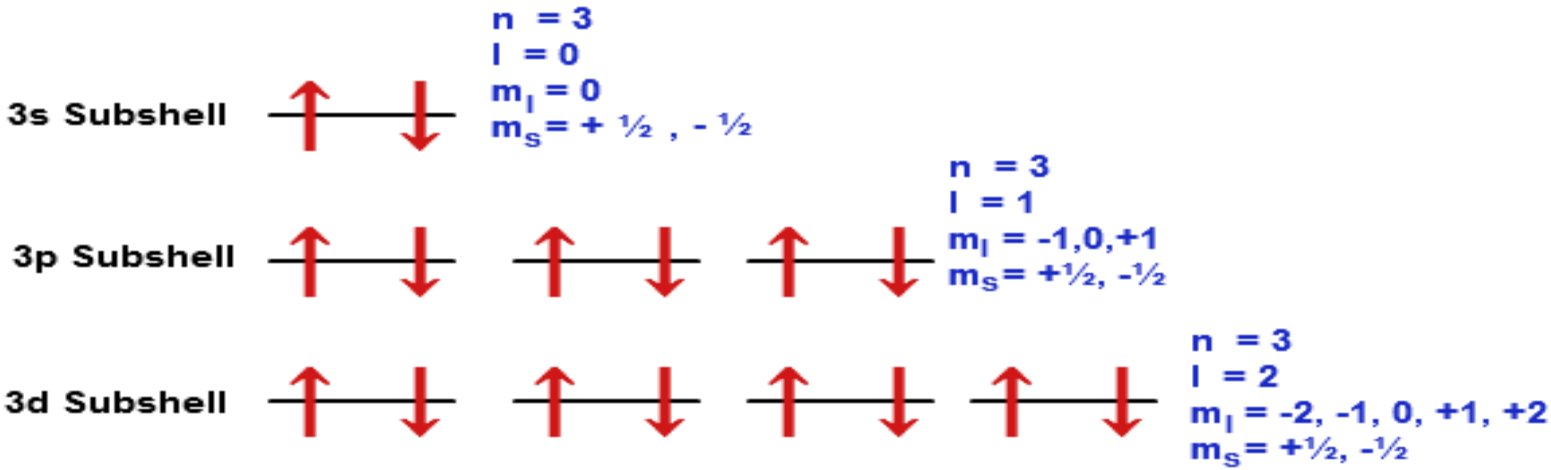


Electron aligned against magnetic field:

$m_s = -\frac{1}{2}$







* The value of l indicates s, p, or d subshell
* Each black line represents one orbital (value count of m_l)
* The direction of the arrow represent m_s

Multielectronic atoms

The repulsion between electrons translates in which the electrons in a multielectronic atom try to stay away of others and their movements are entangled with each other.

In multielectronic atoms, the attractive force of the nucleus to a given electron increases with the nuclear charge.

In the atoms multielectronics, the energies of the orbitals depend on the type of orbital; the Orbitals with different values of E within the same main layer are not degenerate.

Penetration and shielding

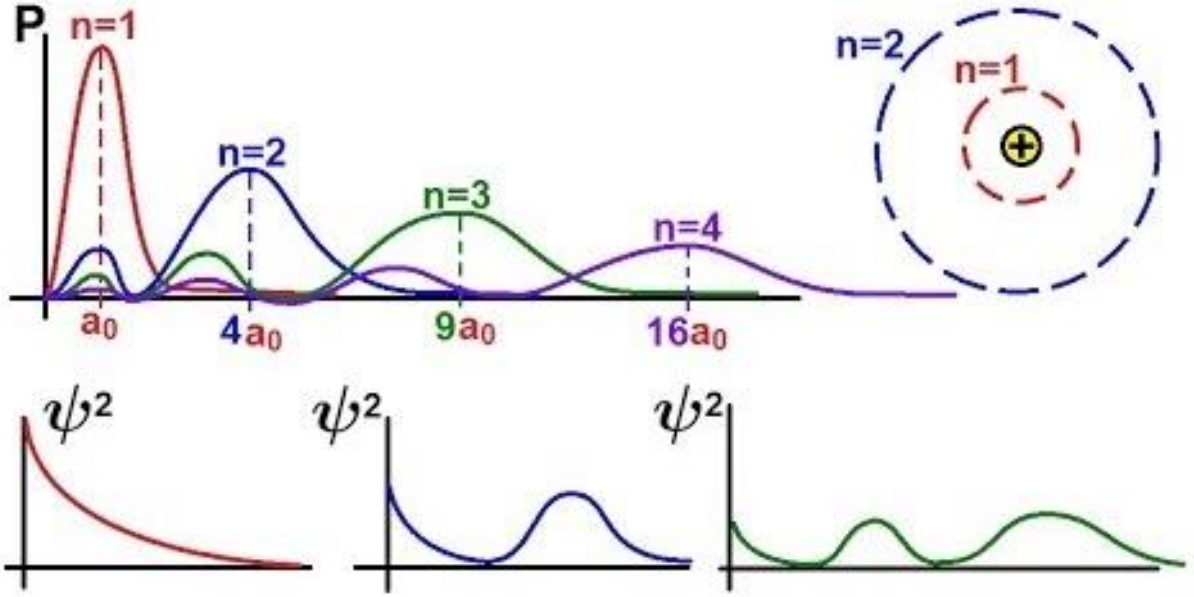
The electrons in the orbitals closest to the nucleus shield the core of the most external electrons. In effect, electron shielding reduces the efficiency of the attraction of the nucleus makes the electron more distant.

