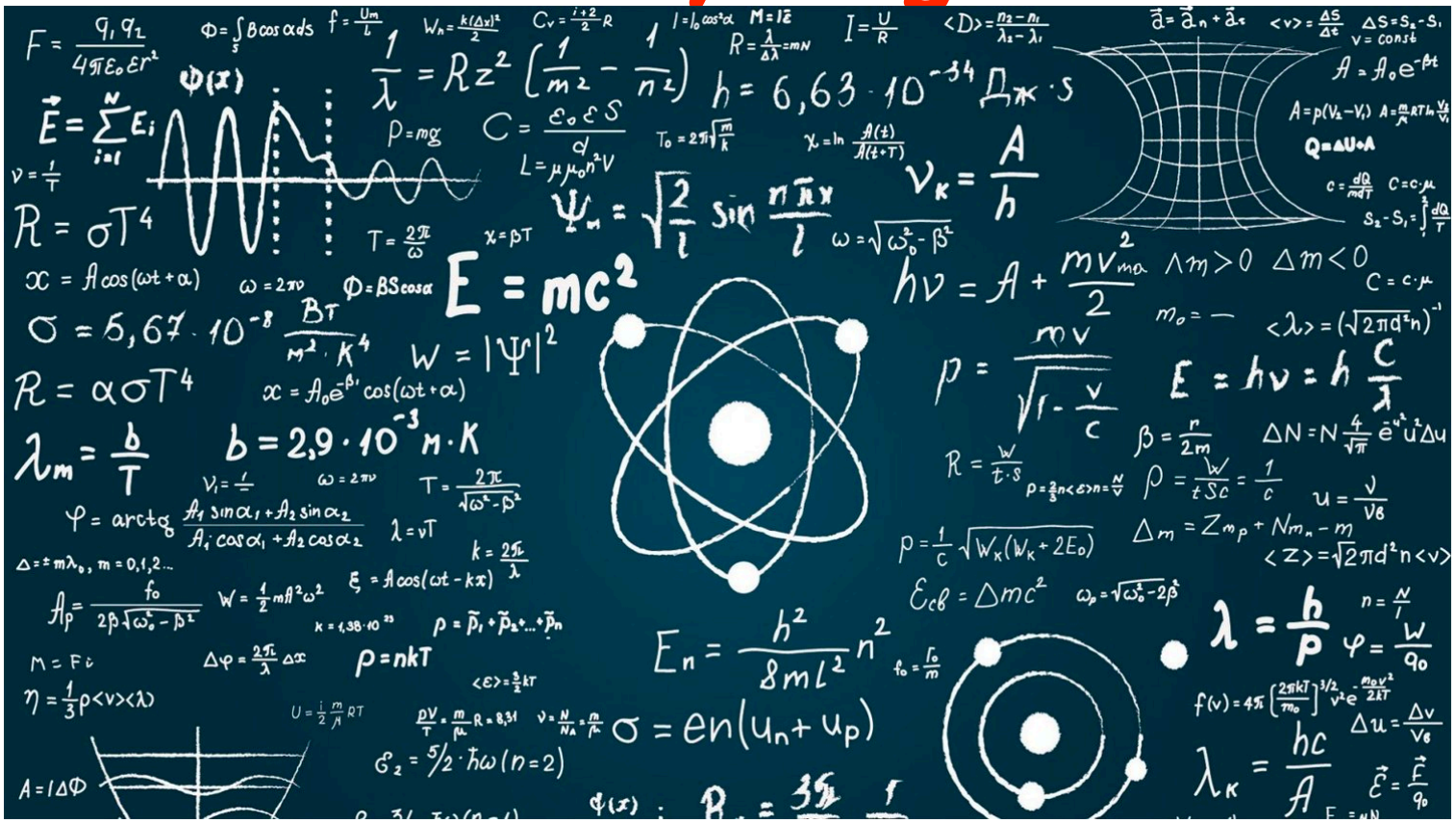
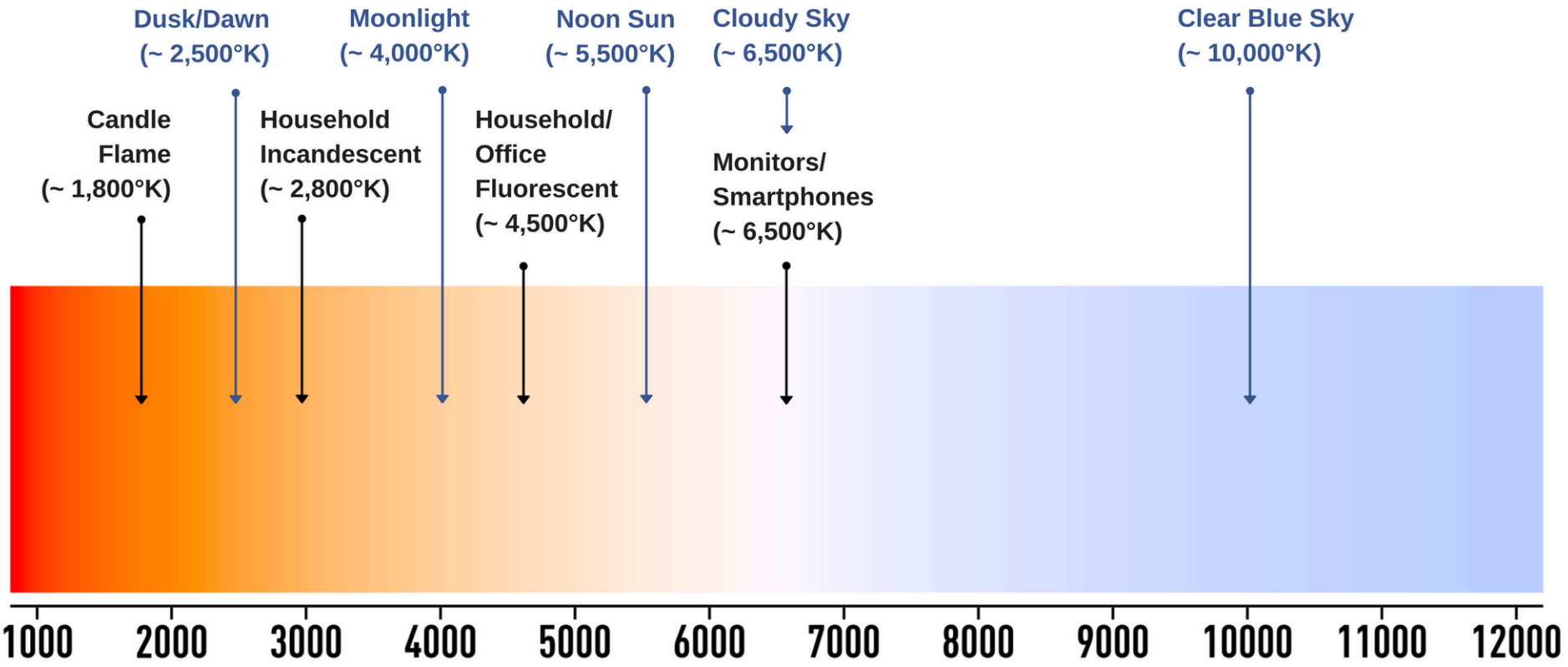
Atomic Physics

