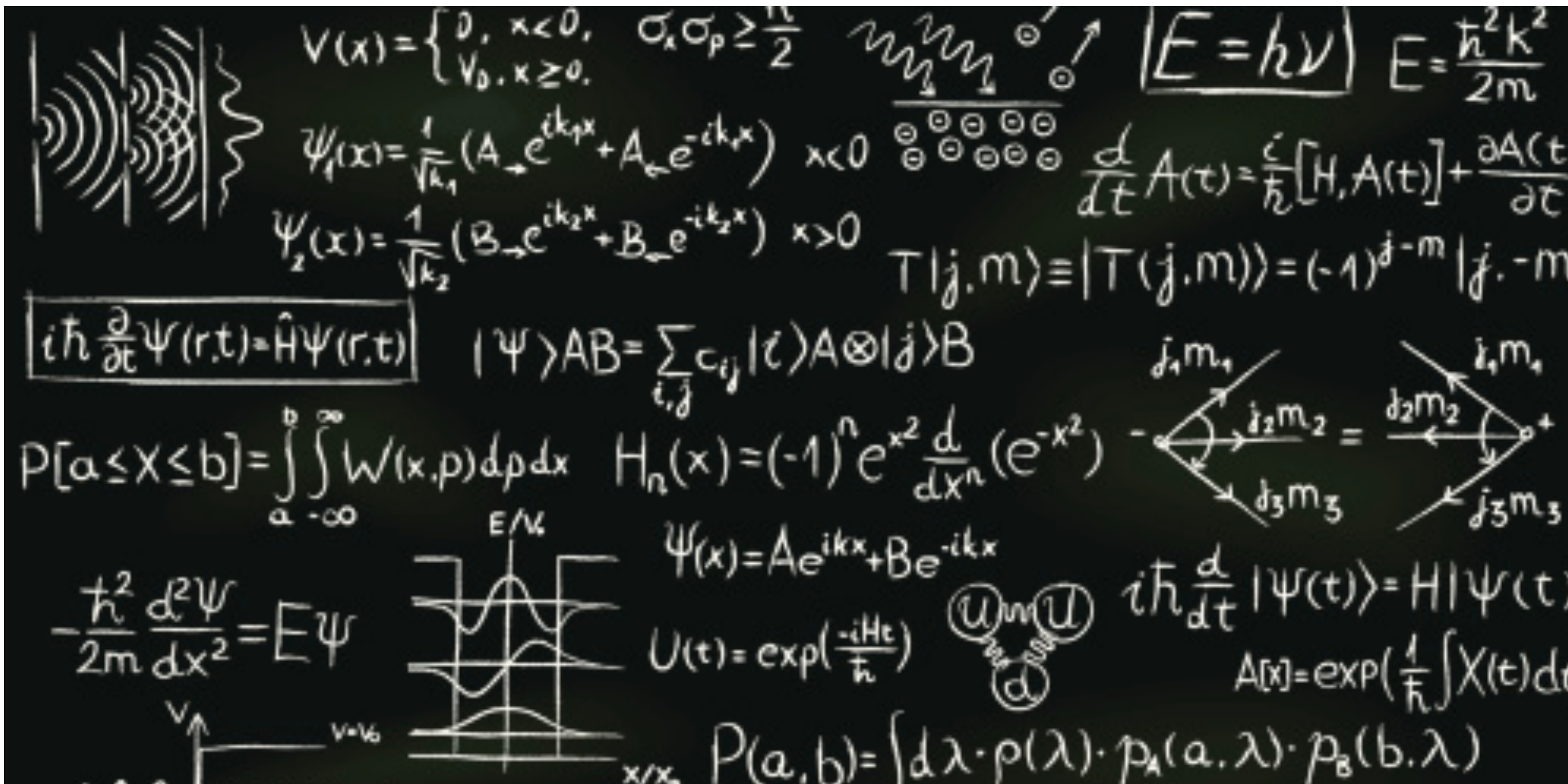
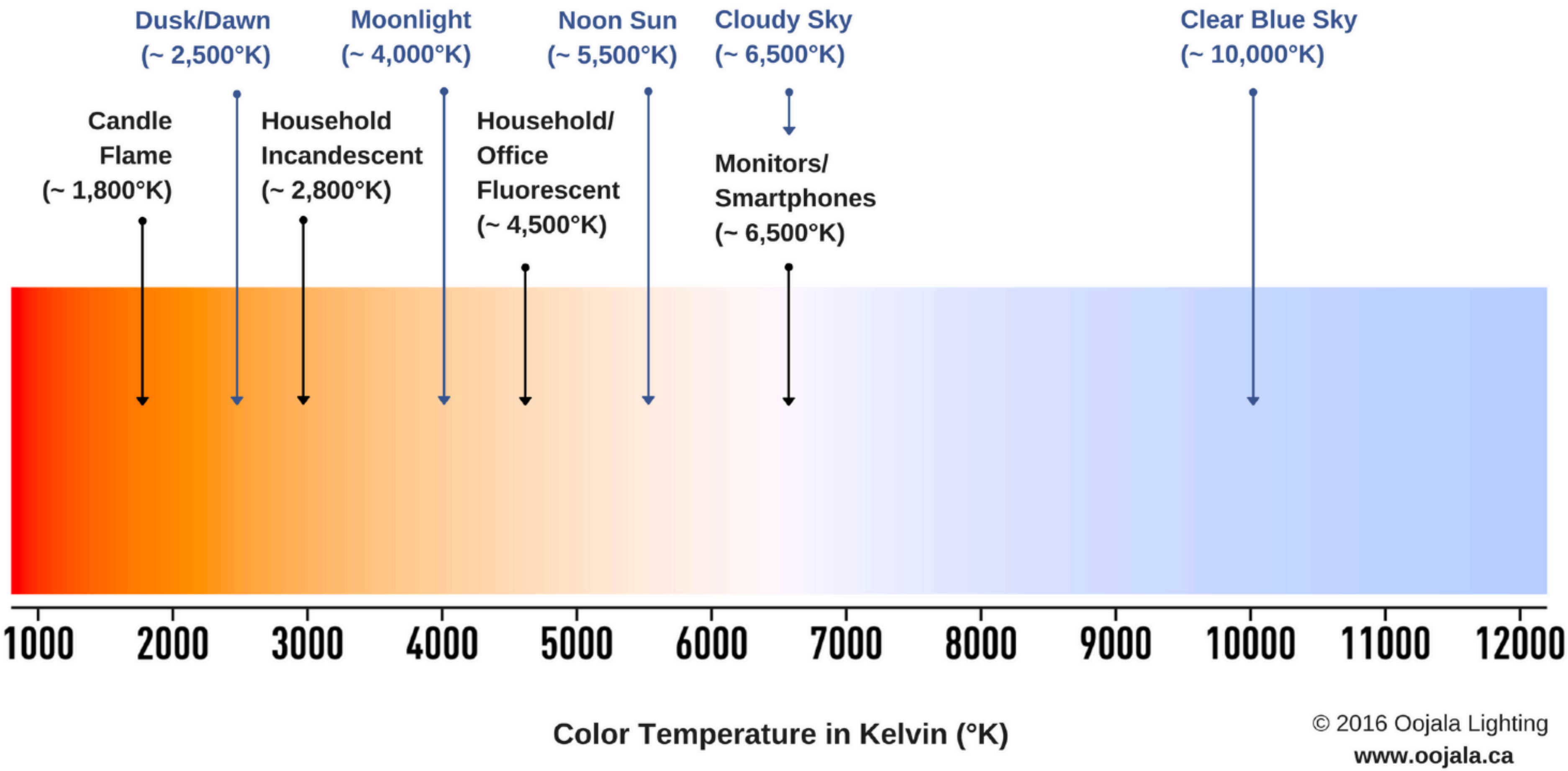
Atomic Physics

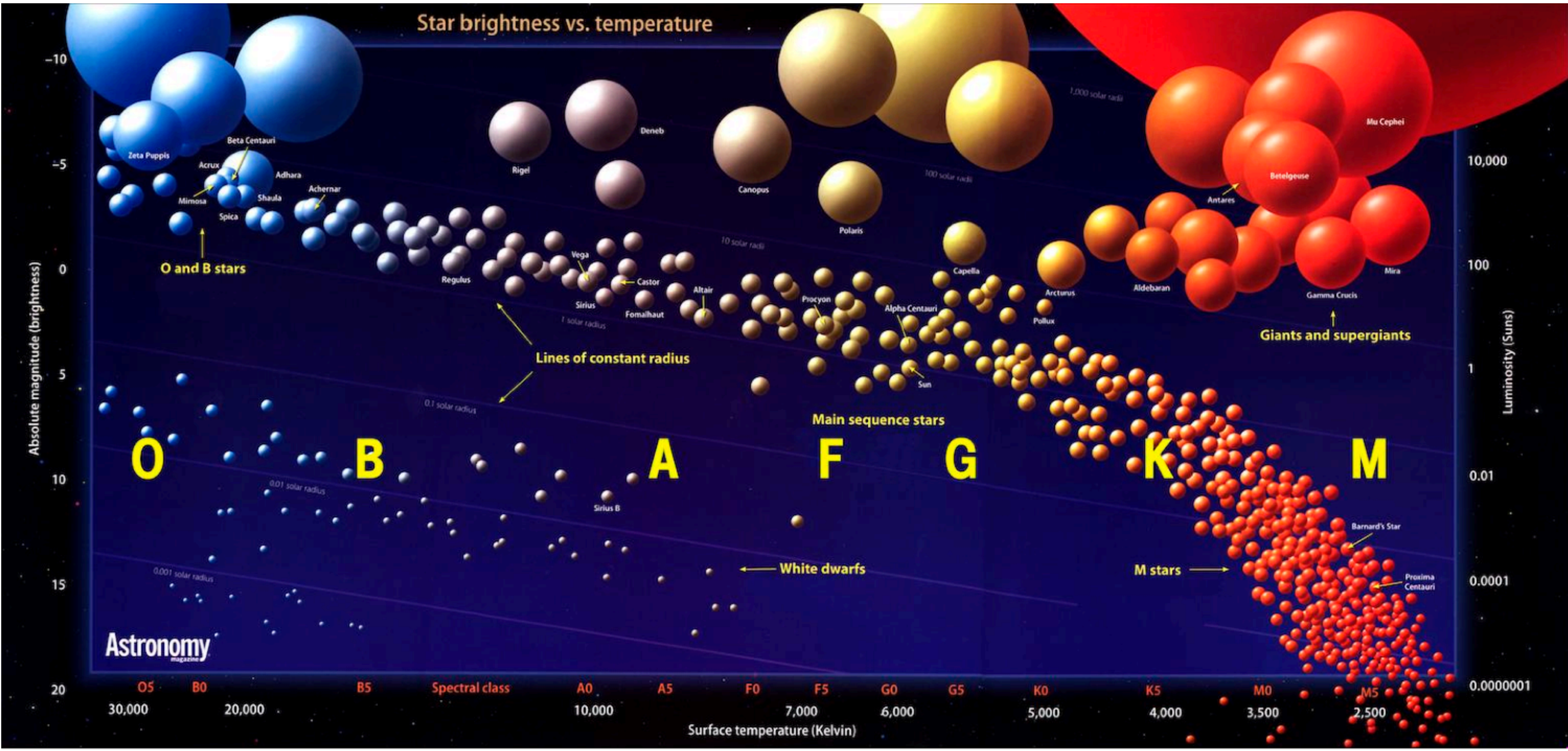
Chapter 3 Quantum Mechanics of the Hydrogen Atom



Blackbody Radiation

If the temperature were increased still further, the color would progress through orange, yellow, and finally white.



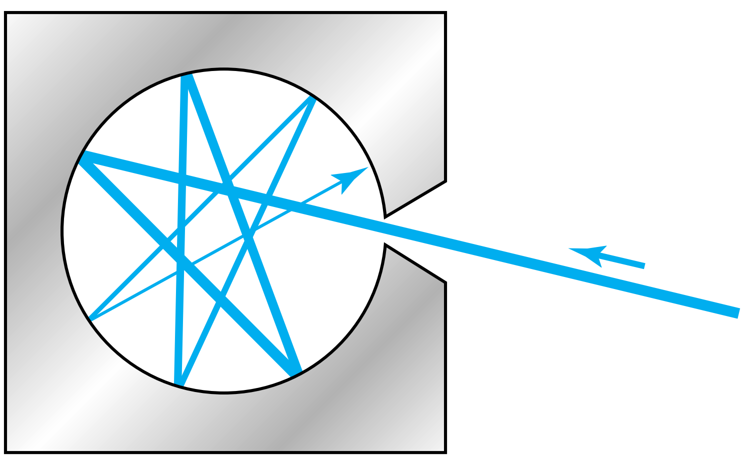

Star brightness vs. temperature
Absolute magnitude (brightness)
-10
-5
0
5
10
15
20
Luminosity (Suns)
10,000
100
1
0.01
0.0001
0.0000001
Zeta Puppis
Beta Centauri
Acrux
Adhara
Mimosa
Shaula
Spica
Achernar
Rigel
Deneb
Canopus
Polaris
Capella
Mu Cephei
Betelgeuse
Antares
Aldebaran
Mira
Gamma Crucis
Arcturus
Pollux
Regulus
Vega
Castor
Sirius
Fomalhaut
Altair
Procyon
Alpha Centauri
Sun
O and B stars
Lines of constant radius
Giants and supergiants
Main sequence stars
1,000 solar radii
100 solar radii
10 solar radii
1 solar radius
0.1 solar radius
0.01 solar radius
0.001 solar radius
O
B
A
F
G
K
M
Sirius B
White dwarfs
Barnard's Star
Proxima Centauri
M stars
Astronomy
O5
B0
B5
Spectral class
A0
A5
F0
F5
G0
G5
K0
K5
M0
M5
30,000
20,000
10,000
7,000
6,000
5,000
4,000
3,500
2,500
Surface temperature (Kelvin)

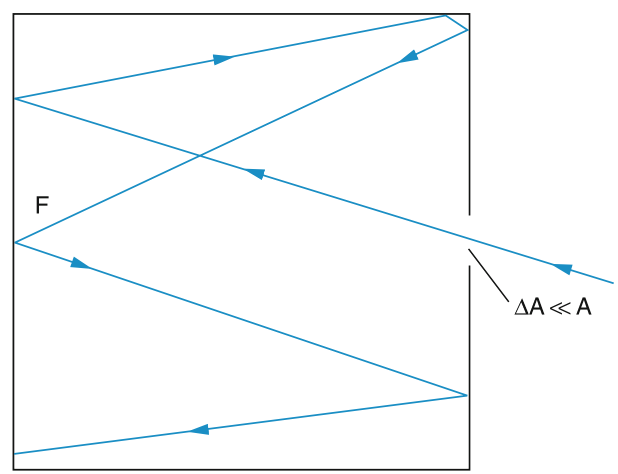
Blackbody Radiation

Thermal equilibrium: one body absorbs thermal energy at the same rate as it emits it.

Blackbody: it absorbs all the radiation falling on it and reflects none. (idealized case)

The simplest way to construct a blackbody is to drill a small hole in the wall of a hollow container.





Blackbody Radiation

The radiation properties of the blackbody are independent of the particular material of which the container is made.

Spectral distribution: properties of intensity versus wavelength at fixed temperatures.

The intensity:

$$\mathcal{R}(\lambda, T)$$

is the total power radiated per unit area per unit wavelength at a given temperature.