The reduction of the nuclear charge depends on the type of orbitals in which they are located

The electrons in the orbitals are more effective in shielding the nucleus to the most external electrons, that the electrons in the orbitals p or d. This ability is called **penetration**. An electron in an orbital with good penetration shields better than one with low penetration.

The radial portion of the wavefunction really only tells us if there is high or low probability at various distances from the nucleus.

Multiplying this probability by the area available at that distance will give us the ***Radial Distribution Function*** for the given electron. The concentric spherical shells have areas equal to the surface area of a sphere which is $4\pi r^2$.



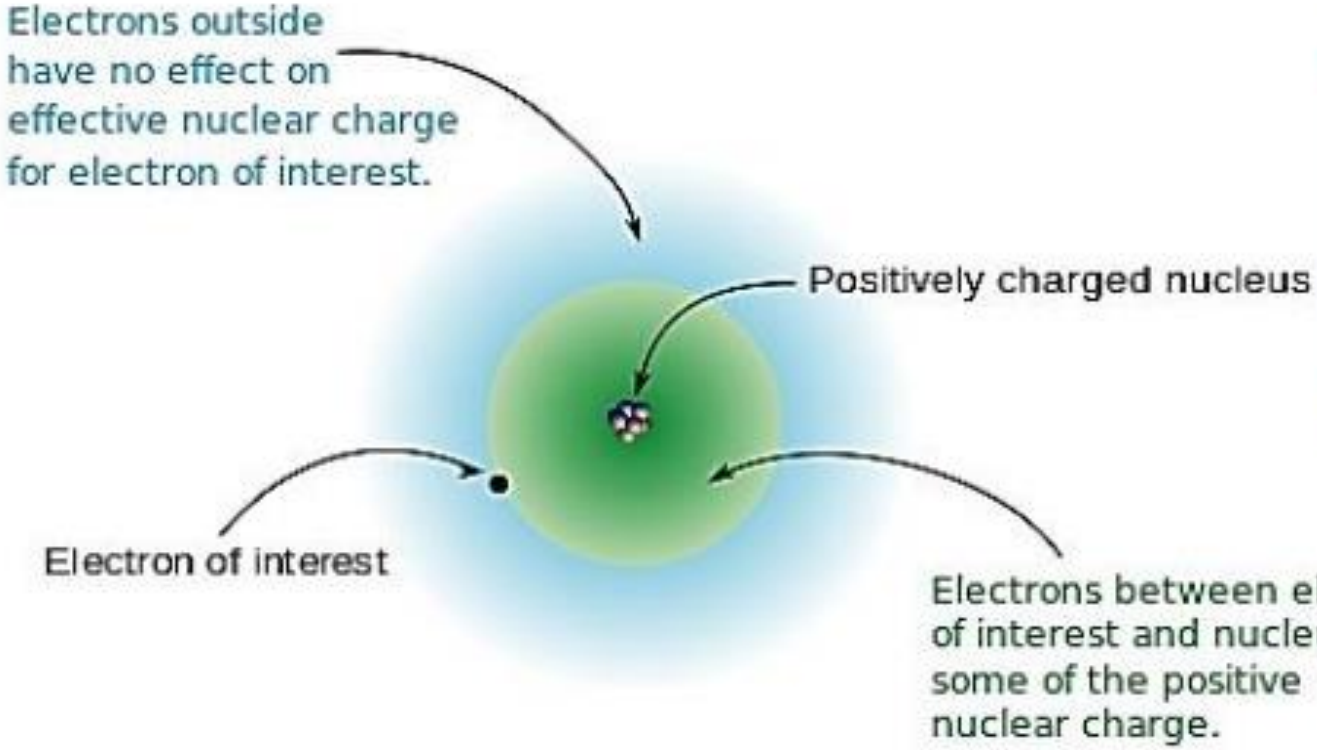
The effective nuclear charge

The magnitude of the shielding effect is difficult to calculate precisely. As an approximation, we can estimate the effective nuclear charge on each electron.

The effective nuclear charge (often symbolized as Z_{eff} or Z*) is the net positive charge experienced by an electron in a multi-electron atom. The term “effective” is used because the shielding effect of negatively charged electrons prevents higher orbital electrons from experiencing the full nuclear charge.