Chapter 3 Quantum Mechanics of the Hydrogen Atom



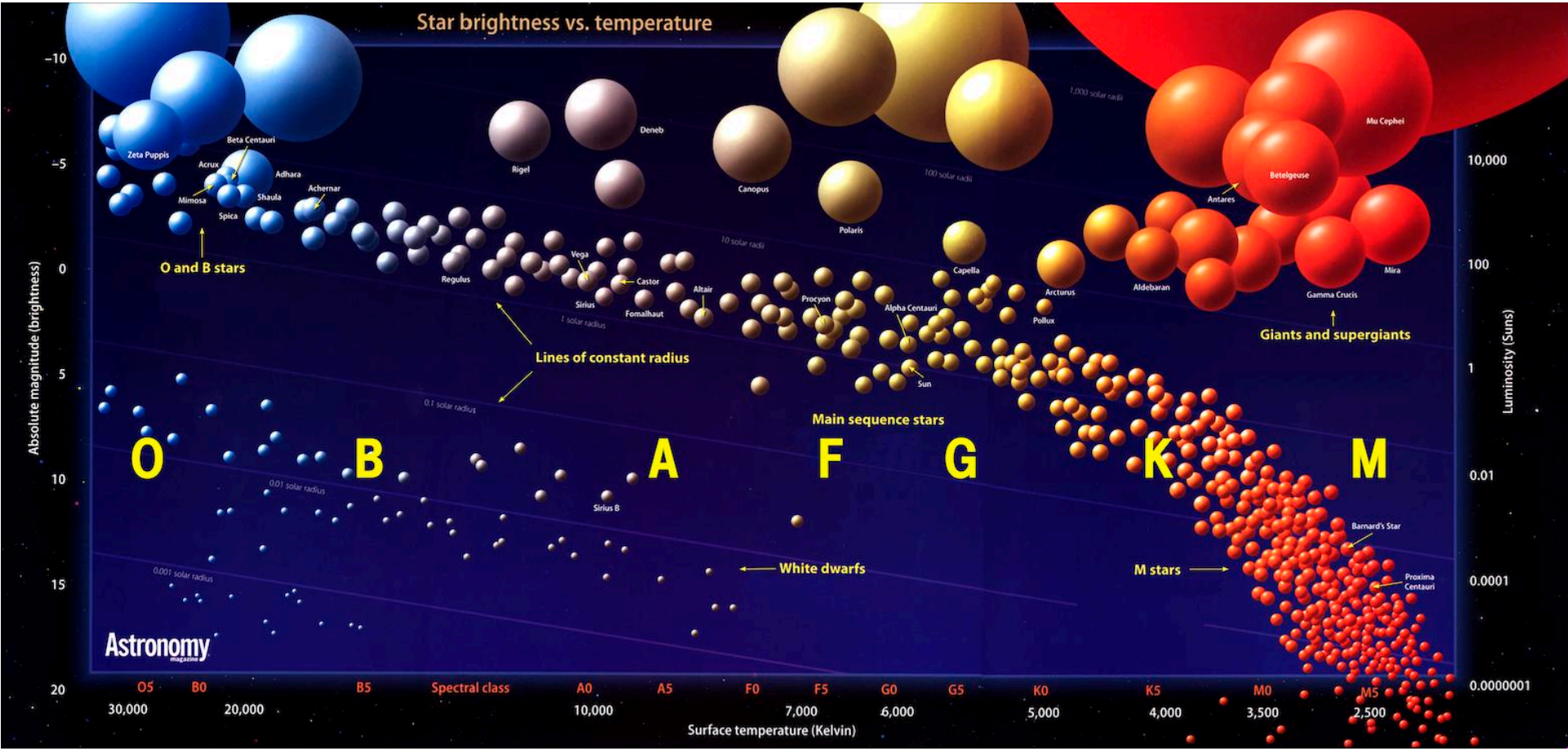
Blackbody Radiation

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



© 2016 Oojala Lighting
www.oojala.ca

Hertzsprung-Russell diagram

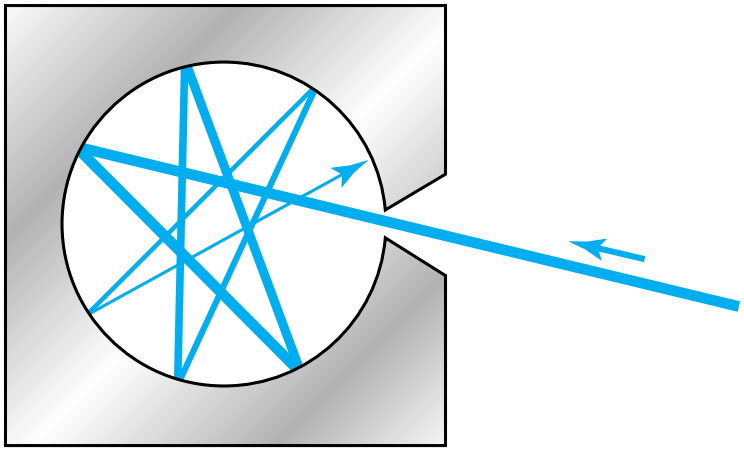


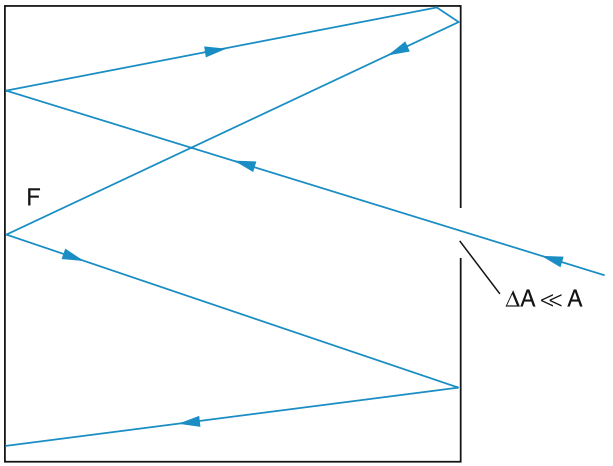
Blackbody Radiation

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 Kirchhoff's law: 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.

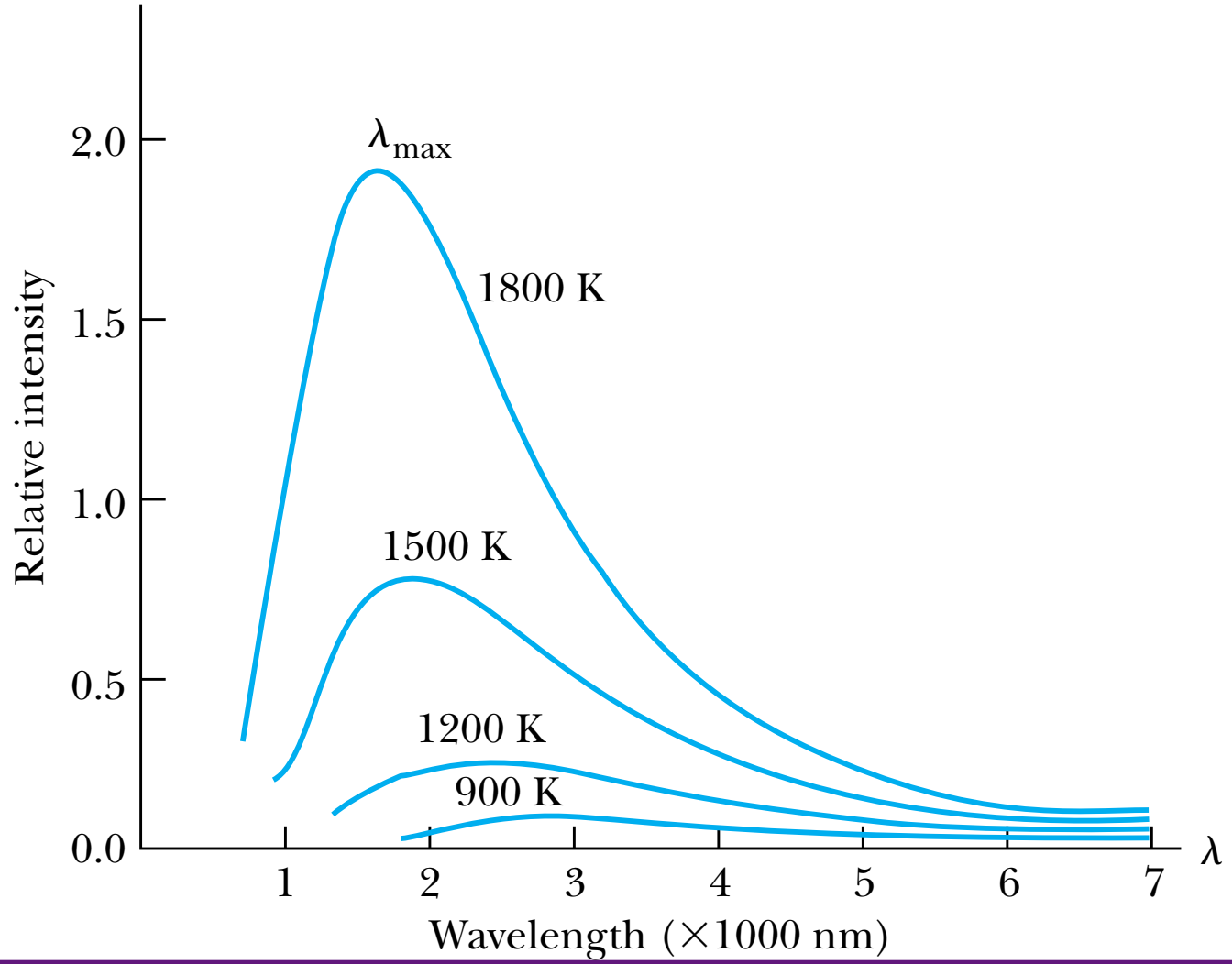
The intensity:

$$e_\nu = J(\nu, T)$$

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

Blackbody Radiation

Measurements of intensity for a blackbody are displayed



Blackbody Radiation

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)

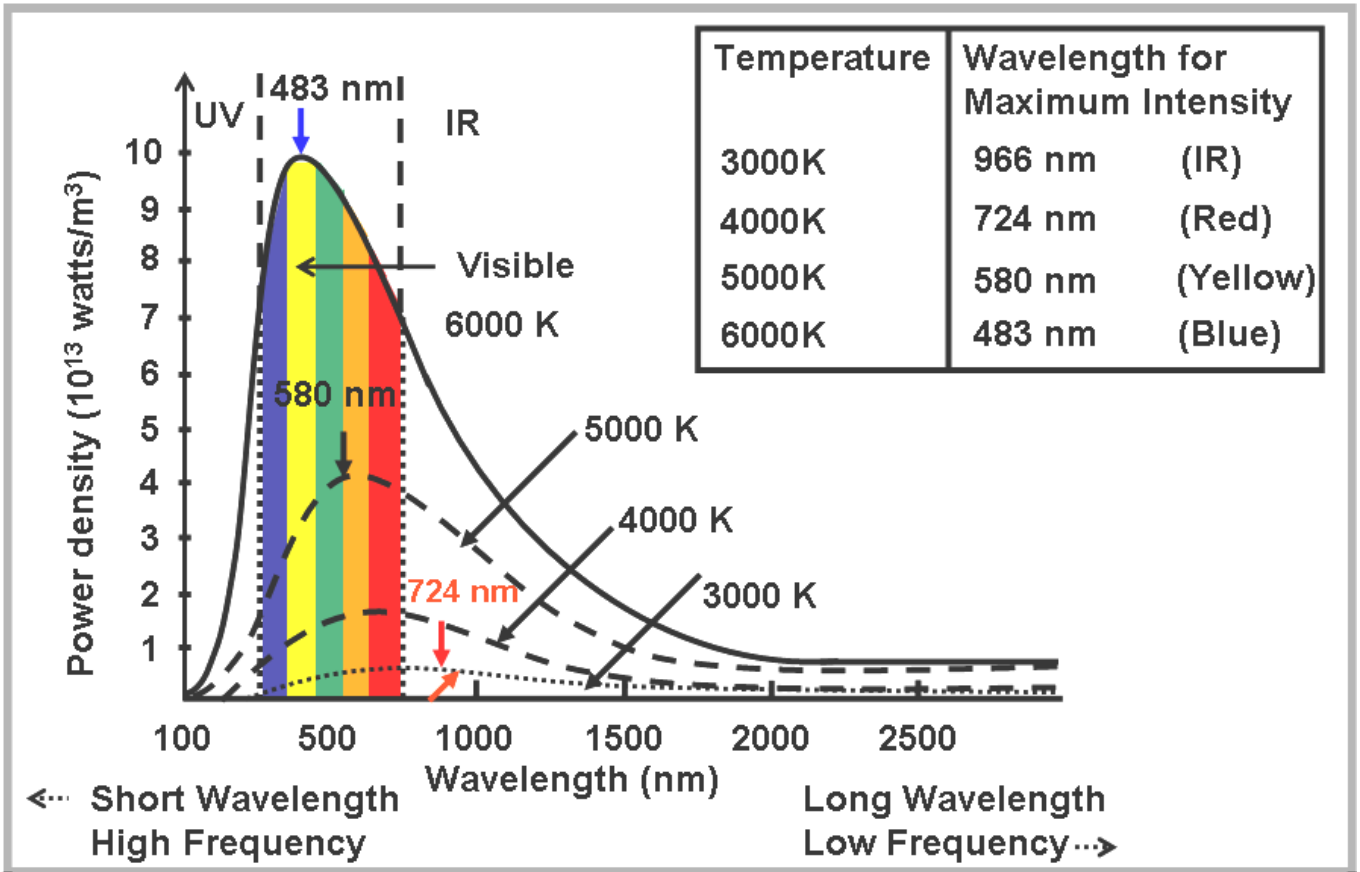


Fig. Spectral intensity distribution of Blackbody Radiation vs Wavelength Intensity Maximum shifts to shorter wavelengths as temperature increases.