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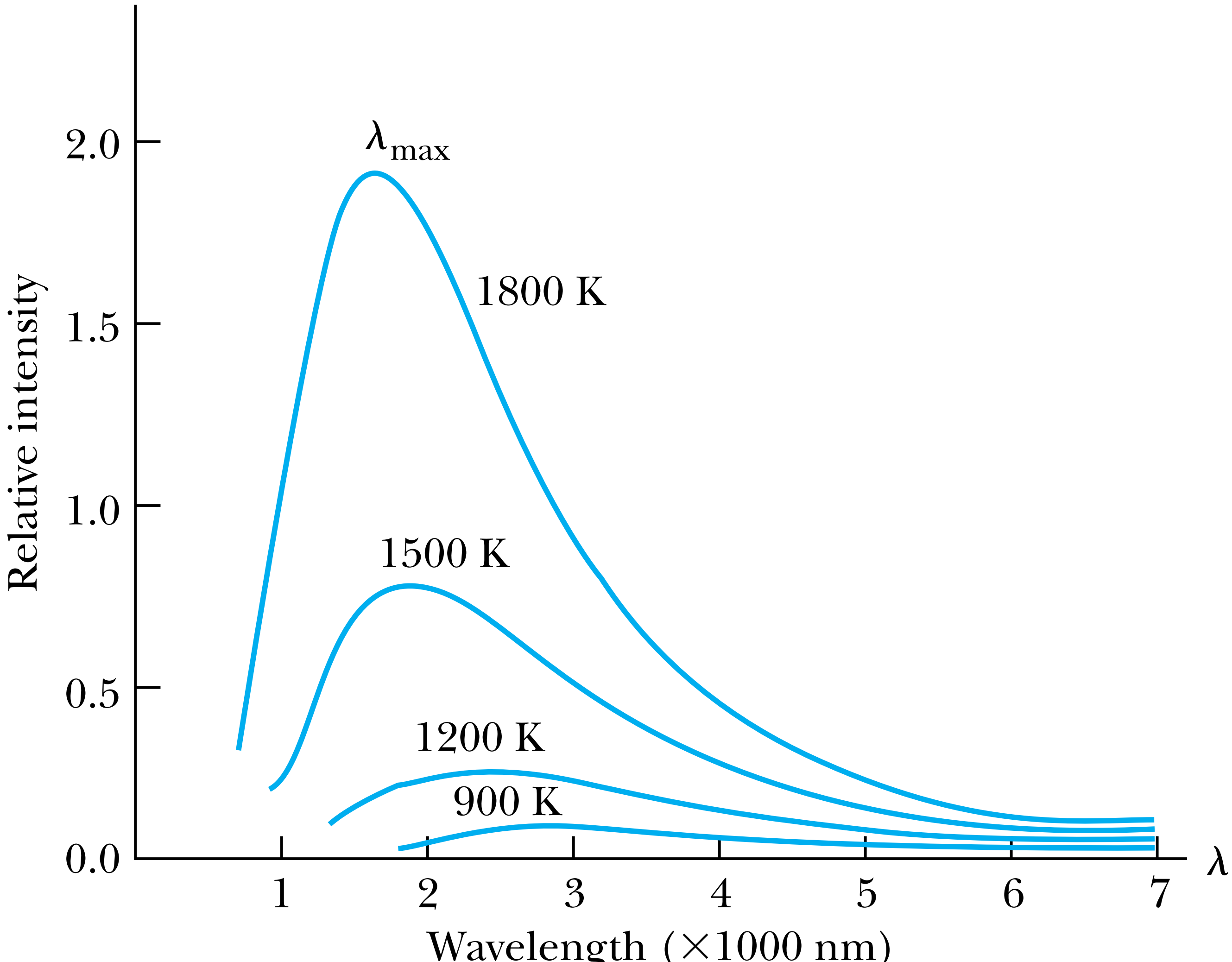
Measurements of intensity for a blackbody are displayed



Measurements of intensity for a blackbody are displayed

Temperature	Wavelength for Maximum Intensity	
3000K	966 nm	(IR)
4000K	724 nm	(Red)
5000K	580 nm	(Yellow)
6000K	483 nm	(Blue)

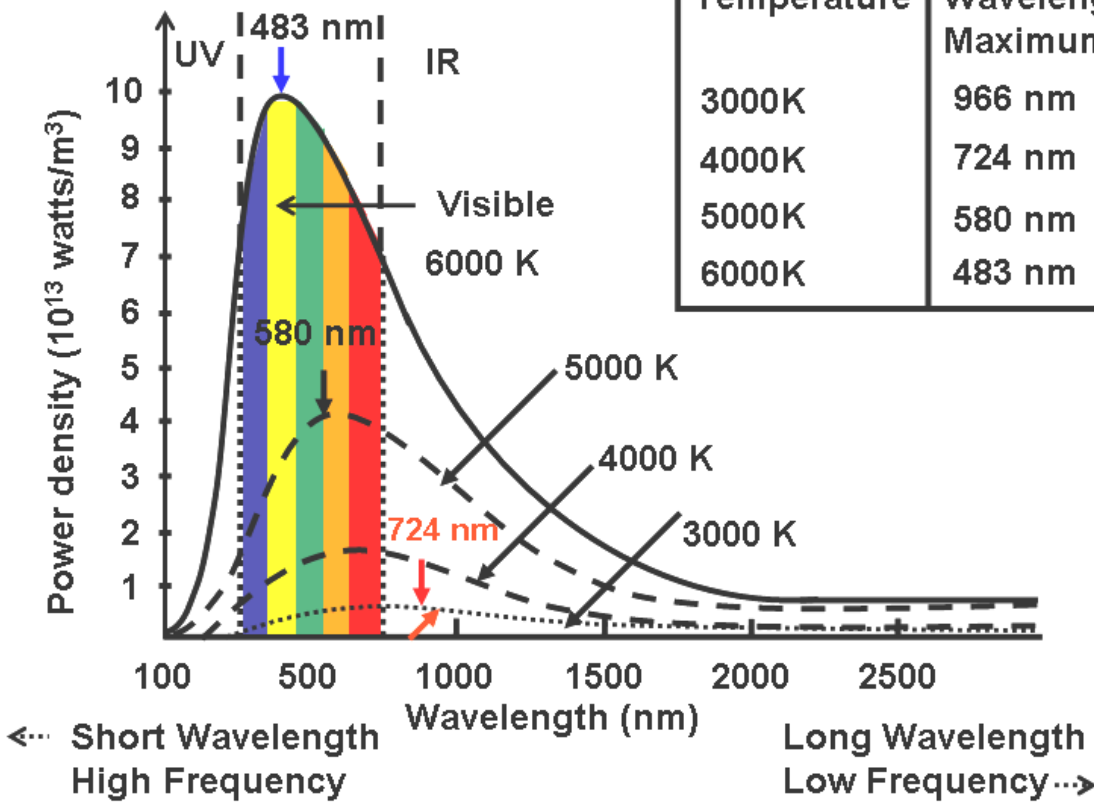


Fig. Spectral intensity distribution of Blackbody Radiation vs Wavelength Intensity Maximum shifts to shorter wavelengths as temperature increases.

Two important observations should be noted:

1. The maximum of the distribution shifts to smaller wavelengths as the temperature is increased.
2. The total power radiated increases with the temperature.

The first observation is expressed in Wien's displacement law:

$$\lambda_{\rm max} T = 2.898 \times 10^{-3}\ {\rm m \cdot K}$$

where λ_{max} is the wavelength of the peak of the spectral distribution at a given temperature.

Wilhelm Wien received the Nobel Prize in 1911 for his discoveries concerning radiation.

We can quantify the second observation by integrating the quantity intensity over all wavelengths to find the power per unit area at temperature T:

$$R(T) = \int_0^\infty \mathcal{R}(\lambda, T) d\lambda$$

Stefan-Boltzmann law:

$$R(T) = \epsilon\sigma T^4$$

with the constant

$$\sigma = 5.6705 \times 10^{-8}\ \mathrm{W/(m^2 \cdot K^4)}$$

The emissivity ε is simply the ratio of the emissive power of an object to that of an ideal blackbody and is always less than 1.

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Rayleigh-Jeans formula:

$$\mathcal{R}(\lambda, T) = \frac{2\pi ckT}{\lambda^4}$$

It is the best formulation that classical theory can provide to describe blackbody radiation.

When

$$\lambda \to 0$$

the total energy of all configurations is infinite. In 1911 Paul Ehrenfest dubbed this situation the "ultraviolet catastrophe," and it was one of the outstanding exceptions that classical physics could not explain.

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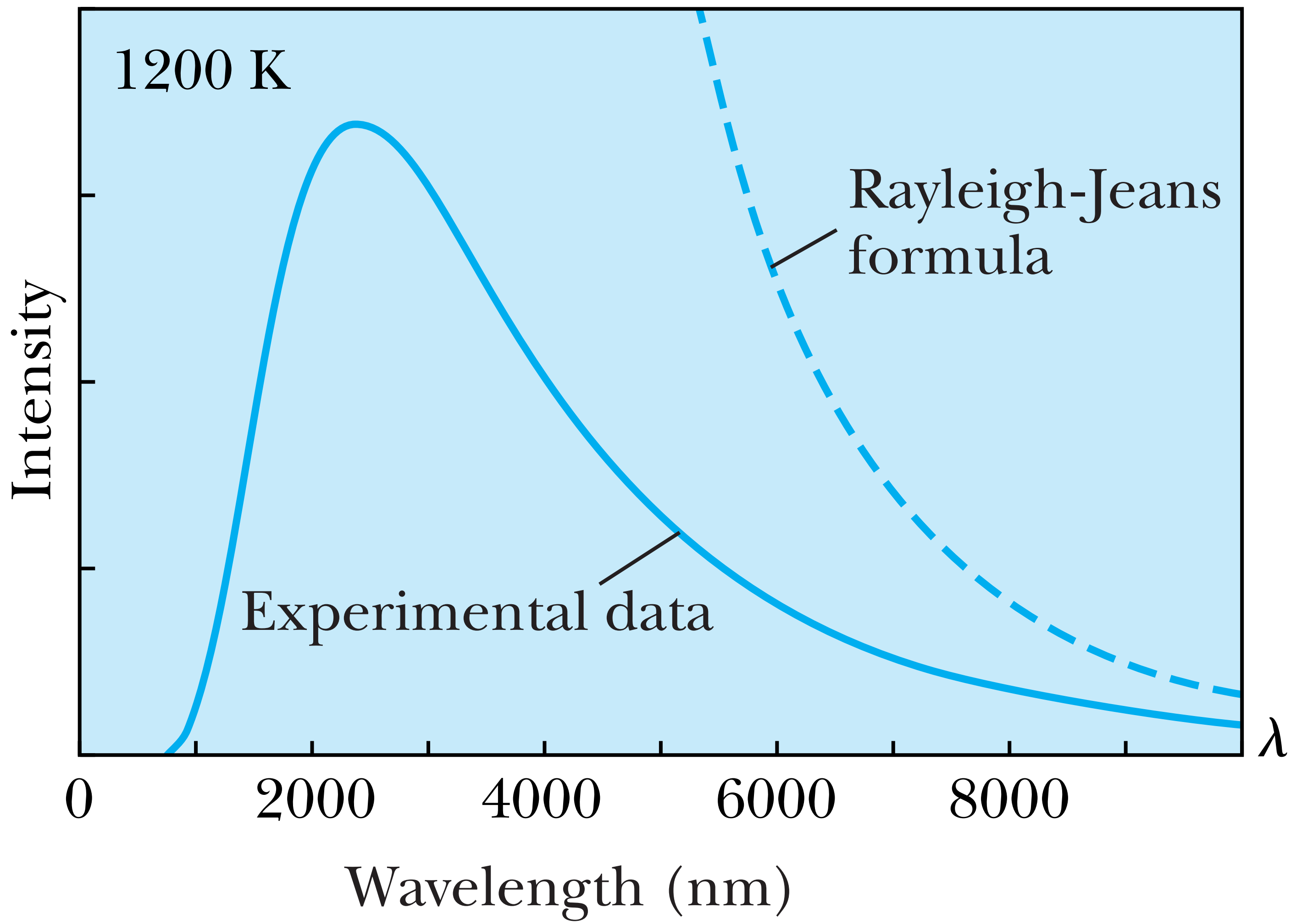
1200 K
Rayleigh-Jeans formula
Experimental data
Intensity
λ
0
2000
4000
6000
8000
Wavelength (nm)

Max Plank

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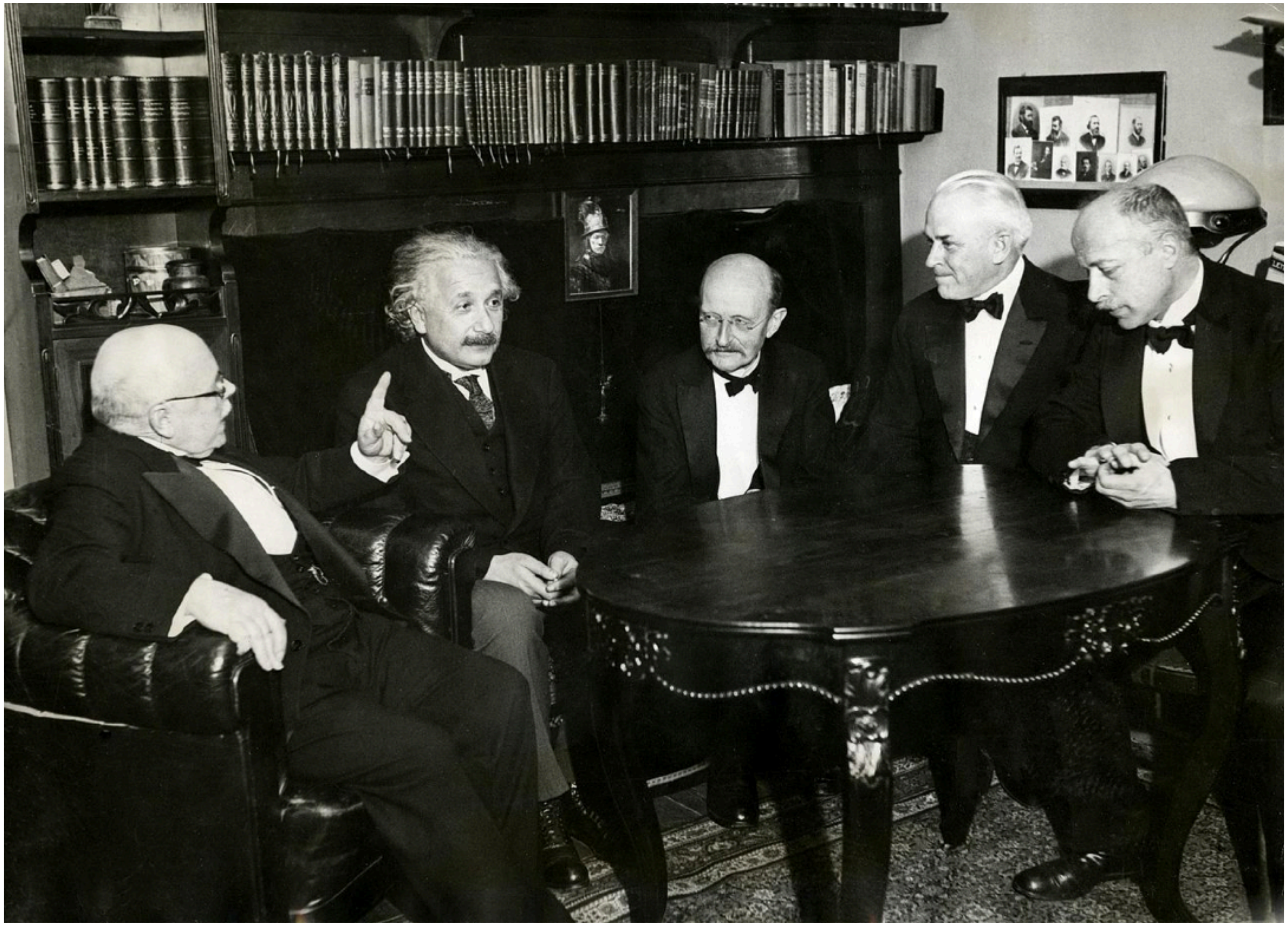
Max Plank



W. Nernst, A. Einstein, **M. Planck**, R.A. Millikan and von Laue

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Planck's radiation law:

$$\mathcal{R}(\lambda, T) = \frac{2\pi c^2 h}{\lambda^5} \frac{1}{e^{hc/\lambda kT} - 1}$$

He could arrive at agreement with the experimental data only by making two important modifications of classical theory:

1. The oscillators (of electromagnetic origin) can only have certain discrete energies determined by

$$E_n = nh\nu$$

where n is an integer, f is the frequency, and h is called Planck's constant and has the value

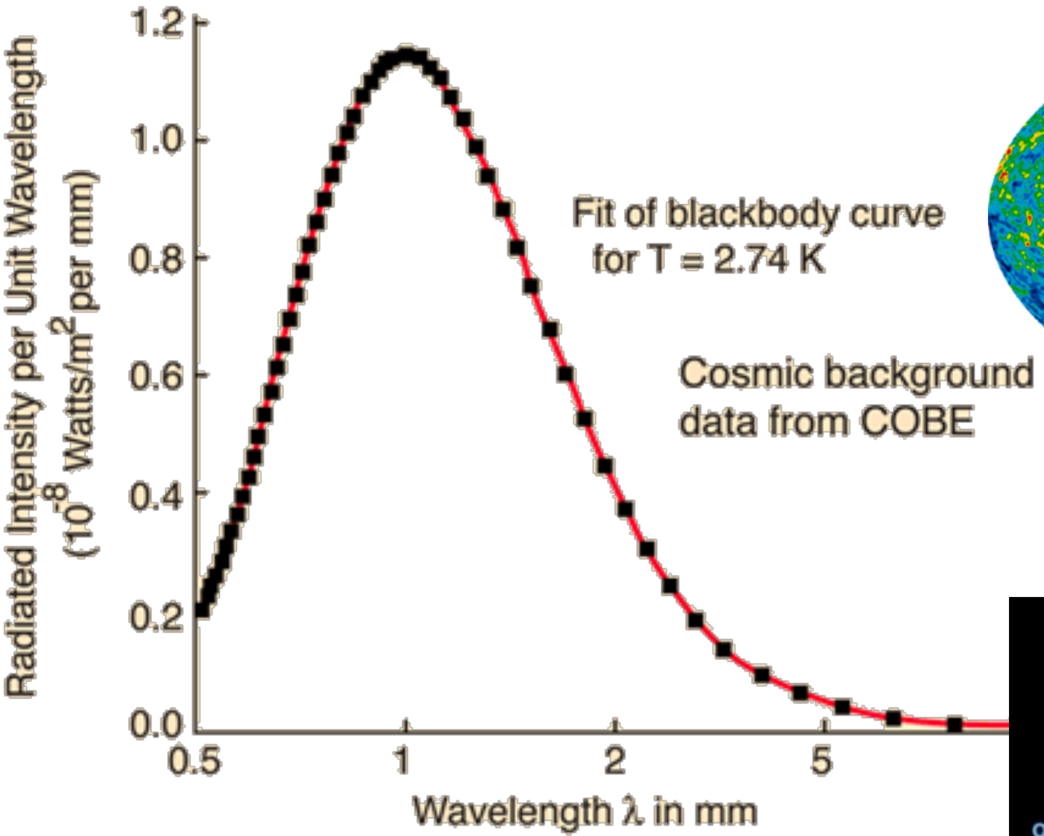
$$h = 6.6261 \times 10^{-34} \mathrm{J \cdot s}$$