Effective nuclear charge Z_{eff} vs. nuclear charge Z

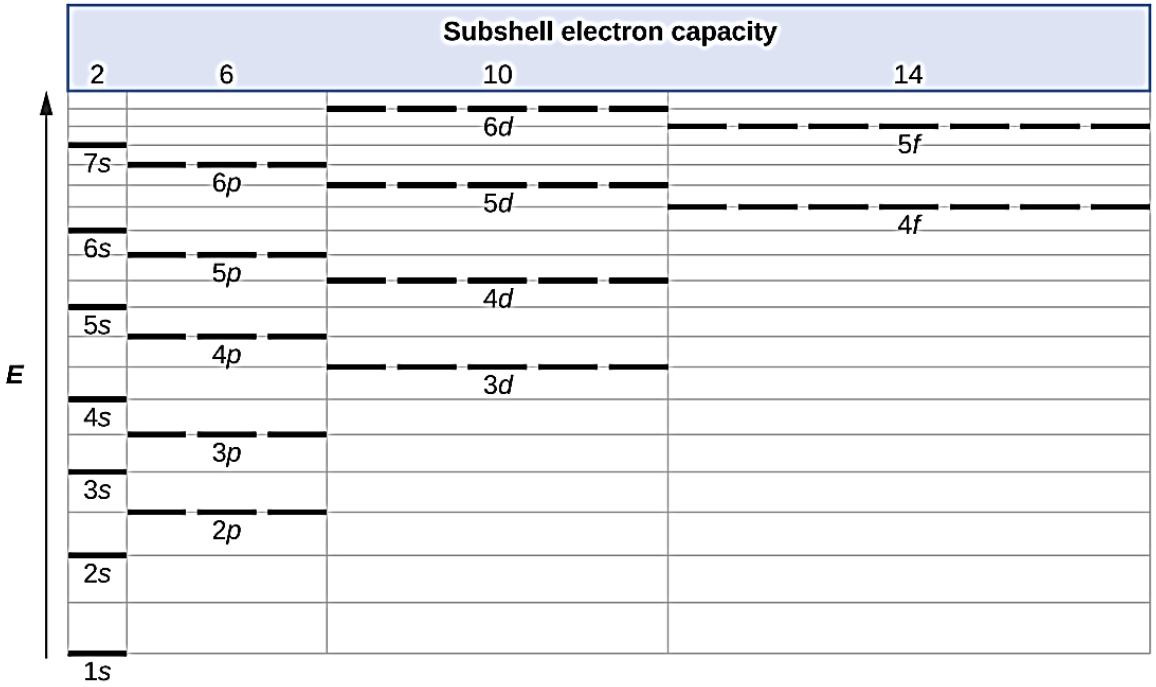
$$Z_{\text{eff}} = Z - \sigma$$



Average nr of electrons between the electron and the nucleus

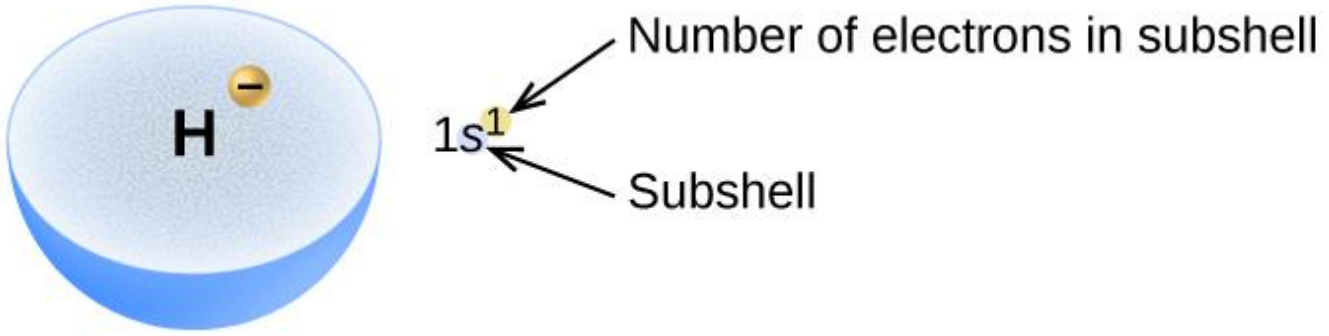
Electronic configuration

The energy of atomic orbitals increases as the principal quantum number, *n*, increases. In any atom with two or more electrons, the repulsion between the electrons makes energies of subshells with different values of *l* differ so that the energy of the orbitals increases within a shell in the order *s* < *p* < *d* < *f*.



The arrangement of electrons in the orbitals of an atom is called the **electron configuration** of the atom. We describe an electron configuration with a symbol that contains three pieces of information The number of the principal quantum shell, *n*,

The letter that designates the orbital type (the subshell, *l*), and A superscript number that designates the number of electrons in that particular subshell.



Rules for the distribution of electrons in orbitals

1. The electrons occupy the orbitals in a way that minimizes the energy of the atom.
2. The **principle of exclusion of Pauli**: two electrons of an atom can not have the four equal quantum numbers.
3. **Hund's principle:** When there are orbitals with the same energy (degenerate), the electrons occupy initially these orbitals individually.

The Aufbau principle

Aufbau is a German word meaning "progressive construction", and we will use this method to assign the electronic configurations to the elements in order of their number atomic credential

When we move from one atom to the next, we add a proton and some neutrons to the nucleus and then we describe the orbital where the added electron goes.

Filling order Diagram



Aufbau Principle

Electronic configurations and the periodic table