Blackbody Radiation

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:

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

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:

$$e_{\text{total}} = \int J(\nu, T) d\nu = \sigma T^4$$

Stefan-Boltzmann law:

$$e_{\text{total}} = a\sigma T^4$$

with the constant

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

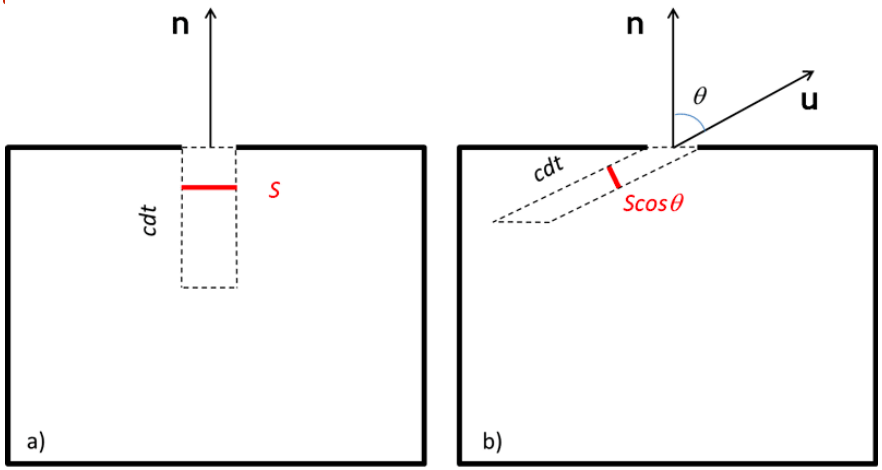
The emissivity a is simply the ratio of the emissive power of an object to that of an ideal blackbody and is always less than 1.

Blackbody Radiation

It is more convenient to consider the spectral energy density, or energy per unit volume per unit frequency of the radiation within the blackbody cavity, u(ν, T).

Because the cavity radiation is isotropic and unpolarized, one can average over direction to show that the constant of proportionality between J(ν, T) and u(ν, T) is c/4, where c is the speed of light. Therefore,

$$J(\nu, T) = u(\nu, T)c/4$$

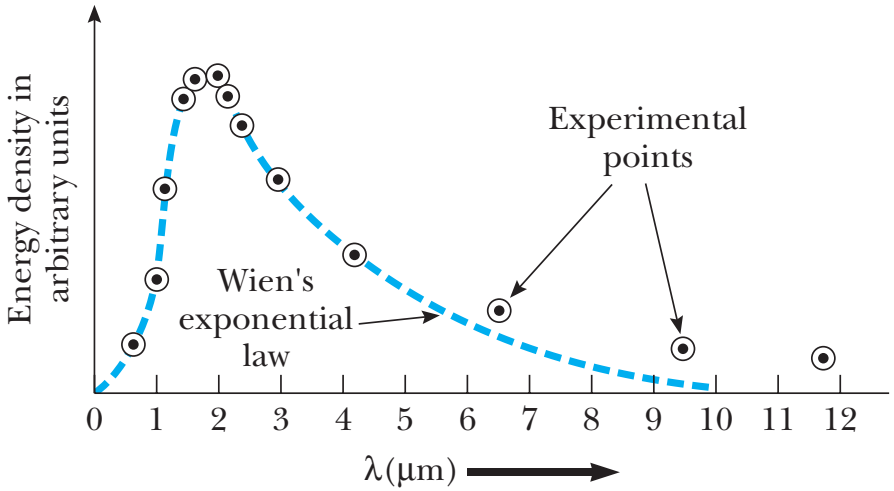


Blackbody Radiation

An important guess as to the form of the universal function u(ν, T) was made in 1893 by Wien and had the form

$$u(\nu, T) = A\nu^3 e^{-\beta\nu/T}$$

where A and β are constants. This result was known as Wien's exponential law; it resembles and was loosely based on Maxwell's velocity distribution for gas molecules.



Blackbody Radiation

In his 1900 attempt, Rayleigh focused on understanding the nature of the electromagnetic radiation inside the cavity.

When the cavity is in thermal equilibrium, the electromagnetic energy density inside the cavity is equal to the energy density of the charged particles in the walls of the cavity.

The average total energy of the radiation leaving the cavity can be obtained by multiplying the average energy of the oscillators by the number of modes (standing waves) of the radiation in the frequency interval ν to ν+dv:

$$N(\nu) = \frac{8\pi\nu^2}{c^3},$$

So the electromagnetic energy density in the frequency range ν to ν+$d\nu$ is given by

$$u(\nu, T) = N(\nu)\langle E\rangle = \frac{8\pi\nu^2}{c^3}\langle E\rangle,$$

where <E> is the average energy of the oscillators present on the walls of the cavity. According to the equipartition theorem of classical thermodynamics, all oscillators in the cavity have the same mean energy, irrespective of their frequencies:

$$\langle E\rangle = \frac{\int_0^\infty E e^{-E/kT} dE}{\int_0^\infty e^{-E/kT} dE} = kT,$$

Blackbody Radiation

Rayleigh-Jeans formula:

$$u(\nu, T) = \frac{8\pi\nu^2}{c^3} kT$$

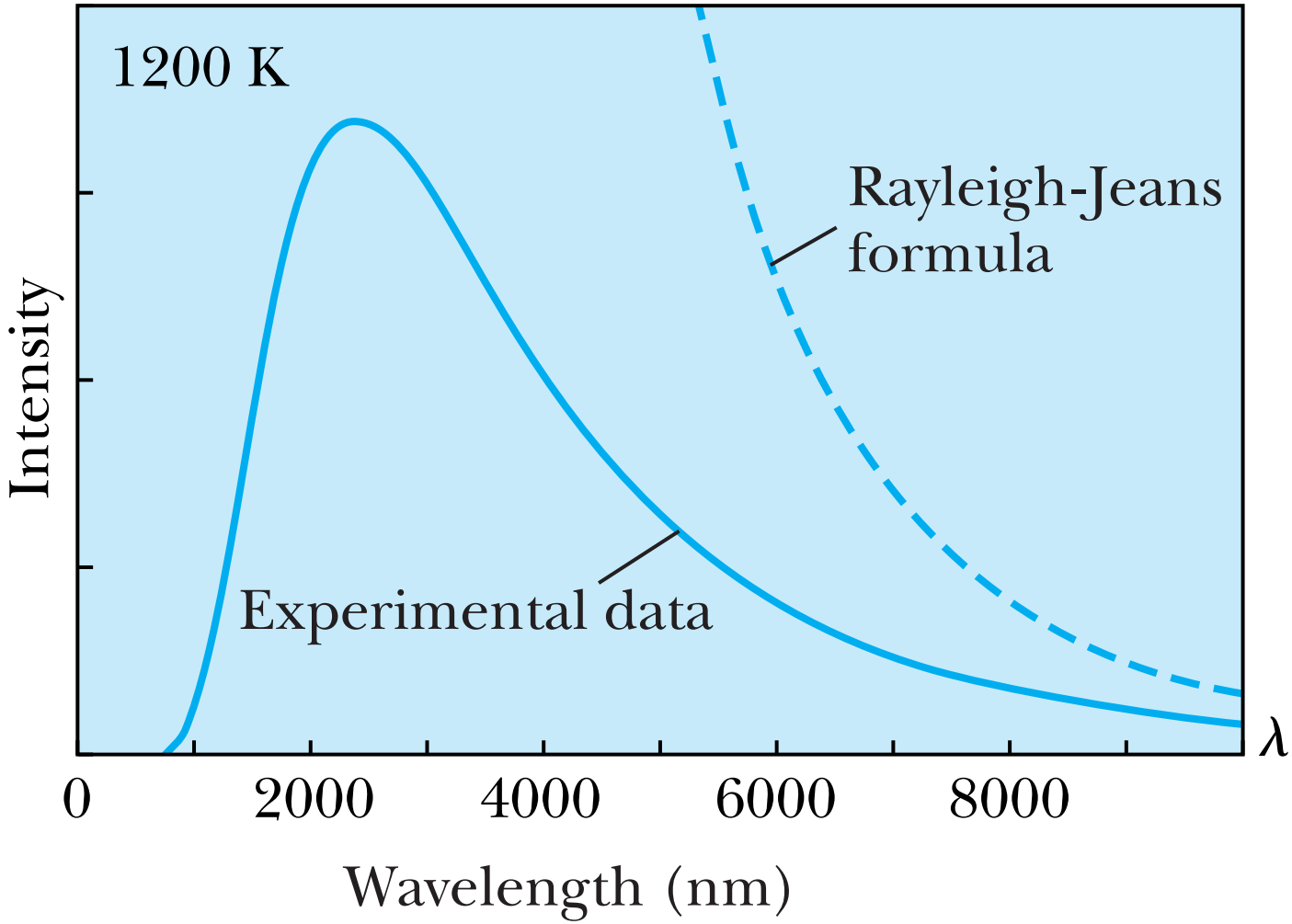
It is the best formulation that classical theory can provide to describe blackbody radiation.