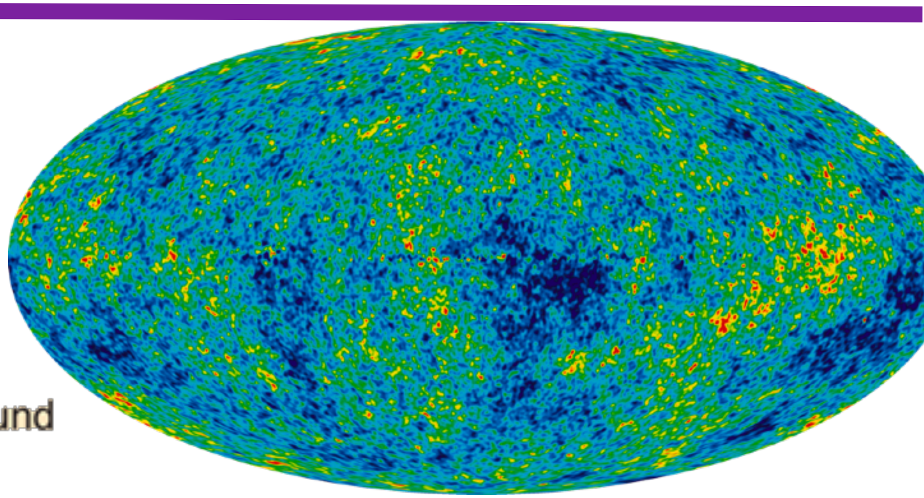
2. The oscillators can absorb or emit energy in discrete multiples of the fundamental quantum of energy given by

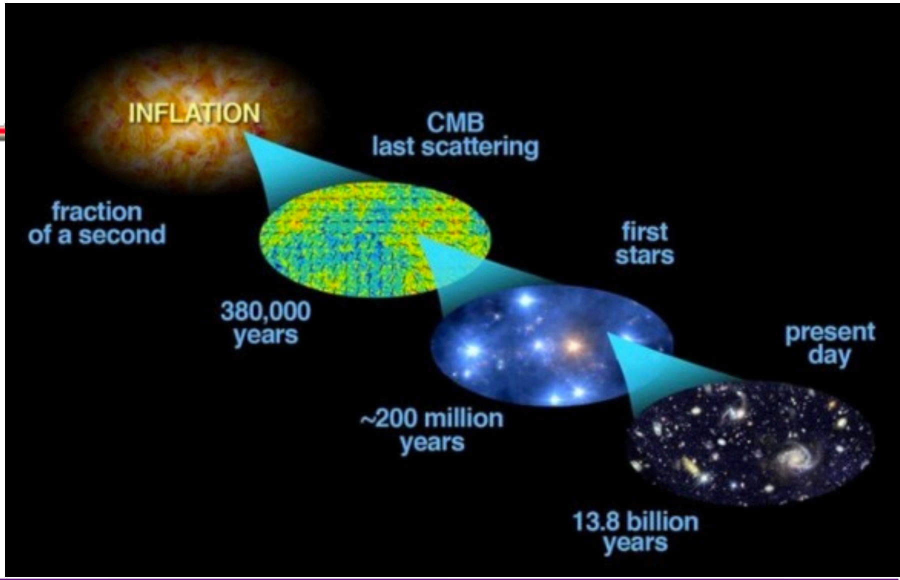
$$\Delta E = h\nu$$

Planck found these results quite disturbing and spent several years trying to find a way to keep the agreement with experiment while letting $h \rightarrow 0$. Each attempt failed, and Planck's quantum result became one of the cornerstones of modern science.

Cosmic microwave background







Problem: show that Wien's displacement law follows from Planck's radiation law.

Solution: To find the value of the Planck radiation law for a given wavelength, we set

$$\frac{d\mathcal{R}(\lambda, T)}{d\lambda} = 0, \text{ for } \lambda = \lambda_{\max}$$

so,

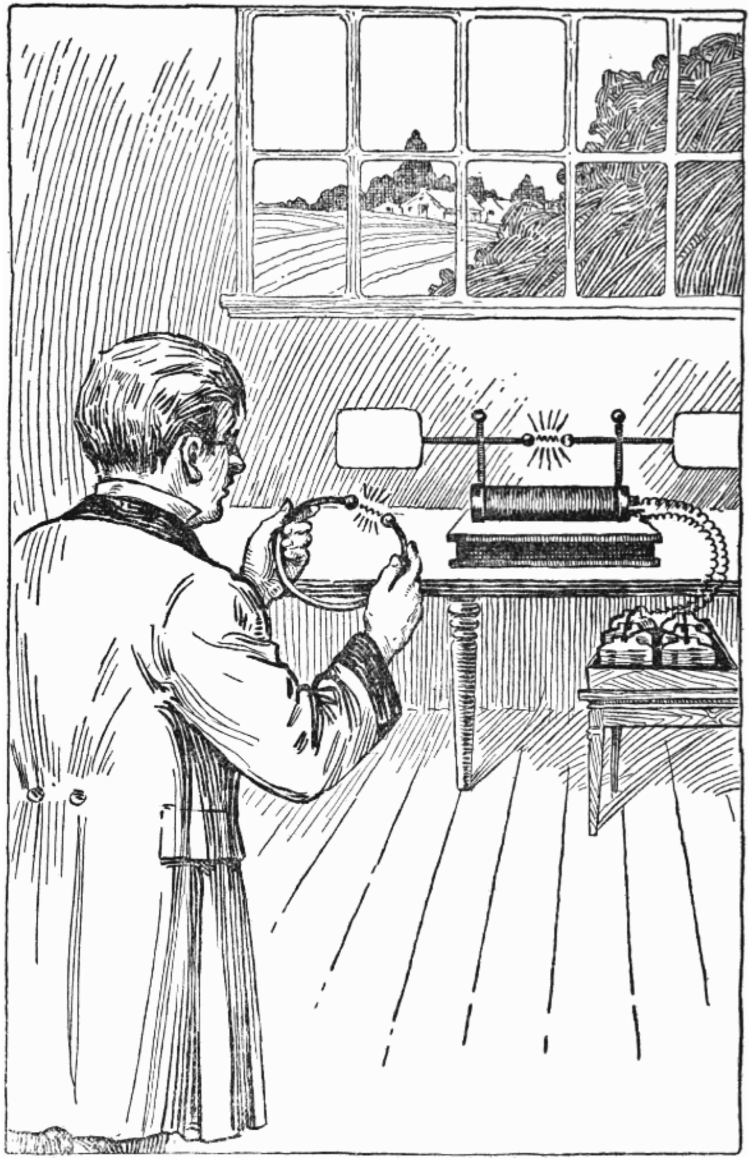
$$\frac{hc}{\lambda_{\max} kT}\left(\frac{e^{hc/\lambda_{\max} kT}}{e^{hc/\lambda_{\max} kT} - 1}\right) = 5,$$

Let,

$$x = \frac{hc}{\lambda_{\max} kT} \longrightarrow \lambda_{\max} = \frac{hc}{4.966k} = 2.898 \times 10^{-3} \text{m} \cdot \text{K}$$

Photoelectric Effect

While Heinrich Hertz was performing his famous experiment in 1887 that confirmed Maxwell's electromagnetic wave theory of light, he noticed that when ultraviolet light fell on a metal electrode, a charge was produced that separated the leaves of his electroscope.



Photoelectric Effect

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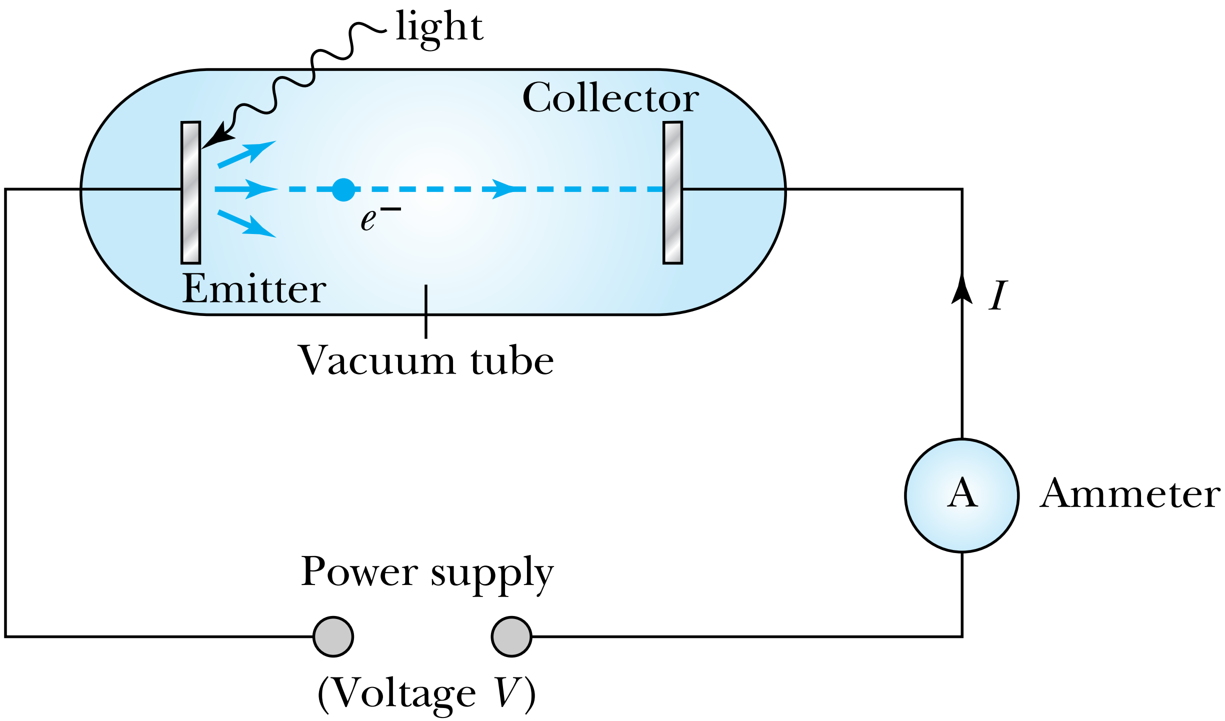
The photoelectric effect is one of several ways in which electrons can be emitted by materials.

The methods known now by which electrons can be made to completely leave the material include:

1. Thermionic emission: Application of heat allows electrons to gain enough energy to escape.
2. Secondary emission: The electron gains enough energy by transfer from a high-speed particle that strikes the material from outside.
3. Field emission: A strong external electric field pulls the electron out of the material.
4. Photoelectric effect: Incident light (electromagnetic radiation) shining on the material transfers energy to the electrons, allowing them to escape.

Experimental Results

Incident light falling on the emitter ejects electrons. Some of the electrons travel toward the collector (also called the anode), where either a negative (retarding) or positive (accelerating) applied voltage V is imposed by the power supply.



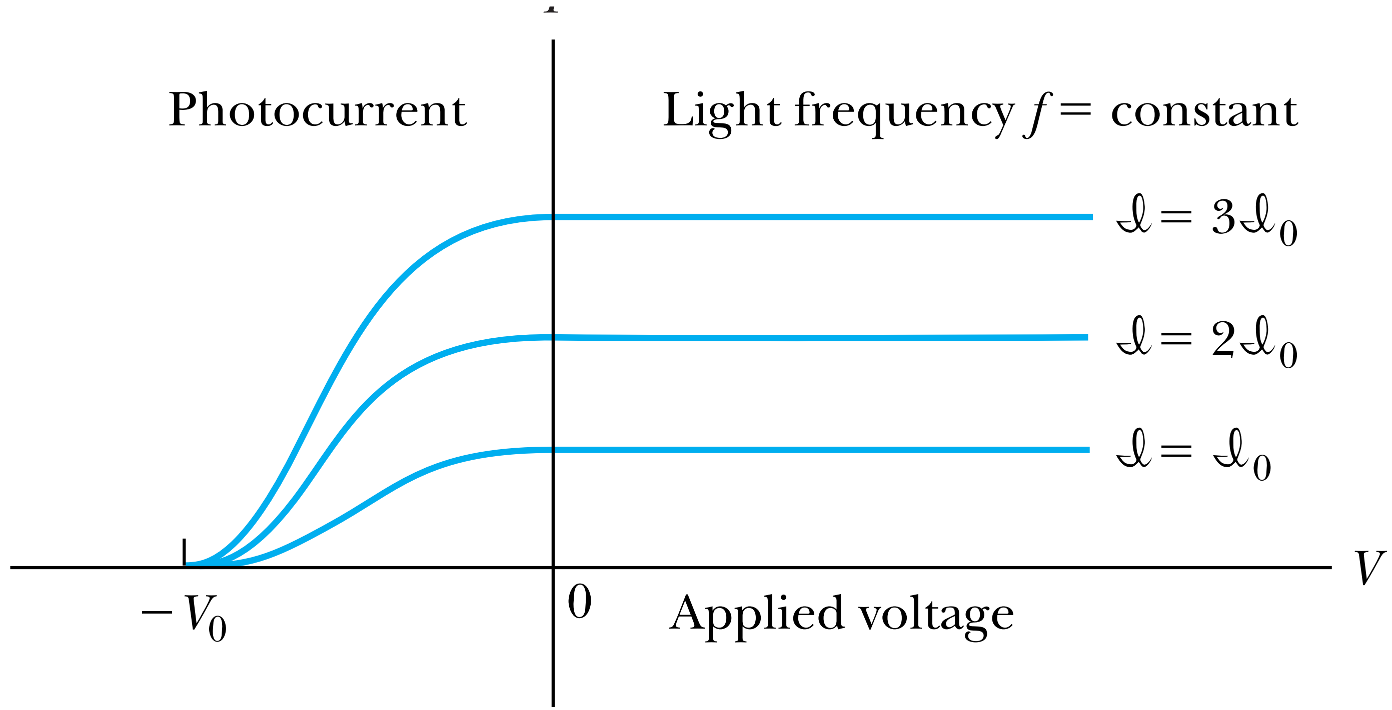
We call the ejected electrons photoelectrons. The minimum extra kinetic energy that allows electrons to escape the material is called the work function ϕ. The work function is the minimum binding energy of the electron to the material

Element	ϕ (eV)	Element	ϕ (eV)	Element	ϕ (eV)
Ag	4.64	K	2.29	Pd	5.22
Al	4.20	Li	2.93	Pt	5.64
C	5.0	Na	2.36	W	4.63
Cs	1.95	Nd	3.2	Zr	4.05
Cu	4.48	Ni	5.22		
Fe	4.67	Pb	4.25		

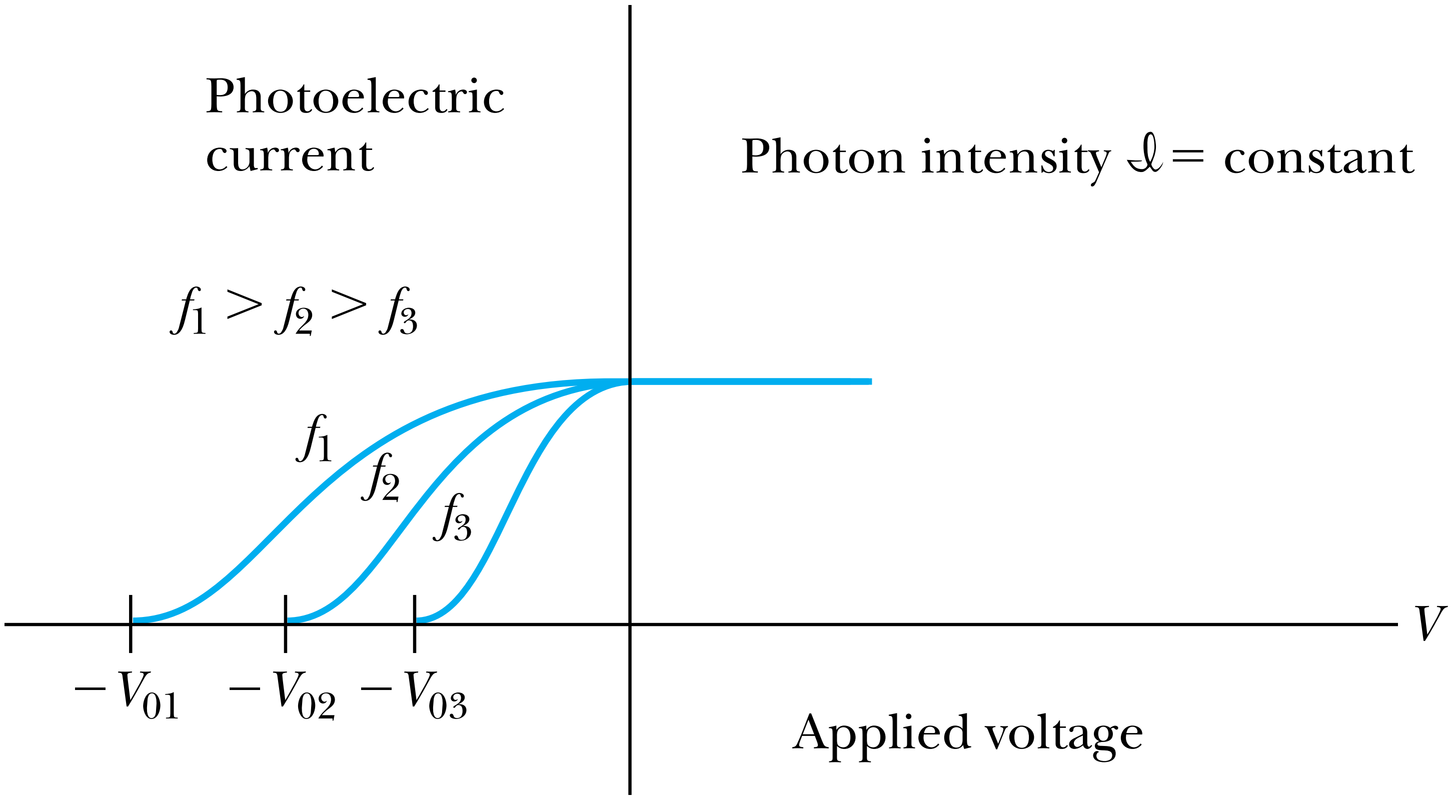
Experimental Results

The pertinent experimental facts about the photoelectric effect are these:

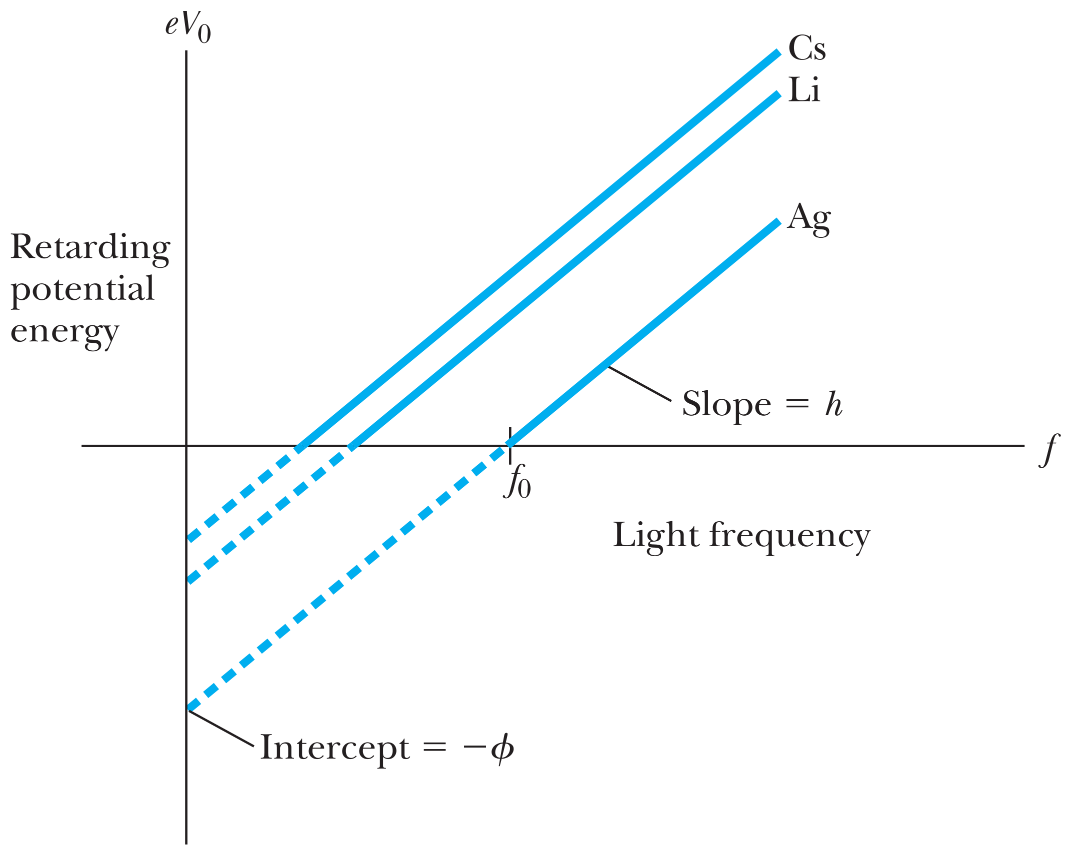
1. The kinetic energies of the photoelectrons are independent of the light intensity.



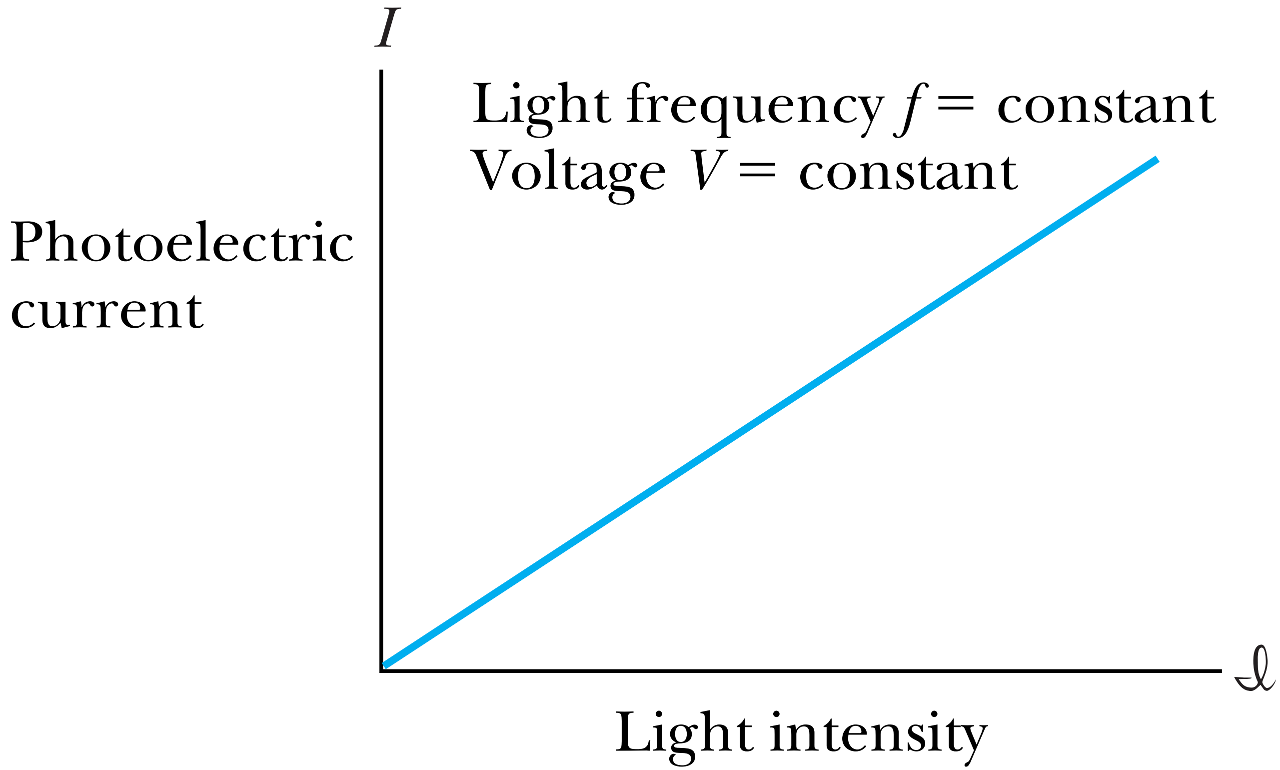
2. The maximum kinetic energy of the photoelectrons, for a given emitting material, depends only on the frequency of the light.



3. The smaller the work function ϕ of the emitter material, the lower is the threshold frequency of the light that can eject photoelectrons.



4. When the photoelectrons are produced, however, their number is proportional to the intensity of light



5. The photoelectrons are emitted almost instantly ($3*10^{-9}$s) following illumination of the photocathode, independent of the intensity of the light.

Except for result 5, these experimental facts were known in rudimentary form by 1902, primarily due to the work of Philipp Lenard, who had been an assistant to Hertz in 1892 after Hertz had moved from Karlsruhe to Bonn.

Lenard, who extensively studied the photoelectric effect, received the Nobel Prize in Physics in 1905 for this and other research on the identification and behavior of electrons.

Classical Interpretation

1. Classical theory allows electromagnetic radiation to eject photoelectrons from matter.

2. Classical theory predicts that the total amount of energy in a light wave increases as the light intensity increases.

3. Classical theory cannot explain that the maximum kinetic energy of the photoelectrons depends on the value of the light frequency ν and not on the intensity.

4. The existence of a threshold frequency is completely inexplicable in classical theory.

5. Classical theory does predict that the number of photoelectrons ejected will increase with intensity.

1. Albert Einstein was intrigued by Planck's hypothesis that the electromagnetic radiation field must be absorbed and emitted in quantized amounts.
2. Einstein took Planck's idea one step further and suggested that the electromagnetic radiation field itself is quantized
3. We now call these energy quanta of light photons. According to Einstein each photon has the energy quantum

$$E = h\nu$$

where ν is the frequency of the electromagnetic wave associated with the light, and h is Planck's constant.

4. Einstein proposed that in addition to its well-known wavelike aspect, amply exhibited in interference phenomena, light should also be considered to have a particle-like aspect.

The conservation of energy requires that

$$h\nu = \phi + E_k$$

We want to experimentally detect the maximum value of the kinetic energy.

$$h\nu = \phi + \frac{1}{2}mv_{\max}^2$$

The retarding potentials are thus the opposing potentials needed to stop the most energetic electrons.

$$eV_0 = \frac{1}{2}mv_{\max}^2$$

Quantum Interpretation

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The kinetic energy of the electrons depends only on the light frequency and the work function of the material.

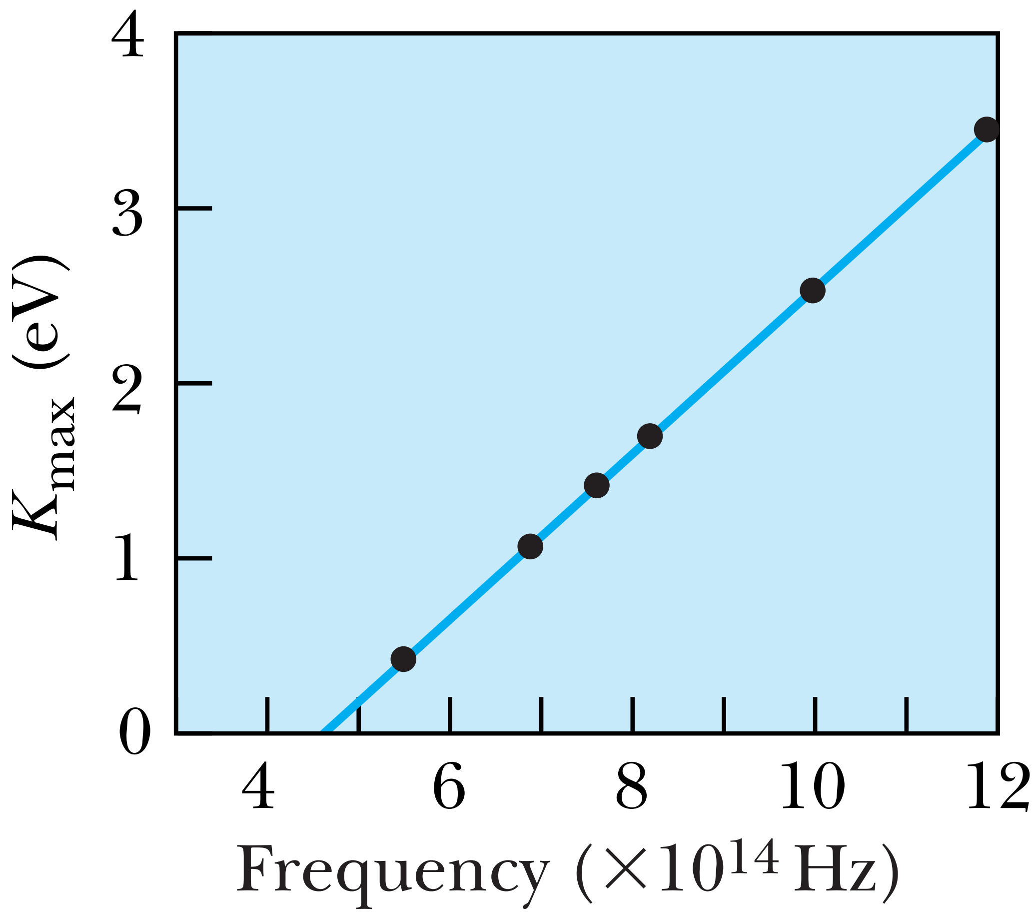
$$\frac{1}{2}mv_{\max}^2 = eV_0 = h\nu - \phi$$

which proposed by Einstein in 1905, predicts that the stopping potential will be linearly proportional to the light frequency, The slope is independent of the metal used to construct the photocathode. This equation can be rewritten as

$$eV_0 = \frac{1}{2}mv_{\max}^2 = h(\nu - \nu_0)$$

The frequency ν_0 represents the threshold frequency for the photoelectric effect. (when the kinetic energy of the electron is precisely zero).

In 1916 Millikan reported data that confirmed Einstein's prediction.



1924, De Broglie established the wave properties of particles. His fundamental relationship is the prediction

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

That is, the wavelength to be associated with a particle is given by Planck's constant divided by the particle's momentum. For a photon in Einstein's special theory of relativity

$$E = pc$$

and quantum theory

$$E = h\nu$$

so

$$pc = h\nu = \frac{hc}{\lambda}$$

De Broglie extended this relation for photons to all particles. Particle waves were called matter waves by de Broglie, and the wavelength is now called the de Broglie wavelength of a particle.

Example: Calculate the de Broglie wavelength of

(a) a tennis ball of mass 57 g traveling 25 m/s and

(b) an electron with kinetic energy 50 eV.

Solution:

(a) For the tennis ball $$\lambda = \frac{h}{p} = \frac{6.63 \times 10^{-34}}{0.057 \times 25} = 4.7 \times 10^{-34}\mathrm{m}$$

(b) For the electron

$$\lambda = \frac{h}{p} = \frac{hc}{\sqrt{2mc^2 E}} = \frac{1240\ \mathrm{ev} \cdot \mathrm{nm}}{\sqrt{2 \times 0.511 \times 10^6 \times 50\ (\mathrm{eV})^2}} = 0.17\mathrm{nm}$$

Bohr's Quantization Condition

Represent the electron as a standing wave in an orbit around the proton. The condition for a standing wave in this configuration is that the entire length of the standing wave must just fit around the orbit's circumference.

$$n\lambda = 2\pi r$$

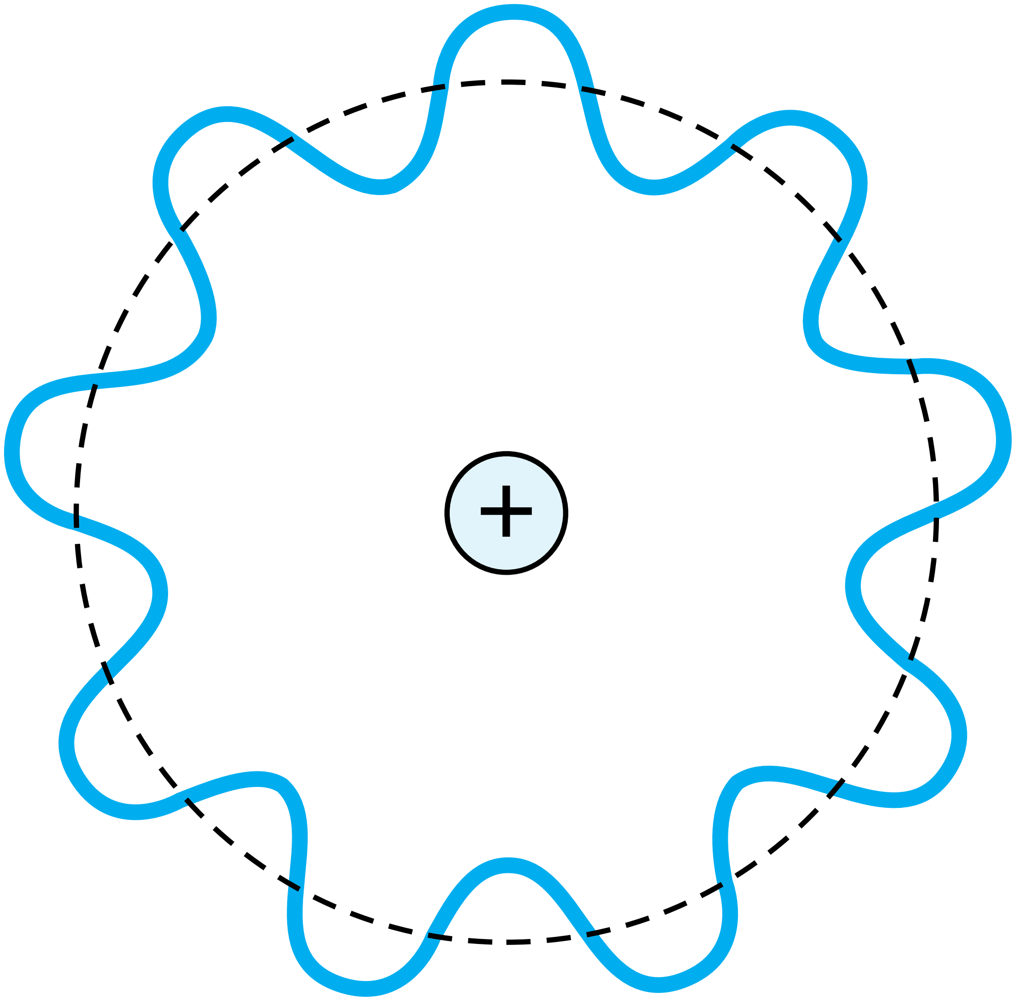
where r is the radius of the orbit. Now we use the de Broglie relation for the wavelength and obtain

$$n\lambda = 2\pi r = n\frac{h}{p}$$

The angular momentum of the electron in this orbit is L=rp, so we have, using the above relation,