When

$$\lambda \to 0 \qquad u(\lambda, T)\, d\lambda = \frac{8\pi}{\lambda^4} k_B T\, d\lambda$$

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.

Blackbody Radiation

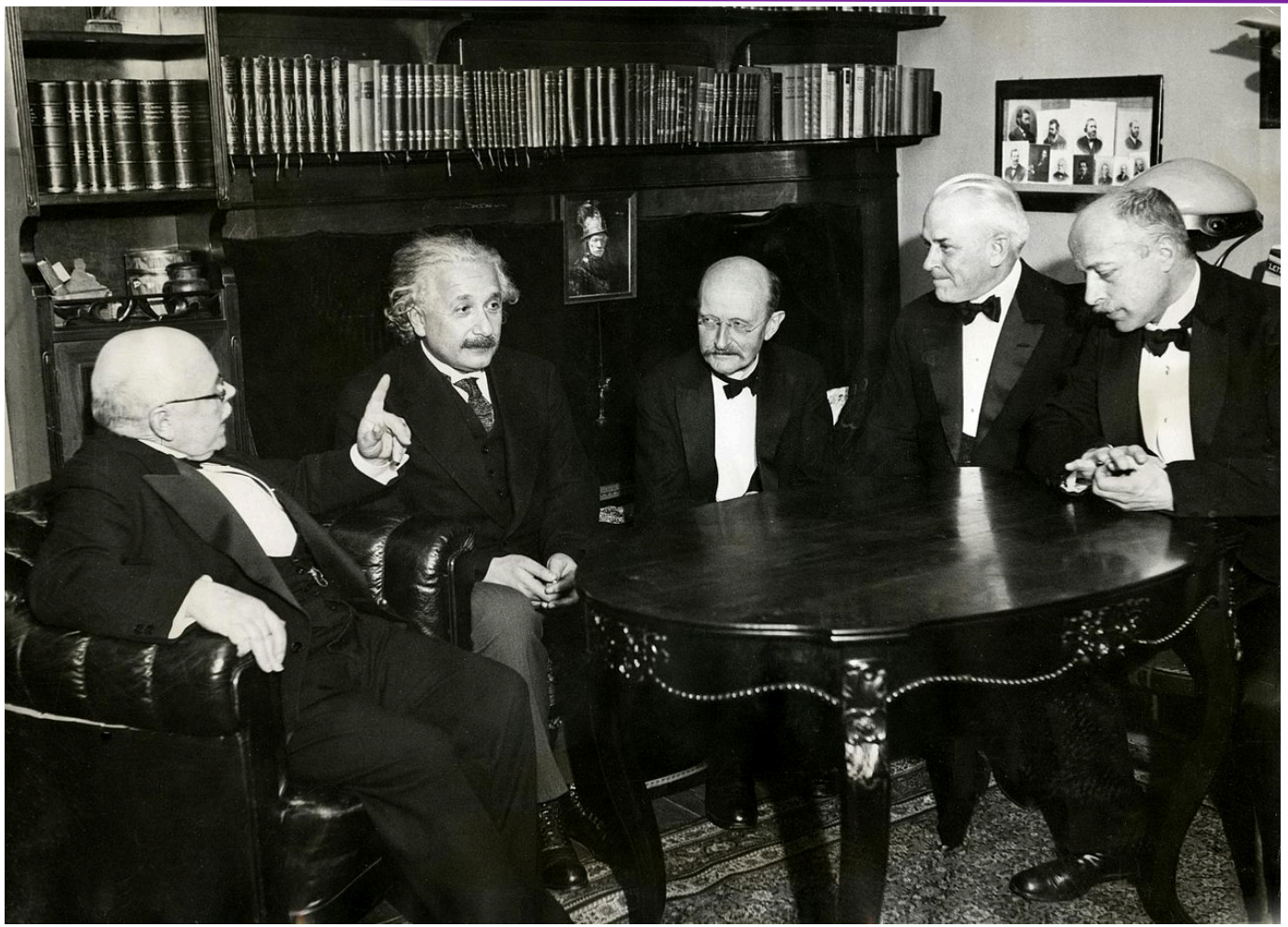


Max Plank





Max Plank



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

Blackbody Radiation

南開大學

Planck's radiation law:

$$u(\nu, T) = \frac{8\pi\nu^2}{c^3}\frac{h\nu}{e^{h\nu/kT} - 1}$$

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

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

A *discrete* summation corresponding to the discreteness of the oscillators' energies[4]:

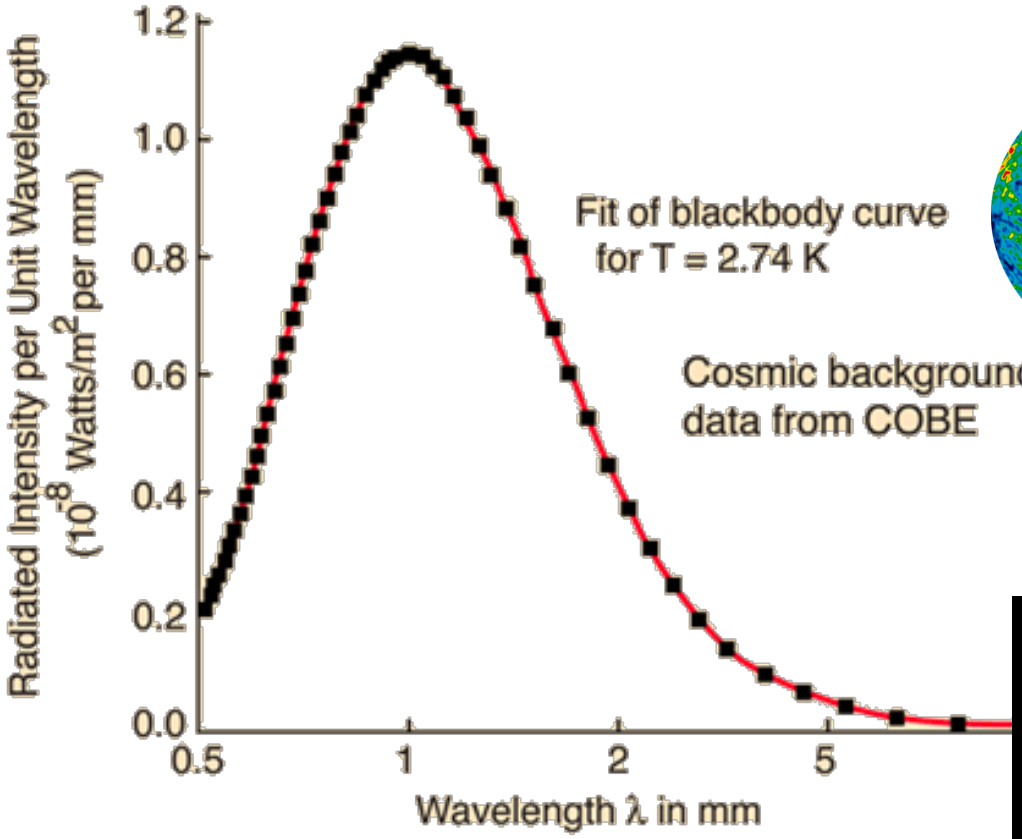
$$\langle E \rangle = \frac{\sum_{n=0}^{\infty} nh\nu e^{-nh\nu/kT}}{\sum_{n=0}^{\infty} e^{-nh\nu/kT}} = \frac{h\nu}{e^{h\nu/kT} - 1},$$

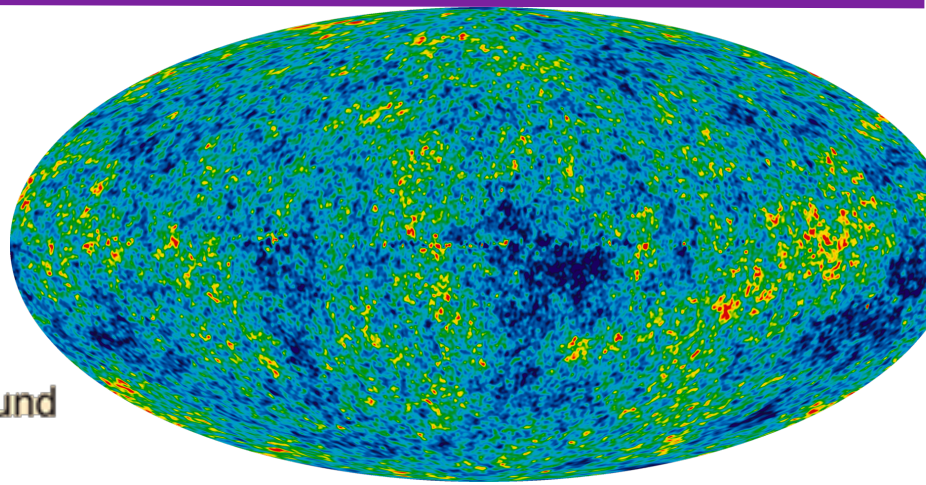
2. The oscillators can absorb or emit energy in discrete multiples of the fundamental quantum of energy given by