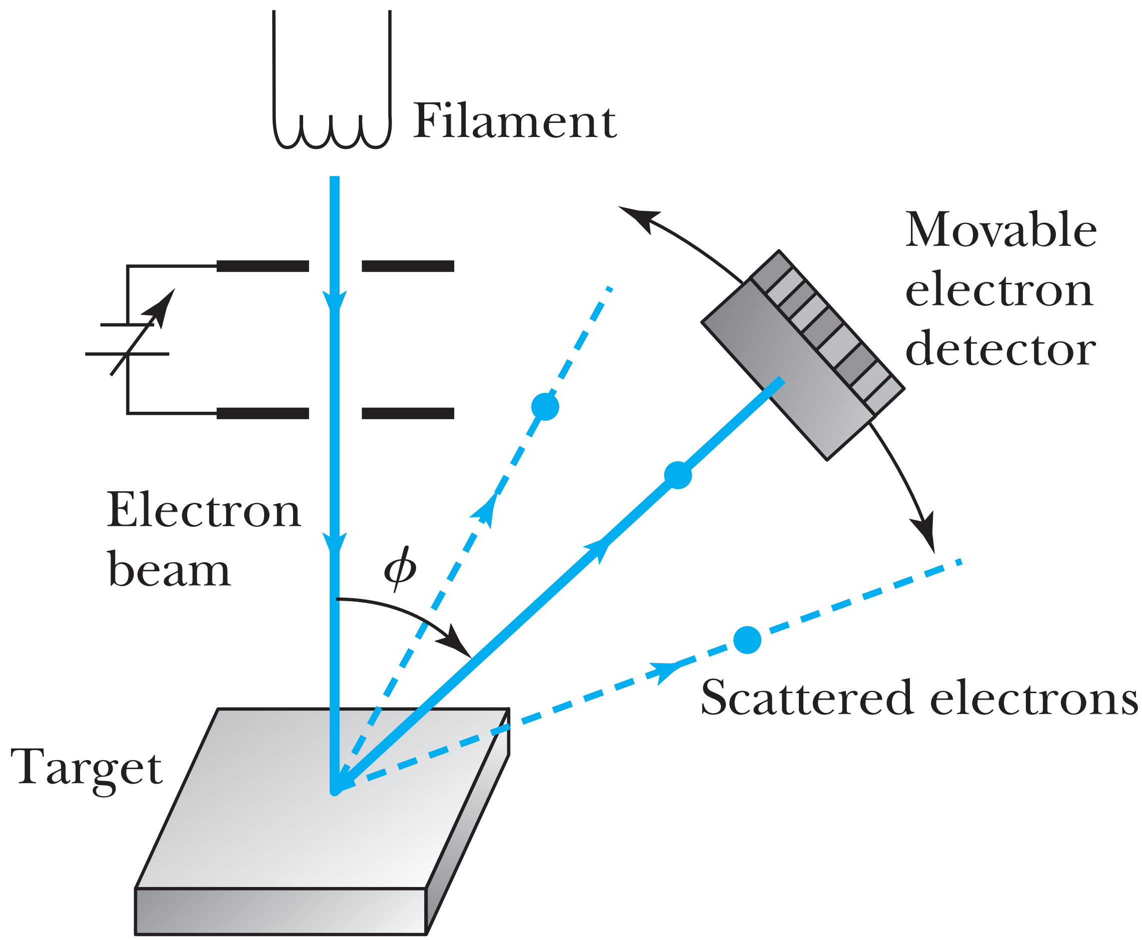
$$L = rp = \frac{nh}{2\pi} = n\hbar$$

Bohr's Quantization Condition

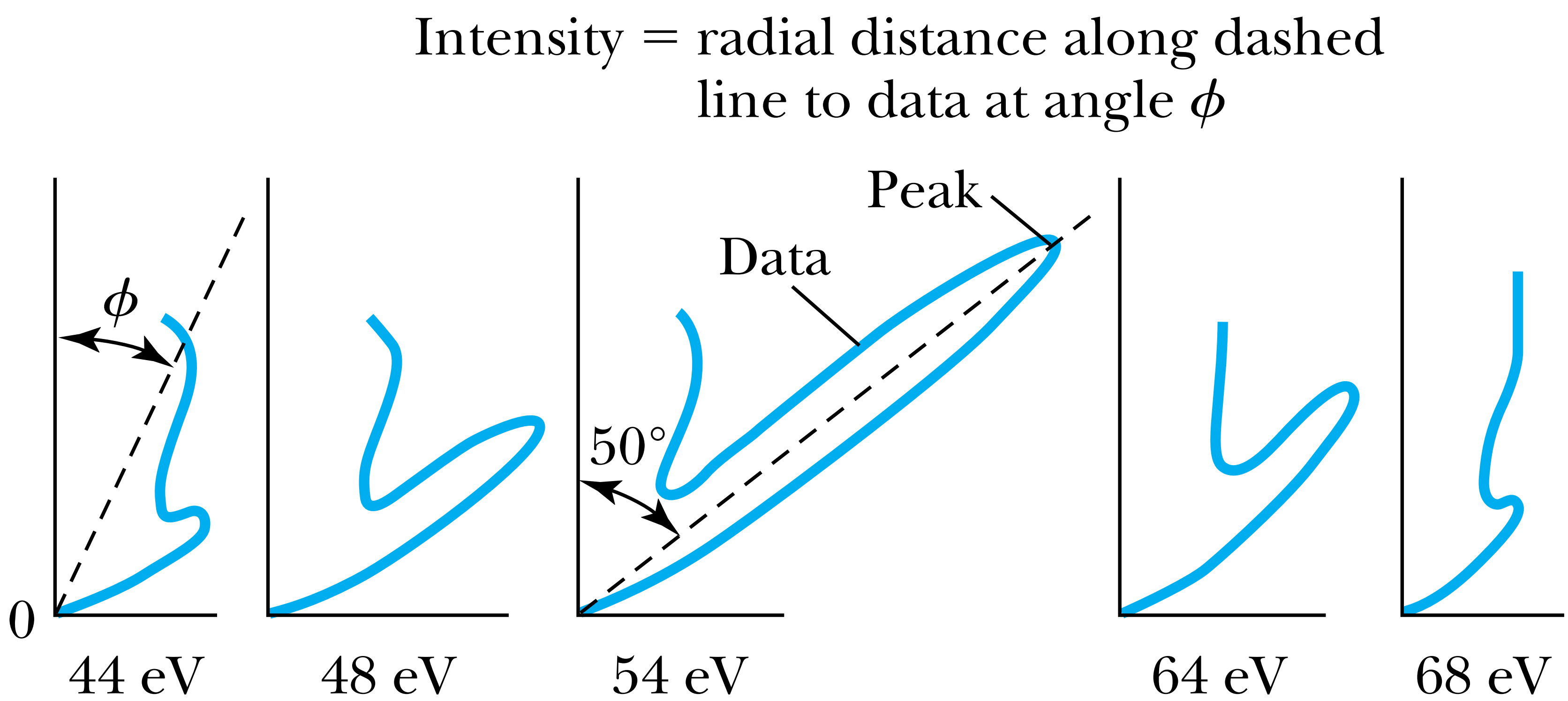


Electron Scattering

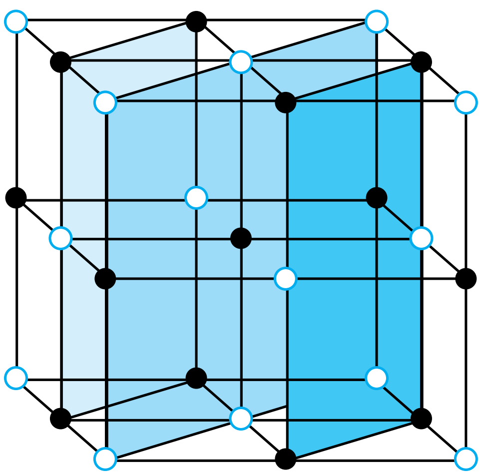
In 1925 a laboratory accident led to experimental proof for de Broglie's wavelength hypothesis by C. Davisson and L. H. Germer.

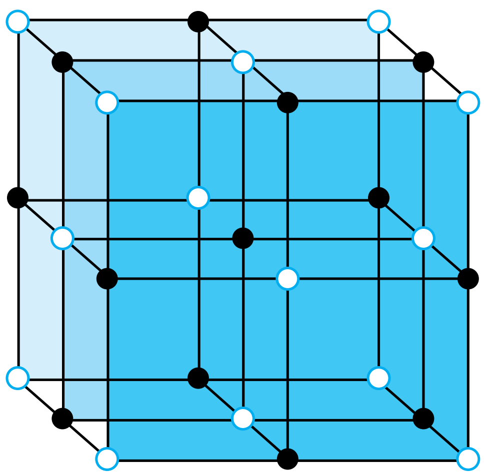


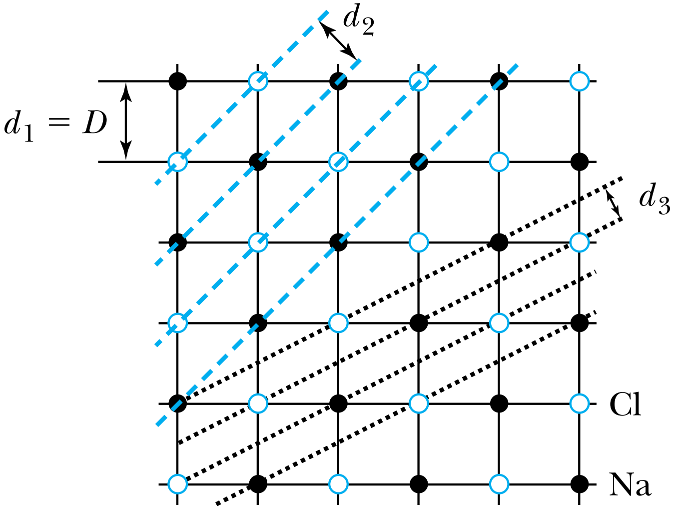
The relationship between the incident electron beam and the nickel crystal scattering planes is shown



The atoms of crystals like NaCl form lattice planes, called **Bragg planes.** It is possible to have many Bragg planes in a crystal, each with different densities of atoms.



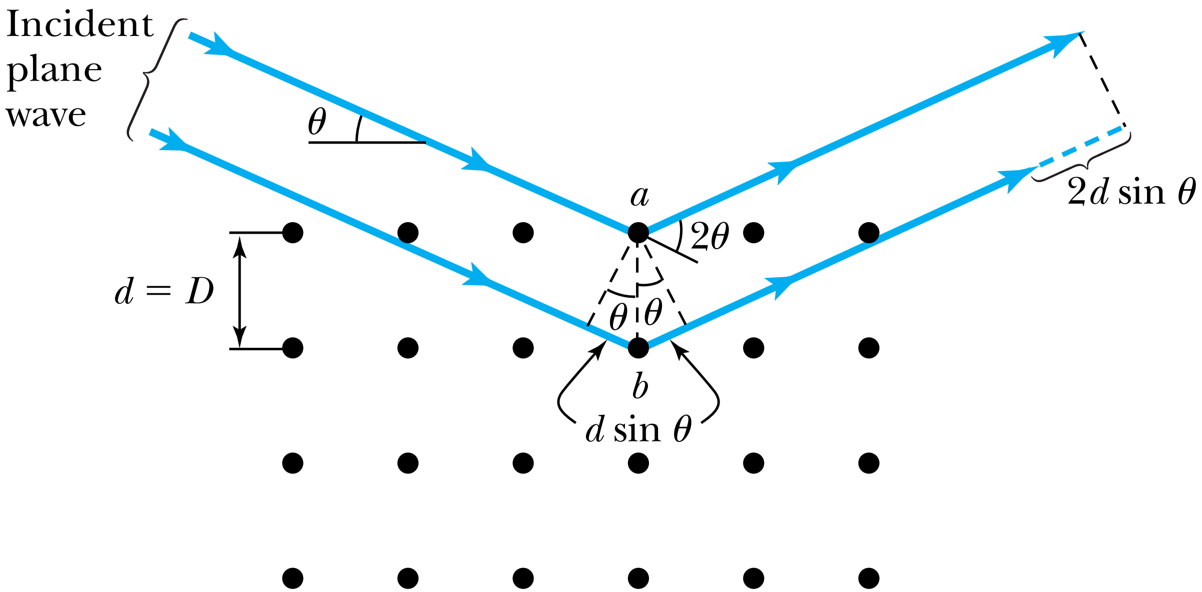




Bragg Law

There are two conditions for constructive interference of the scattered matter wave of electron:

1. The angle of incidence must equal the angle of reflection of the outgoing wave.
2. The difference in path lengths (2d sinθ) shown lower panel must be an integral number of wavelengths.



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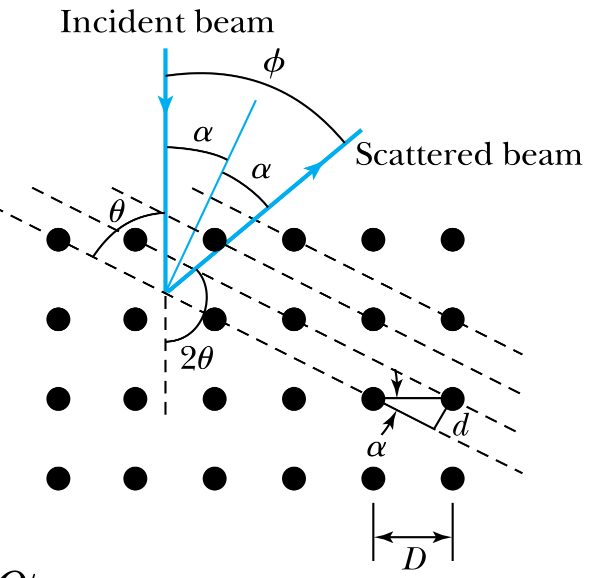
Bragg's Law with condition 2

$$n\lambda = 2d\sin\theta$$

The integer n is called the order of reflection, following the terminology of ruled diffraction gratings in optics.

In the Bragg law, 2θ is the angle between the incident and exit beams. Therefore

$$\phi = \pi - 2\theta = 2\alpha$$



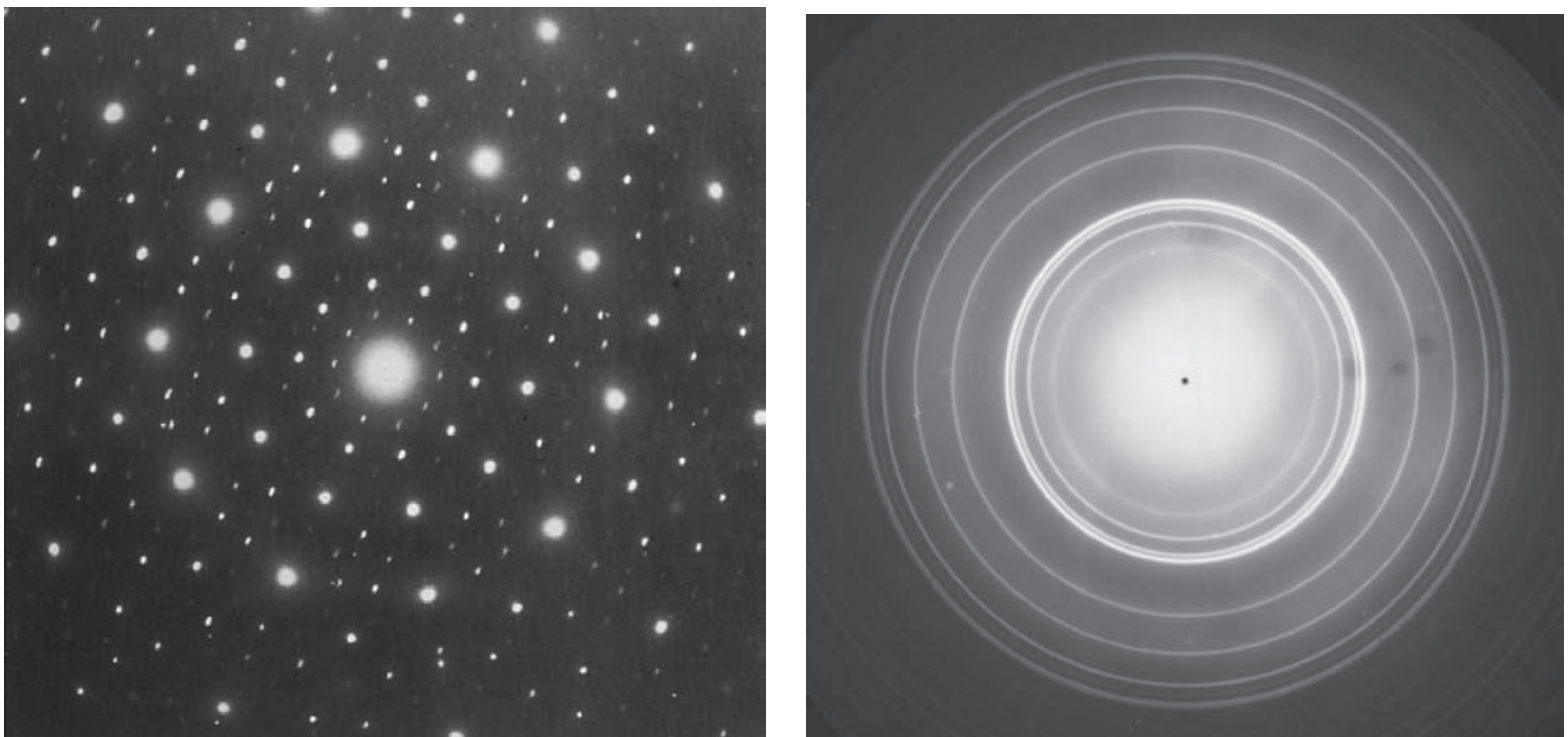
So

$$n\lambda = 2d\cos\alpha = 2D\sin\alpha\cos\alpha$$
$$= D\sin\phi$$

Electron scattering

For nickel the interatomic distance is D=0.215 nm. If the peak found by Davisson and Germer at 50° was n=1, then the electron wavelength should be

$$\lambda = 0.215 \sin(50\pi/180) = 0.165 \text{ nm}$$



Courtesy of David Follstaedt, Sandia National Laboratory

Omikron/Photo Researchers, Inc.