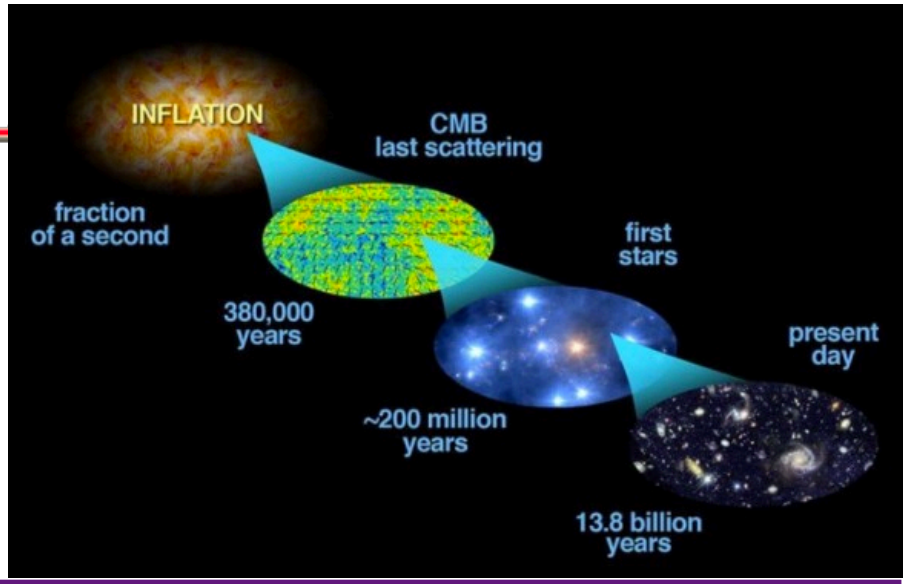
$$\Delta E = h\nu$$

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

Cosmic microwave background







Blackbody Radiation

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

$$\tilde{u}(\lambda, T) = u(\nu, T)\left|\frac{d\nu}{d\lambda}\right| = \frac{8\pi hc}{\lambda^5}\frac{1}{e^{hc/\lambda kT} - 1}. \qquad \partial\tilde{u}(\lambda, T)/\partial\lambda = 0,$$

so,

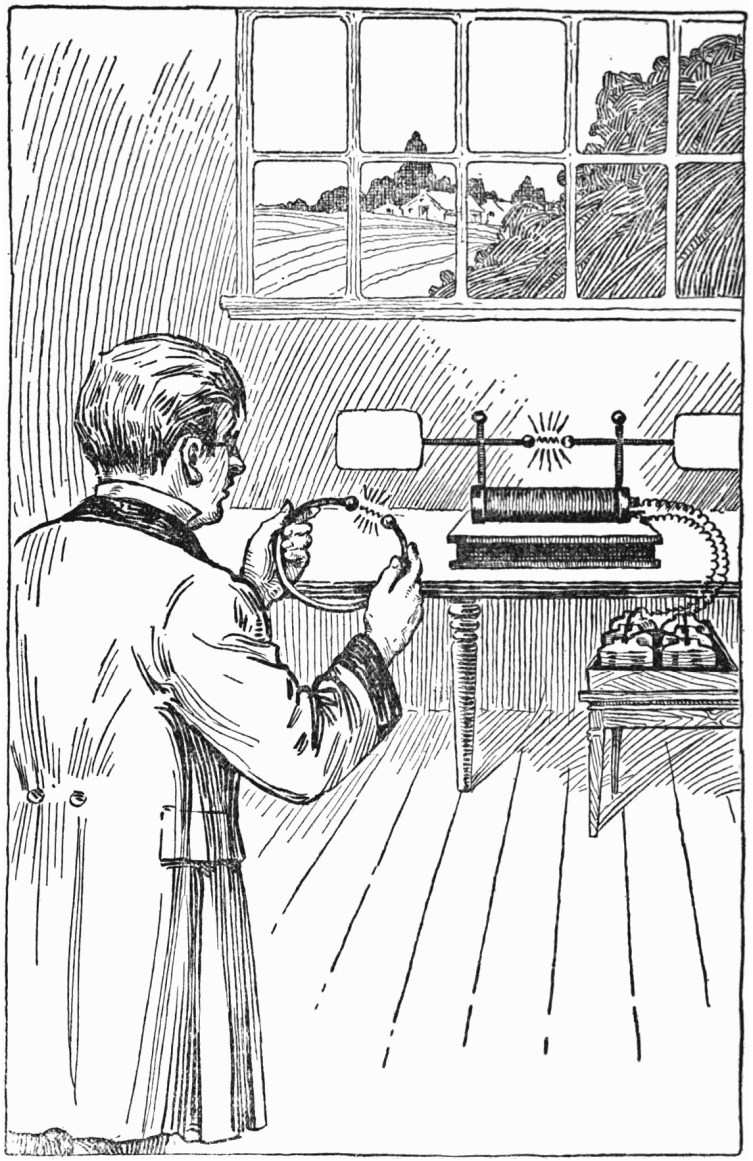
$$\frac{hc}{\lambda_{\max} kT}\left(\frac{e^{hc/\lambda_{\max} kT}}{e^{hc/\lambda_{\max} kT} - 1}\right) = 5,$$

Let,

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

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

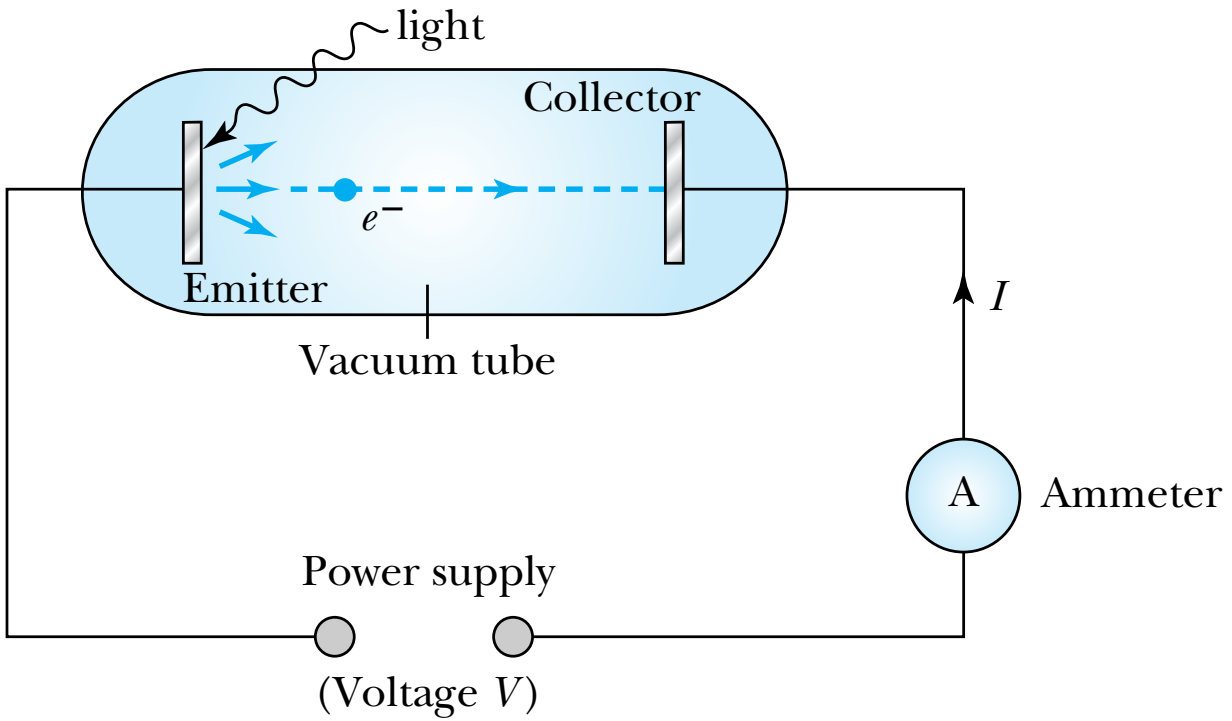
The photoelectric effect is one of several ways in which electrons can be emitted by materials.

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.



Photoelectric Effect

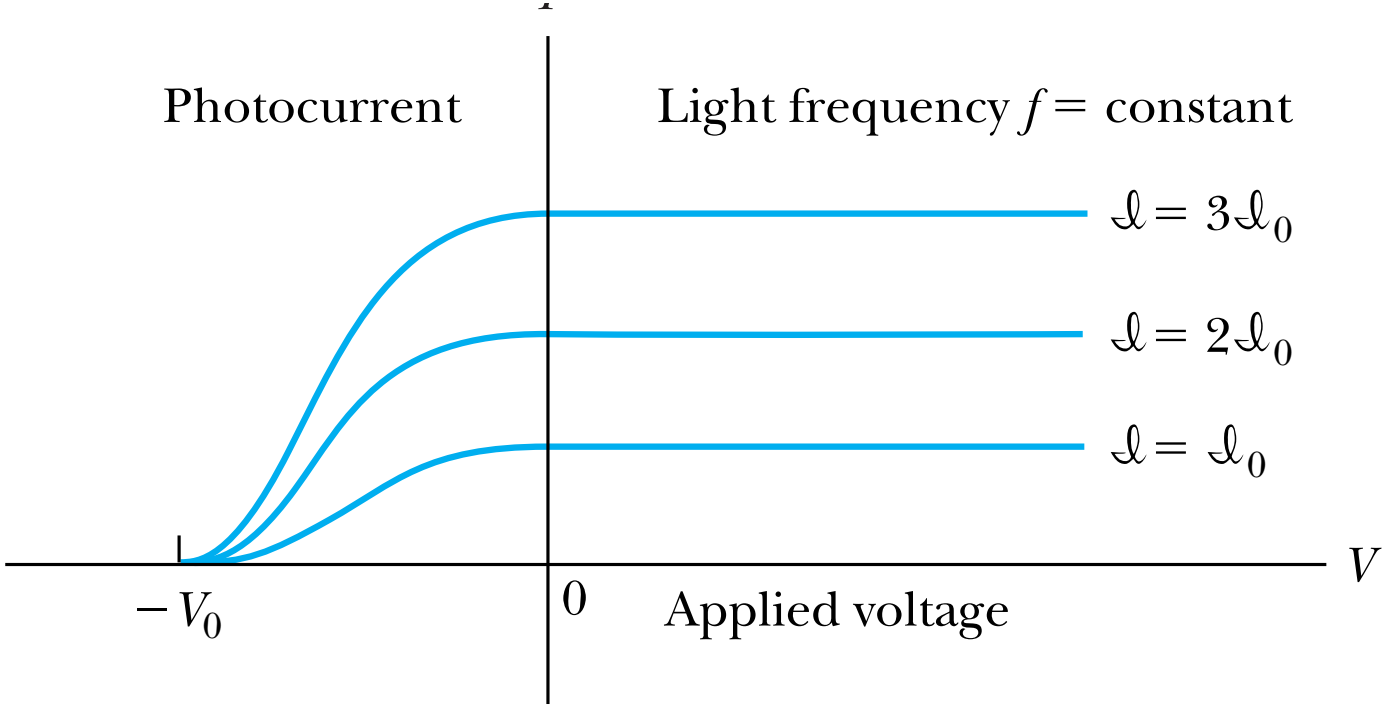
We call the ejected electrons photoelectrons. The minimum extra kinetic energy that allows electrons to escape the material is called the work function ϕ. The work function is the minimum binding energy of the electron to the material

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

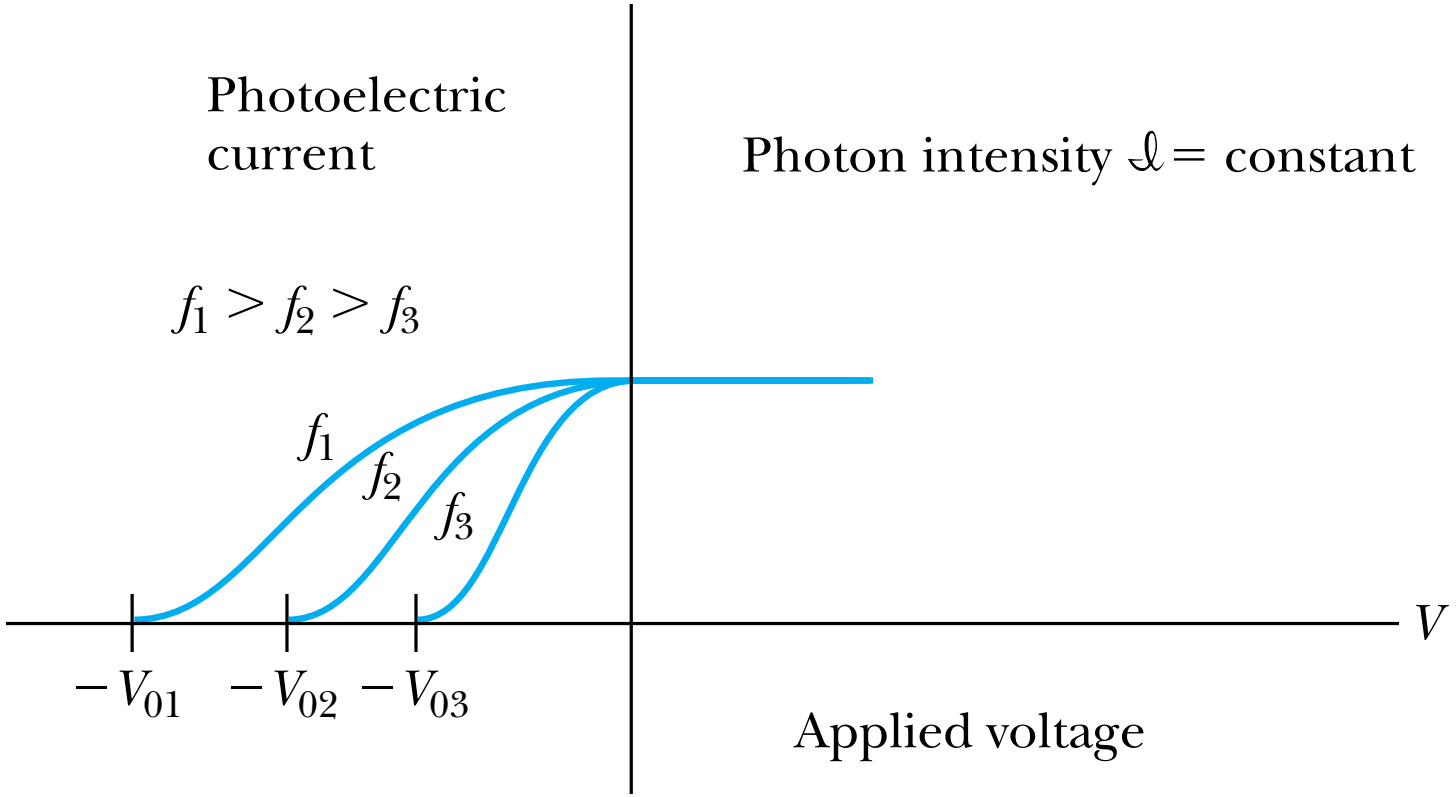
The pertinent experimental facts about the photoelectric effect are these:

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



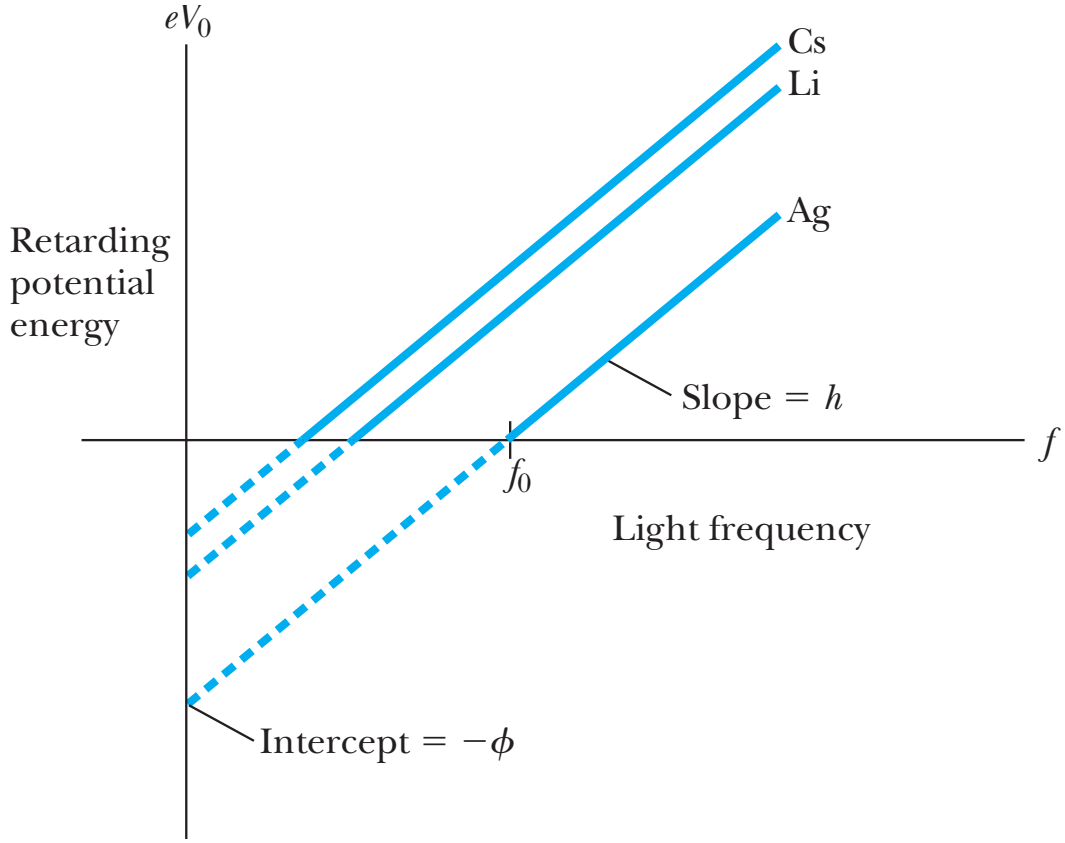
Experimental Results

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

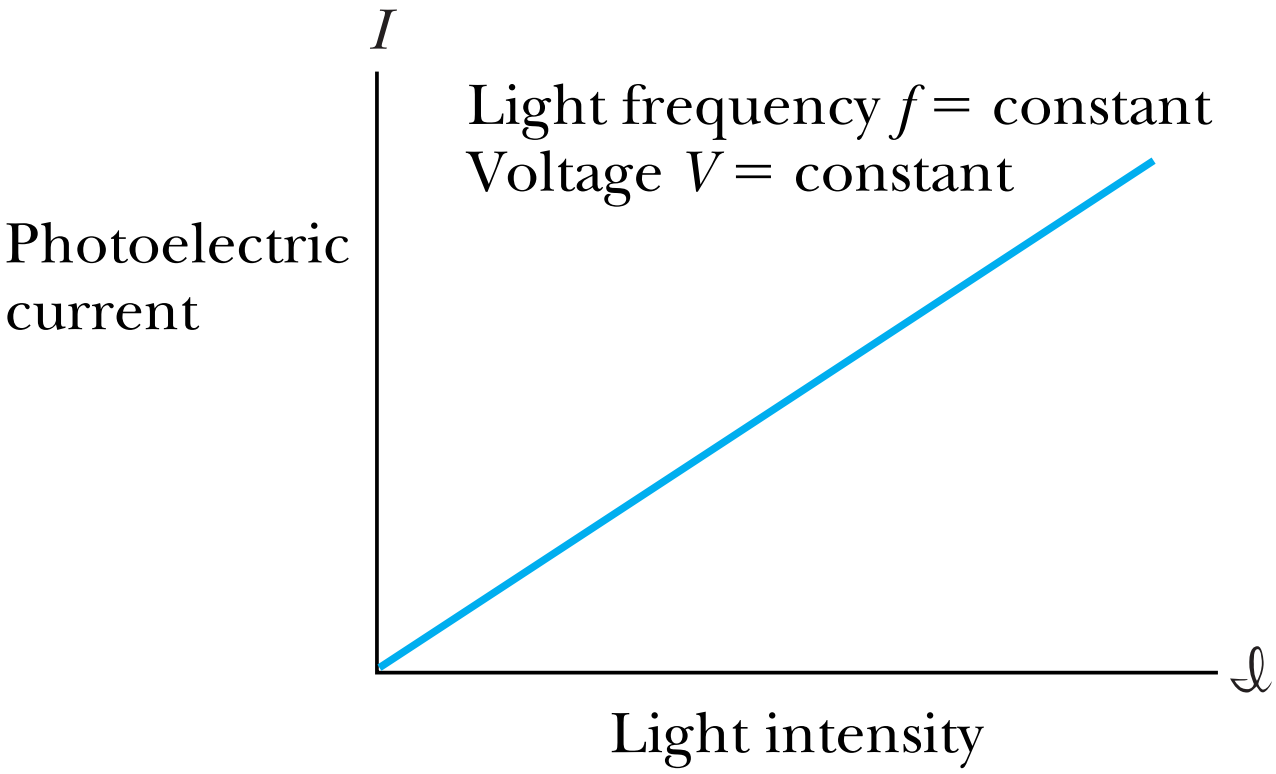


Experimental Results

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



Experimental Results

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.