(a) (b)

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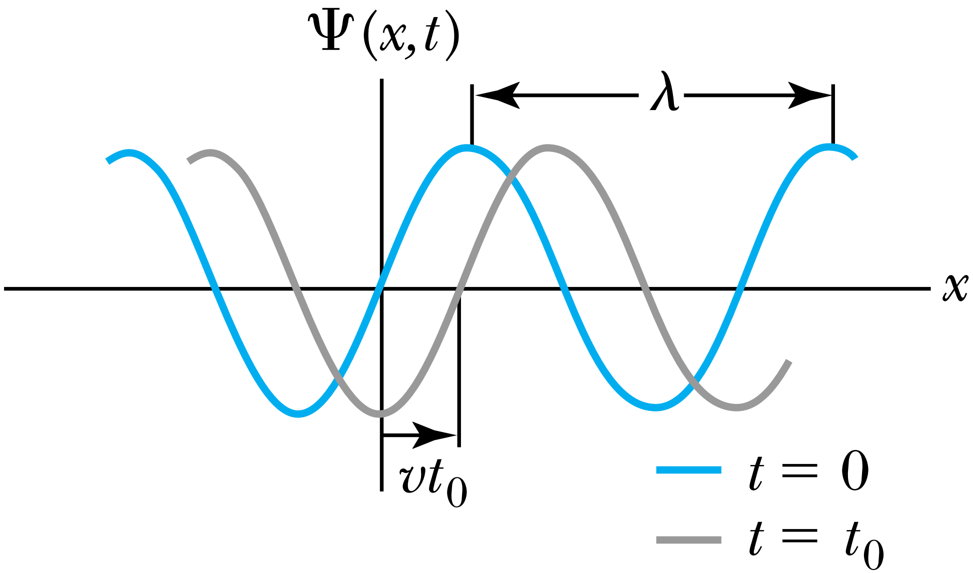
The simplest form of wave has a sinusoidal form; at a fixed time (say, t=0) its spatial variation looks like

$$\Psi(x,t)|_{t=0} = A\sin\left(\frac{2\pi}{\lambda}x\right)$$

The function $\Psi(x, t)$ represents the instantaneous amplitude or displacement of the wave as a function of position x and time t.



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As time increases, the position of the wave will change, so the general expression for the wave is

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

A traveling wave satisfies the wave equation

$$\frac{\partial^2\Psi}{\partial x^2} = \frac{1}{v^2}\frac{\partial^2\Psi}{\partial t^2}$$

We can write wave function more compactly by defining the wave number k and angular frequency ω by

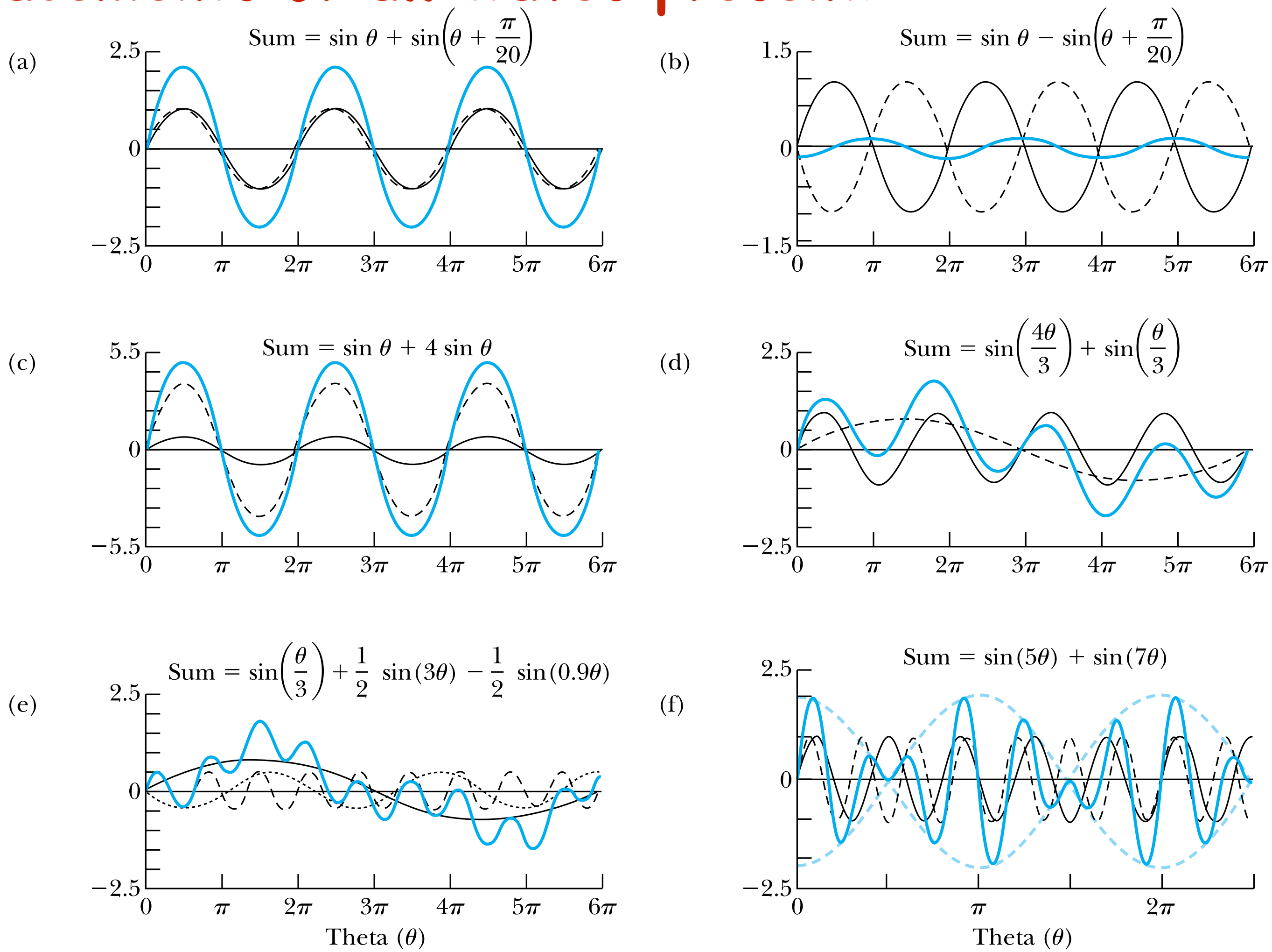
$$k \equiv \frac{2\pi}{\lambda} = \frac{2\pi}{vT}, \quad \text{and}, \quad \omega = \frac{2\pi}{T}$$

as

$$\Psi(x,t) = A\sin[kx - \omega t + \phi]$$

← Phase constant

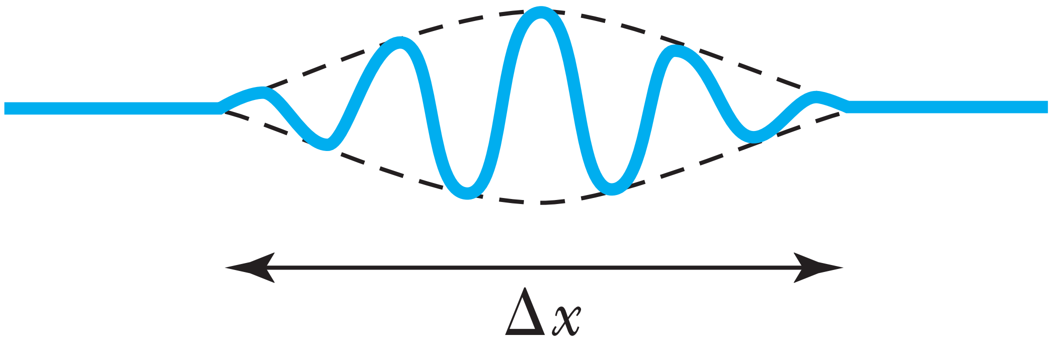
According to the principle of superposition, we add the displacements of all waves present.



Wave motion

If we add many waves of different amplitudes and frequencies in particular ways, it is possible to obtain what is called a wave packet.

The important property of the wave packet is that its net amplitude differs from zero only over a small region Δx



We can localize the position of a particle in a particular region by using a wave packet description

Let us examine in detail the superposition of two waves,

$$\Psi(x,t) = \Psi_1(x,t) + \Psi_2(x,t)$$
$$= 2A\cos\left(\frac{\Delta k}{2}x - \frac{\Delta\omega}{2}t\right)\cos\left(k_{\rm av}x - \omega_{\rm av}t\right)$$

where,

$$\Delta k = k_1 - k_2, \Delta\omega = \omega_1 - \omega_2, k_{\rm av} = (k_1 + k_2)/2, \omega_{\rm av} = (\omega_1 + \omega_2)/2$$

The combined wave oscillates within this envelope with the wave number k_{av} and angular frequency ω_{av}.

The envelope is described by the first cosine factor, which has the wave number $\Delta k/2$ and angular frequency $\Delta\omega/2$.

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Phase velocity,

$$v_{\mathrm{ph}} = \frac{\omega_{\mathrm{av}}}{k_{\mathrm{av}}}$$

Group velocity,

$$v_{\mathrm{gr}} = \frac{\Delta\omega}{\Delta k}$$

In contrast to the pulse or wave packet, the combination of only two waves is not localized in space. However, for purposes of illustration, we can identify a "localized region"

$$\frac{1}{2}\Delta k \Delta x = \pi$$

where, $\Delta x = x_2 - x_1$, and x_1 and x_2 represent two consecutive points where the envelope is zero

Similarly, for a given value of x we can determine the time Δt over which the wave is localized and obtain

$$\Delta\omega\Delta t = 2\pi$$

If we are to treat particles as matter waves, we have to be able to describe the particle in terms of waves.

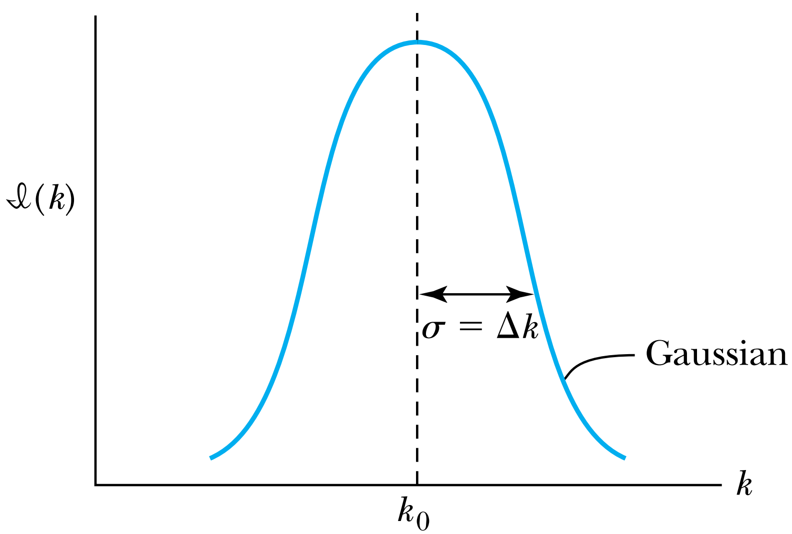
An important aspect of a particle is its localization in space.

That is why it is so important to form the wave packet that we have been discussing.

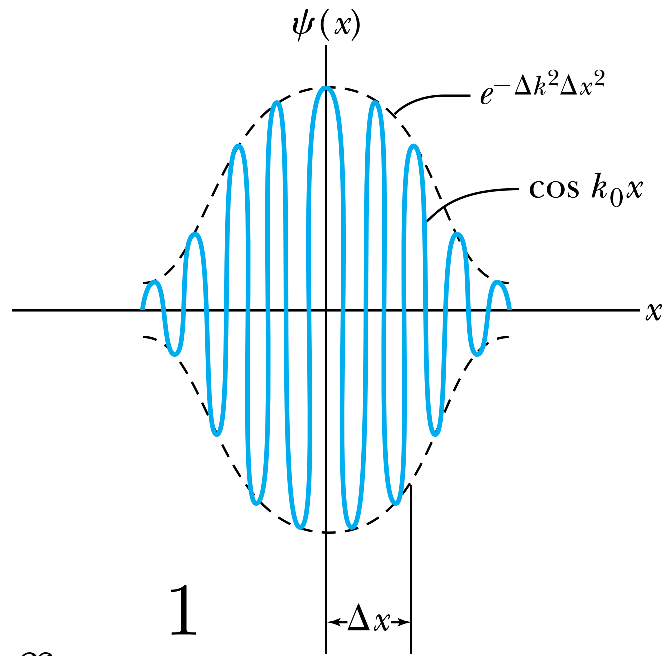
Wave motion

Gaussian Wave Packet are often used to represent the position of particles, because the associated integrals are relatively easy to evaluate.

$$\Psi(x,0) = \psi(x) = Ae^{-\Delta k^2 x^2}\cos(k_0 x)$$



(a)



(b)

$$\Delta k \Delta x = \frac{1}{2}$$


35
Breaking
56
Bad

Uncertainty Principle

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We learned that it is impossible to measure simultaneously, with no uncertainty, the precise values of k and x for the same particle. The wave number k may be rewritten as

$$k = \frac{p}{\hbar}$$

in the case of the Gaussian wave packet,

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

Heisenberg's uncertainty principle can therefore be written

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

It is possible to have a greater uncertainty in the values of p_x and x, but it is not possible to know them with more precision than allowed by the uncertainty principle.

Consider a particle for which the location is known within a width of l along the x axis. The uncertainty principle specifies that Δp is limited by

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

the minimum value of the kinetic energy ,

$$E_{\min} = \frac{p_{\min}^2}{2m} \geq \frac{(\Delta p)^2}{2m} \geq \frac{\hbar^2}{2ml^2}$$

Note that this equation indicates that if we are uncertain as to the exact position of a particle, for example, an electron somewhere inside an atom of diameter l, the particle can't have zero kinetic energy.

Energy-Time Uncertainty Principle

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

Example: Calculate the minimum kinetic energy of an electron that is localized within a typical nuclear radius of $6*10^{-15}$m.

Solution:

$$E_{\min} = \frac{3p_{\min}^2}{2m} \geq \frac{3(\Delta p)^2}{2m} \geq \frac{3\hbar^2}{8mr^2} = \frac{3 * 197^2}{8 * 0.511 * 6^2} = 791 \text{ MeV}$$

Electron Double-Slit Experiment

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In 1961 C. Jönsson of Tübingen, Germany, succeeded in showing double-slit interference effects for electrons

(a) 20 counts

(b) 100 counts

(c) 500 counts

(d) ~4000 counts

Simulation and photos courtesy of Julian V. Noble.

Electron Double-Slit Experiment

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How can we interpret the probability of finding the electron in the wave description?

We used a function $\Psi(x, t)$ named as wave function to denote the superposition of many waves to describe the wave packet.

The quantity

$$|\Psi(x, y, z, t)|^2$$

is called the probability density and represents the probability of finding the particle in a given unit volume at a given instant of time

In general, Ψ(x, y, z, t) is a complex quantity and depends on the spatial coordinates x, y, and z as well as time t.

We are interested here in only a single dimension y along the observing scree and for a give time t. The probability of observing an electron in the interval between y and y+dy at a given time

$$P(y)dy = |\Psi(y,t)|^2 dy$$

Normalization condition

$$\int_{-\infty}^{\infty} P(y)dy = \int_{-\infty}^{\infty} |\Psi(y,t)|^2 dy = 1$$

The Copenhagen Interpretation

Max Born, one of the founders of the quantum theory, first proposed this probability interpretation of the wave function in 1926.

1. The uncertainty principle of Heisenberg

2. The complementarity principle of Bohr: It is not possible to describe physical observables simultaneously in terms of both particles and waves.

3. The statistical interpretation of Born, based on probabilities determined by the wave function

The Schrödinger wave equation in its time-dependent form for a particle moving in a potential V in one dimension is

$$i\hbar\frac{\partial\Psi(x,t)}{\partial t}=-\frac{\hbar^2}{2m}\frac{\partial^2\Psi(x,t)}{\partial x^2}+V\Psi(x,t)$$

Both the potential V and wave function Ψ may be functions of space and time, V(x, t) and Ψ(x, t).

The three-dimensions Schrödinger is fairly straightforward

$$i\hbar\frac{\partial\Psi(x,y,z,t)}{\partial t}=-\frac{\hbar^2}{2m}\nabla^2\Psi(x,y,z,t)+V\Psi(x,y,z,t)$$

Properties of Valid Wave Functions

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1. In order to avoid infinite probabilities, must be finite everywhere.
2. In order to avoid multiple values of the probability, must be single valued.
3. For finite potentials, Ψ and $\partial\Psi/\partial x$ must be continuous. This is required because the second-order derivative term in the wave equation must be single valued. (There are exceptions to this rule when V is infinite.)
4. In order to normalize the wave functions, Ψ must approach zero as x approaches $\pm\infty$.