Einstein's Theory

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

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

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

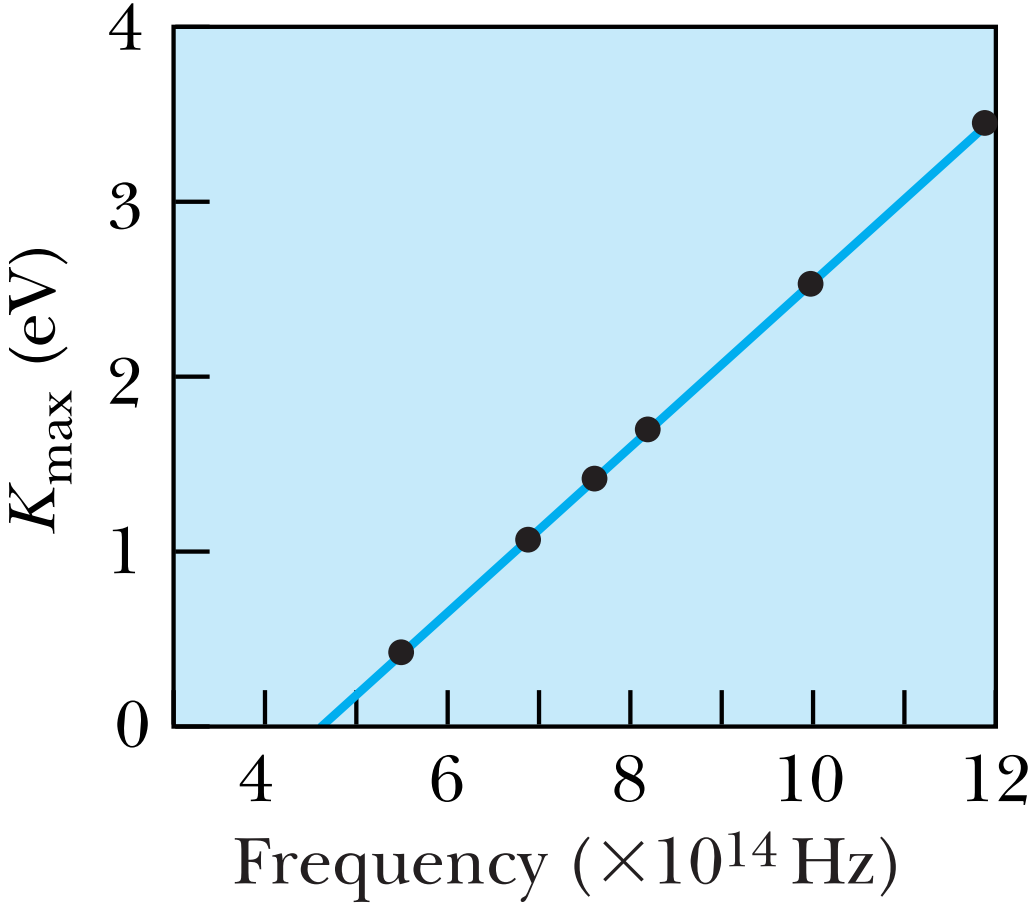
which proposed by Einstein in 1905, predicts that the stopping potential will be linearly proportional to the light frequency, The slope is independent of the metal used to construct the photocathode. This equation can be rewritten as

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

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

Quantum Interpretation

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



Wave properties of matter

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 $\lambda = \frac{h}{p} = \frac{6.63 \times 10^{-34}}{0.057 \times 25} = 4.7 \times 10^{-34}\text{m}$

(b) For the electron

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

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.

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

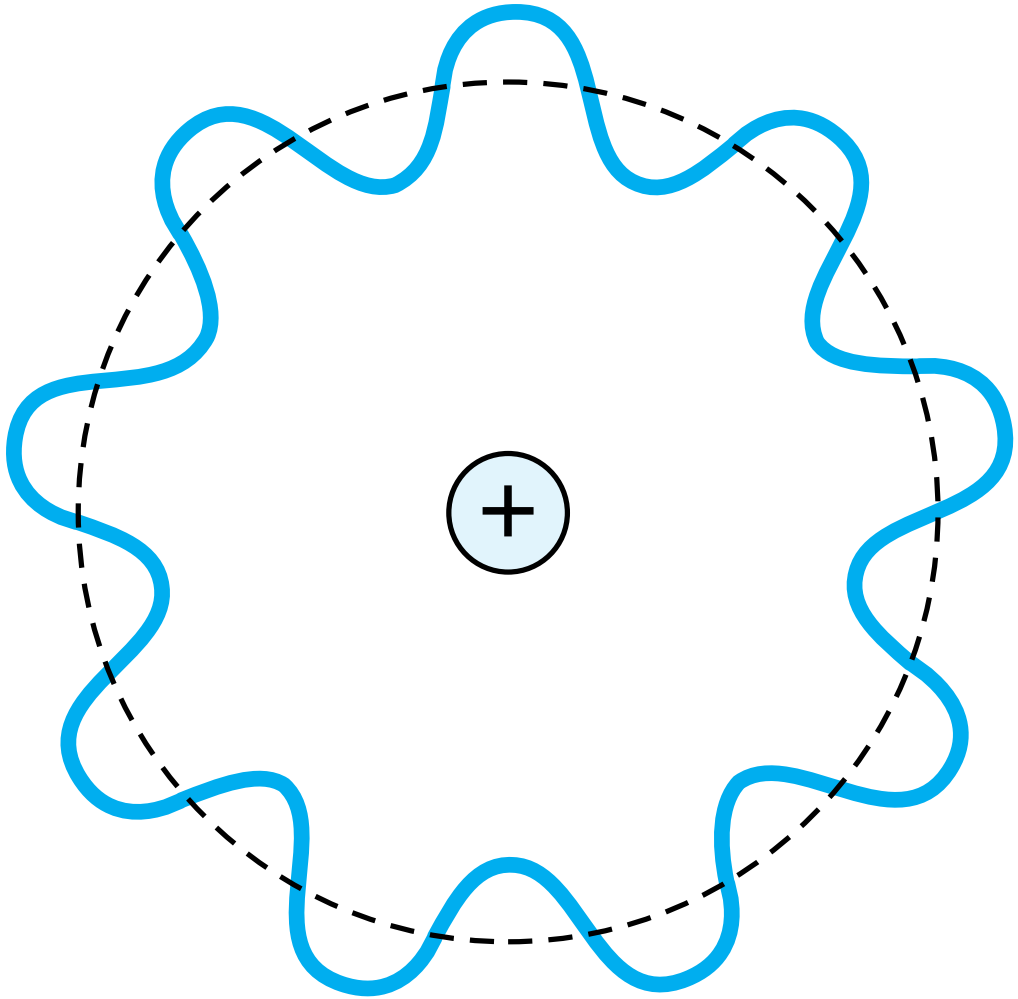
where r is the radius of the orbit. Now we use the de Broglie relation for the wavelength and obtain