In many cases (and in most of the cases discussed here), the potential will not depend explicitly on time. The dependence on time and position can then be separated in the Schrödinger wave equation. Let

$$\Psi(x,t) = \psi(x) f(t)$$

We insert this wave function to Schrödinger equation

$$i\hbar\psi(x)\frac{\partial f(t)}{\partial t} = -\frac{\hbar^2 f(t)}{2m}\frac{\partial^2\psi(x)}{\partial x^2} + V(x)\psi(x)f(t)$$

We divide by $\psi(x)f(t)$ to yield

$$i\hbar\frac{1}{f(t)}\frac{\partial f(t)}{\partial t} = -\frac{\hbar^2}{2m}\frac{1}{\psi(x)}\frac{\partial^2\psi(x)}{\partial x^2} + V(x)$$

It follows that each side must be equal to a constant (which we label B), because one variable may change independently of the other.

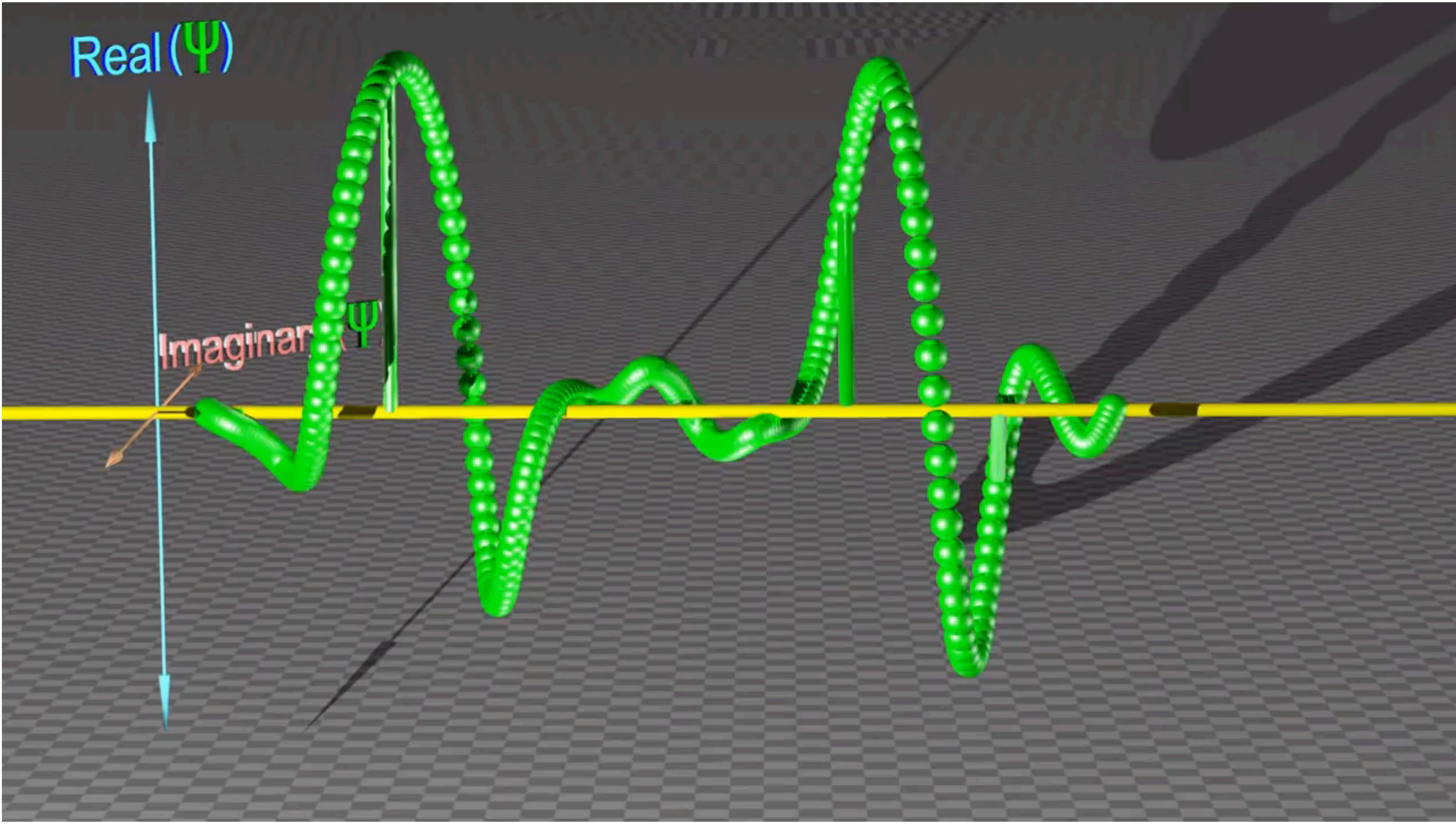
$$i\hbar\frac{1}{f(t)}\frac{\partial f(t)}{\partial t}=B$$

From this equation we determine f to be

$$f(t)=e^{-iBt/\hbar}$$

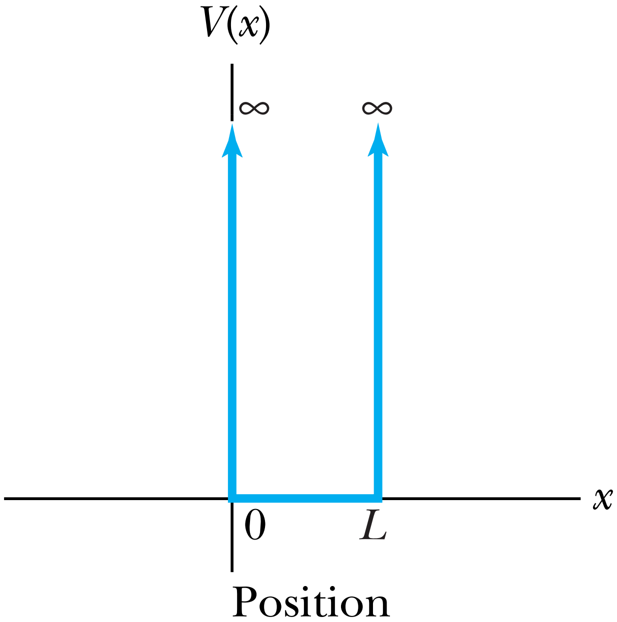
If we compare this function for f (t) to the free-particle wave function that has the time dependence $e^{-i\omega t}$, we see that $B=\hbar\omega=E$. Therefore

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi(x)}{\partial x^2}+V(x)\psi(x)=E\psi(x)$$


Real (Ψ)
Imaginary (Ψ)

Infinite square well

$$V(x) = \begin{cases} \infty & x \le 0,\ x \ge L \\ 0 & 0 < x < L \end{cases}$$



The Schrödinger equation in the well

$$\frac{d^2\psi}{dx^2} = -\frac{2mE}{\hbar^2}\psi = -k^2\psi$$

where,

$$k = \sqrt{\frac{2mE}{\hbar^2}}$$

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A suitable solution to this equation

$$\psi(x) = A\sin kx + B\cos kx$$

where A and B are constants used to normalize the wave function. The wave function must be continuous at x=0 and x=L, therefore

$$B = 0$$

$$kL = n\pi$$

The wave function is now

$$\psi_n(x) = A\sin\left(\frac{n\pi x}{L}\right), \quad n = 1, 2, 3, \ldots$$

A is determined by the normalization condition

$$A^2 \int_0^L \sin^2\left(\frac{n\pi x}{L}\right) = 1$$

and

$$A = \sqrt{\frac{2}{L}}$$

The normalized wave function becomes

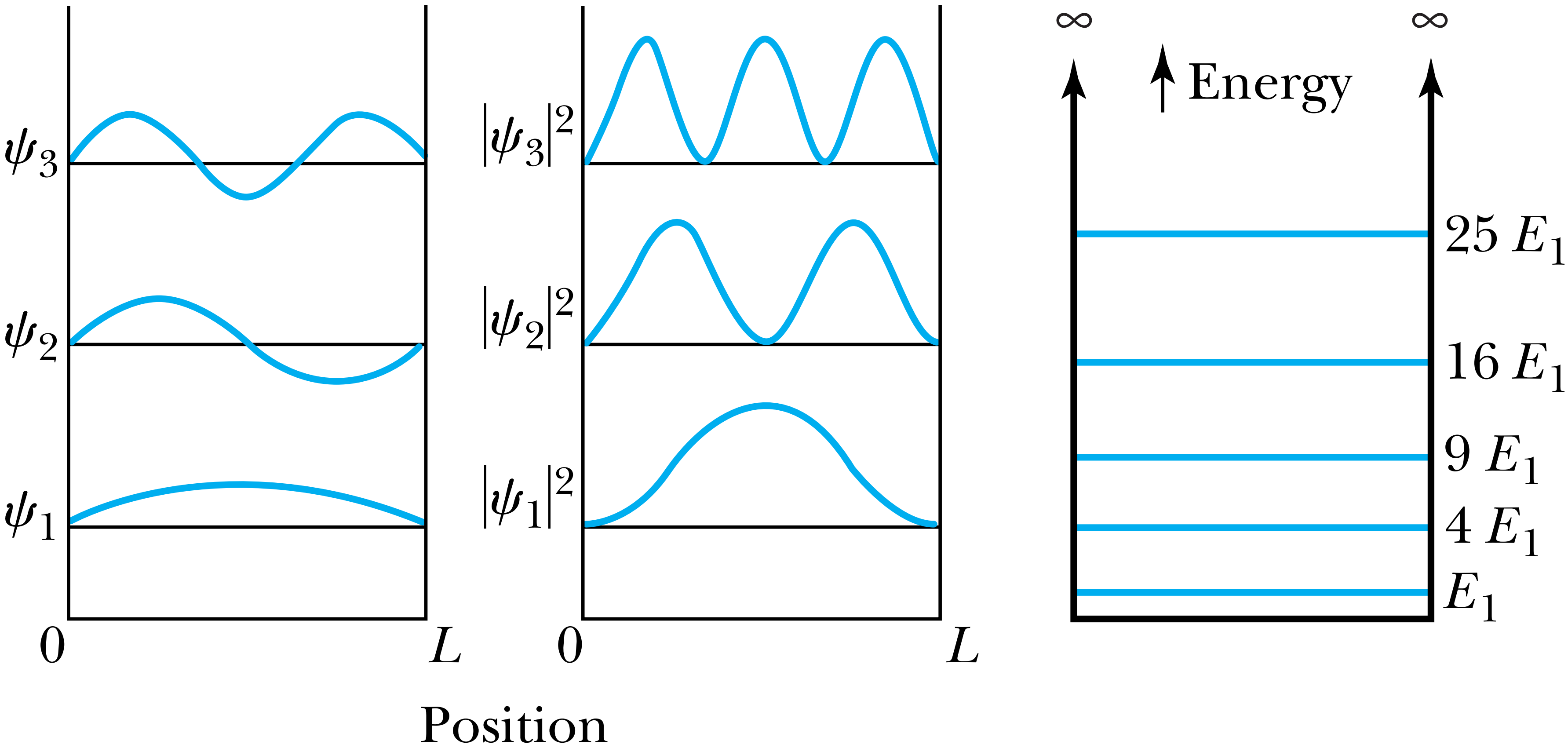
$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right), \quad n = 1, 2, 3, \ldots$$

The quantized energy levels

$$E_n = \frac{n^2\pi^2\hbar^2}{2mL^2}, \quad n = 1, 2, 3, \ldots$$

the integer n is a quantum number

Infinite Square-Well Potential



The Schrödinger Equation for H

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To a good approximation the potential energy of the electron-proton system is electrostatic:

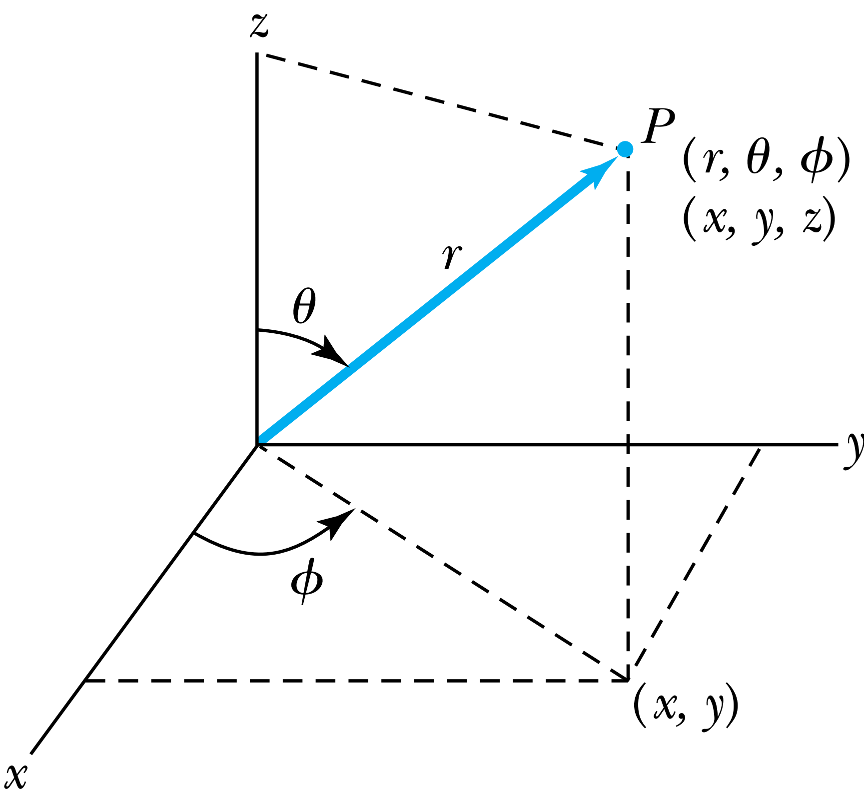
$$V(r) = -\frac{e^2}{4\pi\varepsilon_0 r}$$

We rewrite the three-dimensional time-independent Schrödinger Equation

$$-\frac{\hbar^2}{2m}\frac{1}{\psi(x,y,z)}\left[\frac{\partial^2\psi(x,y,z)}{\partial x^2}+\frac{\partial^2\psi(x,y,z)}{\partial y^2}+\frac{\partial^2\psi(x,y,z)}{\partial z^2}\right] = E - V(r)$$

The potential in this case is due to the central force. To take advantage of the radial symmetry, we transform to spherical polar coordinates.

Relationship between spherical polar coordinates and Cartesian coordinates



$$x = r \sin\theta \cos\phi$$
$$y = r \sin\theta \sin\phi$$
$$z = r \cos\theta$$

$$r = \sqrt{x^2 + y^2 + z^2}$$

$$\theta = \cos^{-1}\frac{z}{r} \quad \text{(Polar angle)}$$

$$\phi = \tan^{-1}\frac{y}{x} \quad \text{(Azimuthal angle)}$$

The Schrödinger equation in spherical polar coordinate

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}+\frac{2\mu}{\hbar^2}(E-V)\psi=0$$

The wave function is now a function of r, θ, ϕ. This equation is separable, meaning a solution may be found as a product of three functions, each depending on only one of the coordinates r, θ, ϕ,

$$\psi(r,\theta,\phi)=R(r)f(\theta)g(\phi)$$

Radial equation

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{2\mu}{\hbar^2}\left[E-V-\frac{\hbar^2}{2\mu}\frac{l(l+1)}{r^2}\right]R=0$$

Angular equation

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{df}{d\theta}\right)+\left[l(l+1)-\frac{m_l^2}{\sin^2\theta}\right]f=0$$

$$\frac{d^2g}{d\phi^2}=-m_l^2 g$$

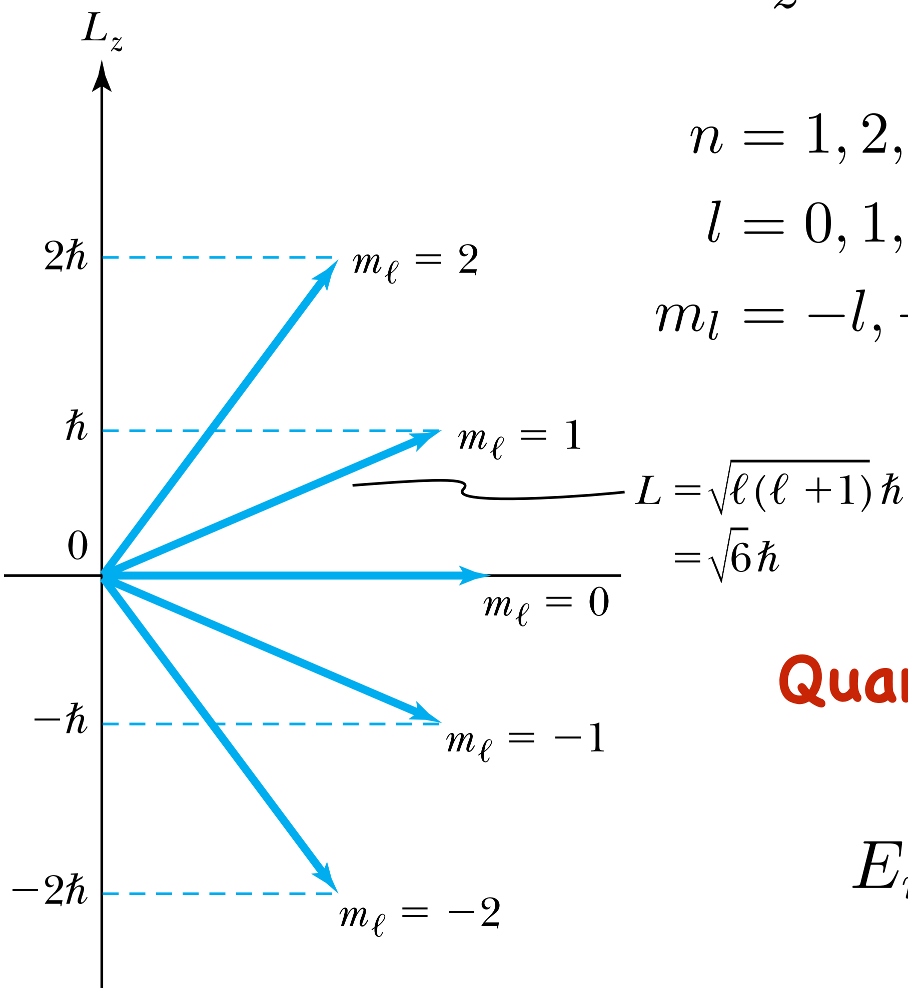
Principal Quantum Number n

Orbital Angular Momentum Quantum Number l

$$L=\sqrt{l(l+1)}\hbar$$

Magnetic Quantum Number m_l

$$L_z = m_l \hbar$$



$$n = 1, 2, 3, 4, \ldots \quad \text{Integer}$$

$$l = 0, 1, 2, 3, \ldots, n-1 \quad \text{Integer}$$

$$m_l = -l, -l+1, \ldots, 0, 1, \ldots, l-1, l \quad \text{Integer}$$

Quantized energy of hydrogen

$$E_n = -\frac{\mu}{2}\left(\frac{e^2}{4\pi\varepsilon_0\hbar}\right)^2 \frac{1}{n^2}$$

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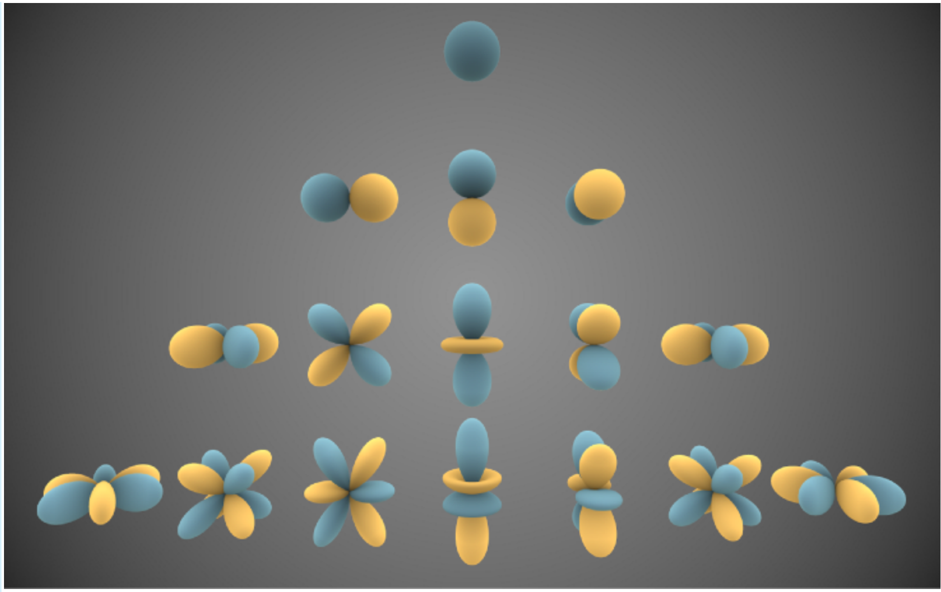
Hydrogen Atom Radial Wave Functions

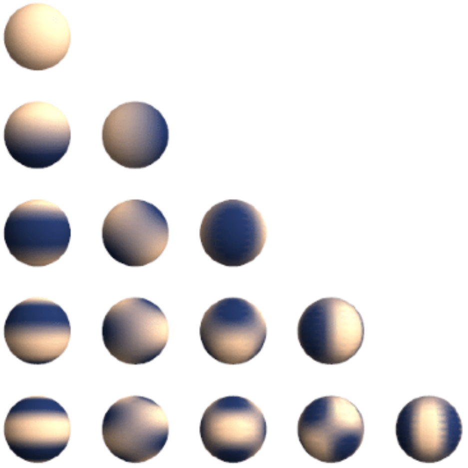
n	ℓ	$R_{n\ell}(r)$
1	0	$\frac{2}{(a_0)^{3/2}} e^{-r/a_0}$
2	0	$\left(2 - \frac{r}{a_0}\right) \frac{e^{-r/2a_0}}{(2a_0)^{3/2}}$
2	1	$\frac{r}{a_0} \frac{e^{-r/2a_0}}{\sqrt{3}(2a_0)^{3/2}}$
3	0	$\frac{1}{(a_0)^{3/2}} \frac{2}{81\sqrt{3}} \left(27 - 18\frac{r}{a_0} + 2\frac{r^2}{a_0{}^2}\right) e^{-r/3a_0}$
3	1	$\frac{1}{(a_0)^{3/2}} \frac{4}{81\sqrt{6}} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0}$
3	2	$\frac{1}{(a_0)^{3/2}} \frac{4}{81\sqrt{30}} \frac{r^2}{a_0{}^2} e^{-r/3a_0}$

Normalized Spherical Harmonics

$$Y(\theta,\phi) = f(\theta)g(\phi)$$

ℓ	m_ℓ	$Y_{\ell m_\ell}$
0	0	$\frac{1}{2\sqrt{\pi}}$
1	0	$\frac{1}{2}\sqrt{\frac{3}{\pi}}\cos\theta$
1	±1	$\mp\frac{1}{2}\sqrt{\frac{3}{2\pi}}\sin\theta\, e^{\pm i\phi}$
2	0	$\frac{1}{4}\sqrt{\frac{5}{\pi}}(3\cos^2\theta - 1)$
2	±1	$\mp\frac{1}{2}\sqrt{\frac{15}{2\pi}}\sin\theta\cos\theta\, e^{\pm i\phi}$
2	±2	$\frac{1}{4}\sqrt{\frac{15}{2\pi}}\sin^2\theta\, e^{\pm 2i\phi}$
3	0	$\frac{1}{4}\sqrt{\frac{7}{\pi}}(5\cos^3\theta - 3\cos\theta)$
3	±1	$\mp\frac{1}{8}\sqrt{\frac{21}{\pi}}\sin\theta(5\cos^2\theta - 1)\, e^{\pm i\phi}$
3	±2	$\frac{1}{4}\sqrt{\frac{105}{2\pi}}\sin^2\theta\cos\theta\, e^{\pm 2i\phi}$
3	±3	$\mp\frac{1}{8}\sqrt{\frac{35}{\pi}}\sin^3\theta\, e^{\pm 3i\phi}$





Expectation Values

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In quantum mechanics we use wave functions to calculate the expected result of the average of many measurements of a given quantity.

Any measurable quantity for which we can calculate the expectation value is called a physical observable.

If we make many measurements of the particle at x axis, we may find the particle N_1 times at x_1, N_2 times at x_2, N_i times at x_i, and so forth. The average value of x,

$$\bar{x} = \frac{N_1 x_1 + N_2 x_2 + N_3 x_3 + \ldots}{N_1 + N_2 + N_3 + \ldots} = \frac{\sum_i N_i x_i}{\sum_i N_i}$$

We can change from discrete to continuous variables by using the probability P(x, t) of observing the particle at a particular x. The previous equation then becomes

$$\bar{x} = \frac{\int_{-\infty}^{\infty} xP(x)dx}{\int_{-\infty}^{\infty} P(x)dx}$$

In quantum mechanics we must use the probability distribution given in wave function

$$\langle x \rangle = \int_{-\infty}^{\infty} x\Psi^*(x,t)\Psi(x,t)dx$$

The same general procedure can be used to find the expectation value of any function g(x)

$$\langle g(x) \rangle = \int_{-\infty}^{\infty} \Psi^*(x,t)g(x)\Psi(x,t)dx$$

To find the expectation value of p, we first need to represent p in terms of x and t. Let's consider the wave function of the free particle,

$$\Psi(x,t) = e^{i(kx-\omega t)}$$

If we take the derivative of wave function with respect to x, we have

$$\frac{\partial \Psi(x,t)}{\partial x} = ik\Psi(x,t)$$

After rearrangement, this yields

$$p[\Psi(x,t)] = -i\hbar \frac{\partial \Psi(x,t)}{\partial x}$$

Operator

An operator is a mathematical operation that transforms one function into another. For example, an operator, transforms one function into another

$$\hat{Q}f(x) = g(x)$$

Momentum operator

$$\hat{p} = -i\hbar\frac{\partial}{\partial x}$$

Energy operator

$$\hat{E} = i\hbar\frac{\partial}{\partial t}$$

The expectation value of the momentum and energy

$$\langle p\rangle = -i\hbar\int_{-\infty}^{\infty}\Psi^*(x,t)\frac{\partial\Psi(x,t)}{\partial x}dx$$

$$\langle E\rangle = i\hbar\int_{-\infty}^{\infty}\Psi^*(x,t)\frac{\partial\Psi(x,t)}{\partial t}dx$$

The Physics of Atoms and Quanta

5.2, 5.3, 5.5, 5.13, 5.14, 6.4, 6.7, 6.8

1. Determine the longest and shortest wavelengths observed in the Paschen series for hydrogen. Which are visible?

1.Determine the longest and shortest wavelengths observed in the Paschen series for hydrogen. Which are visible?

Solution: We insert the values of n into Rydberg equation to obtain

$$\frac{1}{\lambda_{\max}} = (1.0974 \times 10^7)\left(\frac{1}{3^2} - \frac{1}{4^2}\right) = 5.335 \times 10^5 \ \mathrm{m}^{-1}$$

$$\lambda_{\max} = 1875 \ \mathrm{nm}$$

and

$$\frac{1}{\lambda_{\min}} = (1.0974 \times 10^7)\left(\frac{1}{3^2} - \frac{1}{\infty^2}\right) = 1.219 \times 10^6 \ \mathrm{m}^{-1}$$

$$\lambda_{\min} = 820 \ \mathrm{nm}$$

The minimum and maximum wavelengths are both not visible and are both in the infrared.

2.Calculate the wavelength for the $n_u=3$ to $n_l=2$ transition (called the H_α line) for the atoms of hydrogen, deuterium, and tritium.

2.Calculate the wavelength for the $n_u=3$ to $n_l=2$ transition (called the H_α line) for the atoms of hydrogen, deuterium, and tritium.

Solution: The masses of proton, deuteron and triton are

$$\text{Proton} = 1.007276\ \text{u}$$

$$\text{Deuteron} = 2.013553\ \text{u}$$

$$\text{Triton (tritium nucleus)} = 3.015500\ \text{u}$$

2.Calculate the wavelength for the $n_u=3$ to $n_l=2$ transition (called the H_α line) for the atoms of hydrogen, deuterium, and tritium.

The corresponding Rydberg constants are

$$R_H = \frac{1}{1 + \frac{0.0005486}{1.00728}} R_\infty = 0.99946 R_\infty \quad \text{Hydrogen}$$

$$R_D = \frac{1}{1 + \frac{0.0005486}{2.01355}} R_\infty = 0.99973 R_\infty \quad \text{Deuterium}$$

$$R_T = \frac{1}{1 + \frac{0.0005486}{3.01550}} R_\infty = 0.99982 R_\infty \quad \text{Tritium}$$

The wavelengths are

$$\frac{1}{\lambda} = R\left(\frac{1}{2^2} - \frac{1}{3^2}\right) = 0.13889 R$$

$$\lambda(H_\alpha, \text{hydrogen}) = 656.47 \text{ nm}$$

$$\lambda(H_\alpha, \text{deuterium}) = 656.29 \text{ nm}$$

$$\lambda(H_\alpha, \text{tritium}) = 656.23 \text{ nm}$$

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3.Calculate the shortest wavelength that can be emitted by the Li^{++} ion.

3.Calculate the shortest wavelength that can be emitted by the Li^{++} ion.

Solution: We used the Rydberg equation for Li^{++}

$$\frac{1}{\lambda} = (3)^2 R\left(\frac{1}{1^2} - \frac{1}{\infty}\right) = 9R$$

$$\lambda = \frac{1}{9R} = 10.1 \text{ nm}$$

4. An atom with one electron has the energy levels $E_n = -a/n^2$. Its spectrum has two neighboring lines with $\lambda_1 = 97.5nm$ and $\lambda_2 = 102.8nm$ in Lyman series. What is the value of the constant a and which atomic element belongs to this spectrum?

4. An atom with one electron has the energy levels $E_n = -a/n^2$. Its spectrum has two neighboring lines with $\lambda_1 = 97.5nm$ and $\lambda_2 = 102.8nm$ in Lyman series. What is the value of the constant a and which atomic element belongs to this spectrum?

Solution: The photon energies are then

$$h\nu_n = a\left(1 - \frac{1}{n^2}\right)$$

$$h\nu_{n+1} = a\left(1 - \frac{1}{(n+1)^2}\right)$$

$$\frac{\lambda_1}{\lambda_2} = \frac{\nu_{n+1}}{\nu_n} = \frac{1 - 1/(n+1)^2}{1 - 1/n^2}$$

so

$$n = 3$$

$$\frac{1}{\lambda_3} = Z^2 R_A \left(1 - \frac{1}{3^2}\right)$$

$$Z = 1$$

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5.Show that the Planck radiation law agrees with the Rayleigh- Jeans formula for large wavelengths.

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5.Show that the Planck radiation law agrees with the Rayleigh- Jeans formula for large wavelengths.

Solution: We follow the strategy and find the result for the term involving the exponential:

$$\frac{1}{e^{hc/\lambda kT}-1}=\frac{1}{\left[1+\frac{hc}{\lambda kT}+\left(\frac{hc}{\lambda kT}\right)^2\frac{1}{2}+\cdots\right]-1}\rightarrow\frac{\lambda kT}{hc}$$

for large λ

So the intensity becomes

$$\mathcal{R}(\lambda,T)=\frac{2\pi c^2 h}{\lambda^5}\frac{\lambda kT}{hc}=\frac{2\pi ckT}{\lambda^4}$$

6. Light of wavelength 400 nm is incident upon lithium (ϕ= 2.93 eV). Calculate (a) the photon energy and (b) the stopping potential V_0.

6. Light of wavelength 400 nm is incident upon lithium (ϕ= 2.93 eV). Calculate (a) the photon energy and (b) the stopping potential V_0.

Solution: (a)

$$E = \frac{hc}{\lambda} = \frac{1.24 \times 10^3}{400} = 3.10 \text{ eV}$$

(b) For the stopping potential,

$$eV_0 = h\nu - \phi = 3.10 - 2.93 = 0.17 \text{ eV}$$

$$V_0 = 0.17 \text{ V}$$

7. (a) What frequency of light is needed to produce electrons of kinetic energy 3.00 eV from illumination of lithium?

(b) Find the wavelength of this light and discuss where it is in the electromagnetic spectrum.

7. (a) What frequency of light is needed to produce electrons of kinetic energy 3.00 eV from illumination of lithium?

(b) Find the wavelength of this light and discuss where it is in the electromagnetic spectrum.

Solution: (a)

$$h\nu = \phi + \frac{1}{2}mv_{\max}^2 = 5.93\ \mathrm{eV}$$

$$\nu = \frac{E}{h} = \frac{5.93 \times 1.6 \times 10^{-19}}{6.626 \times 10^{-34}} = 1.43 \times 10^{15}\ \mathrm{Hz}$$

(b)

$$\lambda = \frac{c}{\nu} = \frac{3.0 \times 10^{8}}{1.43 \times 10^{15}} = 210\ \mathrm{nm}$$

This is ultraviolet light, because the wavelength 210 nm is below the range of visible wavelengths 400 to 700 nm

8. Determine the de Broglie wavelength for a 54 eV electron used by Davisson and Germer.

8. Determine the de Broglie wavelength for a 54 eV electron used by Davisson and Germer.

Solution: the kinetic energy of electron

$$\frac{p^2}{2m} = eV_0$$

The de Broglie wavelength

$$\lambda = \frac{h}{p} = \frac{hc}{\sqrt{2mc^2 eV_0}} = 0.167 \text{ nm}$$

9. In introductory physics, we learned that a particle (ideal gas) in thermal equilibrium with its surroundings has a kinetic energy of $3kT/2$. Calculate the de Broglie wavelength for

(a) a neutron at room temperature (300 K) and

(b) a "cold" neutron at 77 K (liquid nitrogen).

9. In introductory physics, we learned that a particle (ideal gas) in thermal equilibrium with its surroundings has a kinetic energy of 3kT/2. Calculate the de Broglie wavelength for

(a) a neutron at room temperature (300 K) and

(b) a "cold" neutron at 77 K (liquid nitrogen).

Solution: the kinetic energy of particle

$$\frac{p^2}{2m} = \frac{3kT}{2}$$

The de Broglie wavelength

$$\lambda = \frac{h}{p} = \frac{hc}{\sqrt{3mc^2kT}}$$

$$\lambda(300\ \mathrm{K}) = 0.145\ \mathrm{nm}$$

$$\lambda(70\ \mathrm{K}) = 0.287\ \mathrm{nm}$$