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

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

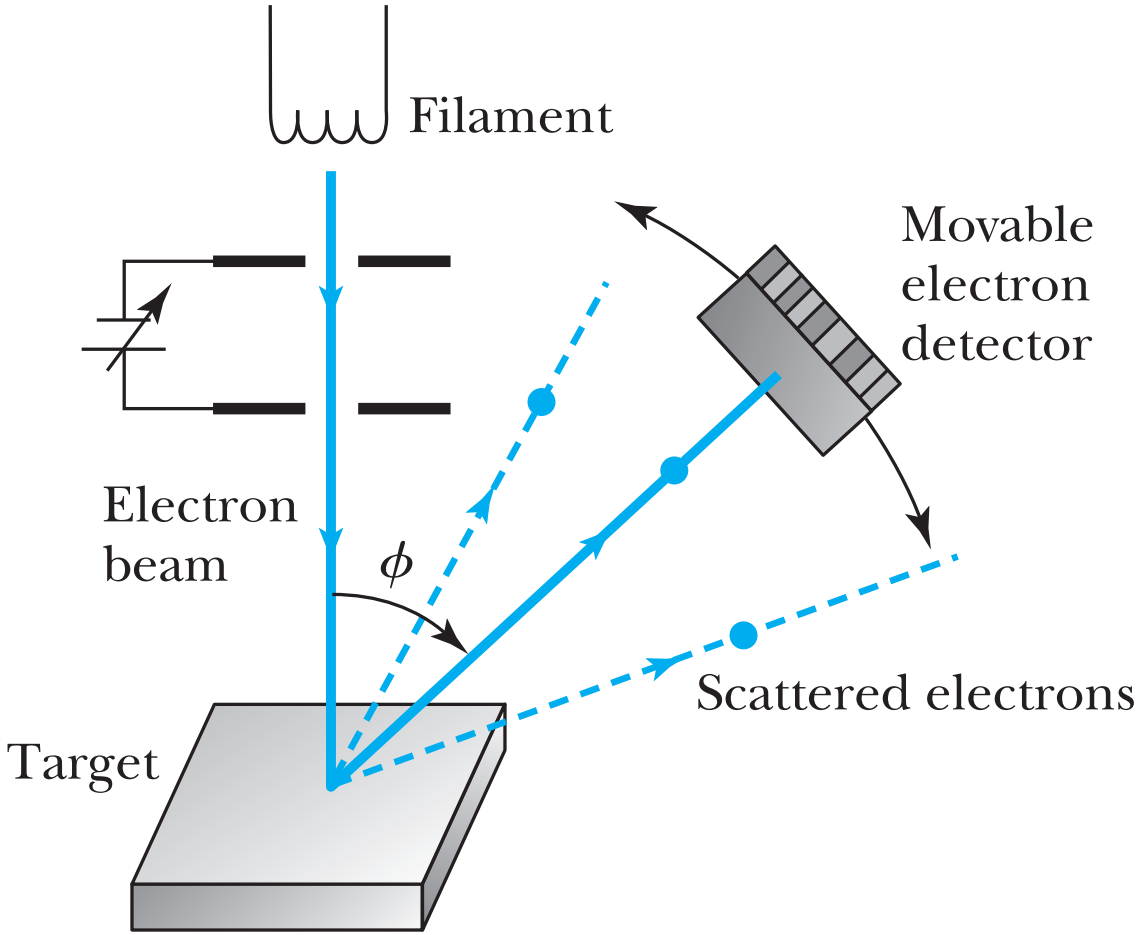
$$L = rp = \frac{nh}{2\pi} = n\hbar$$

Bohr's Quantization Condition

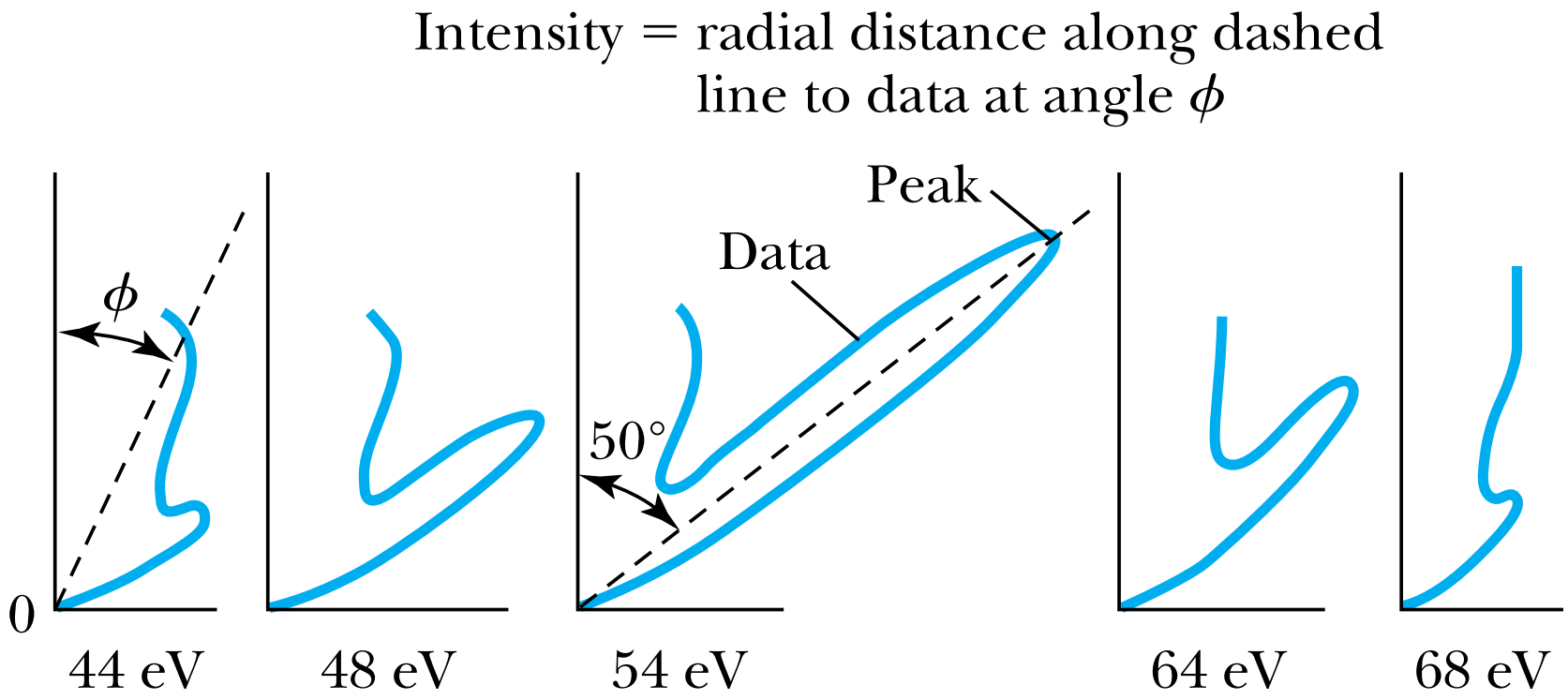


Electron Scattering

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

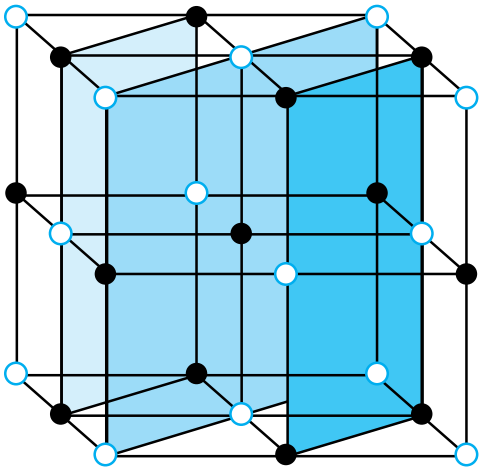


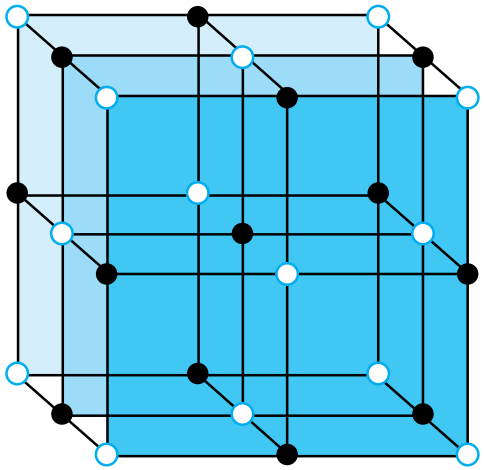
The relationship between the incident electron beam and the nickel crystal scattering planes is shown

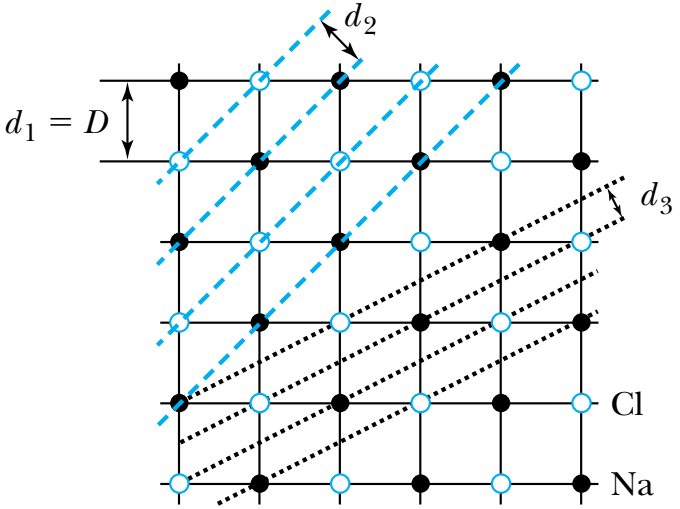


Bragg Law

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.



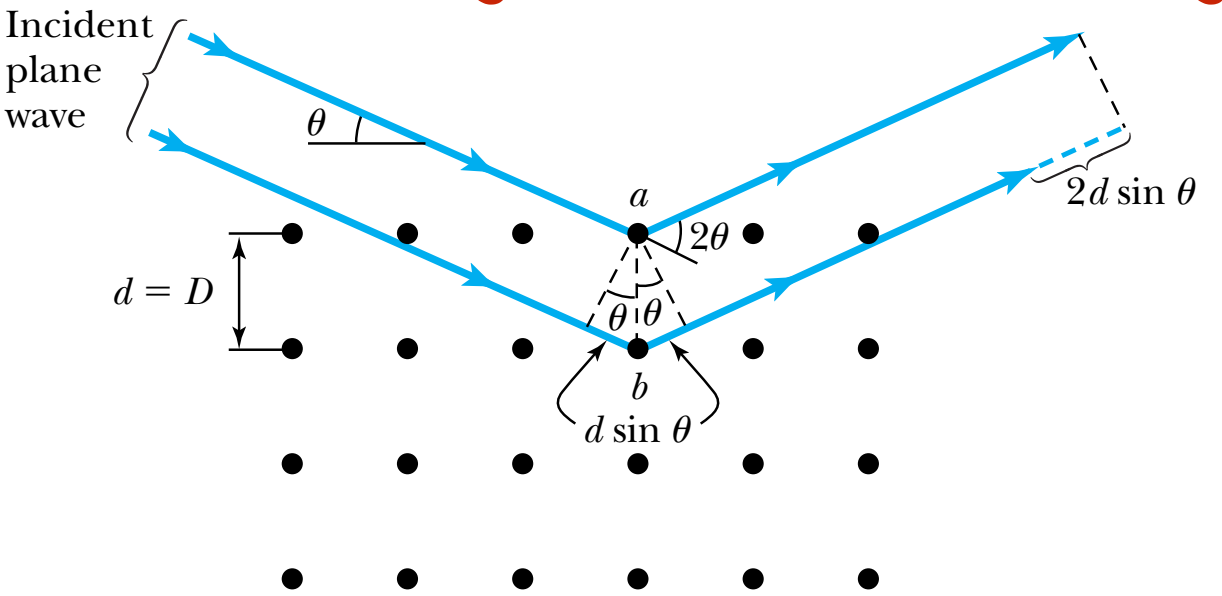




Bragg Law

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.

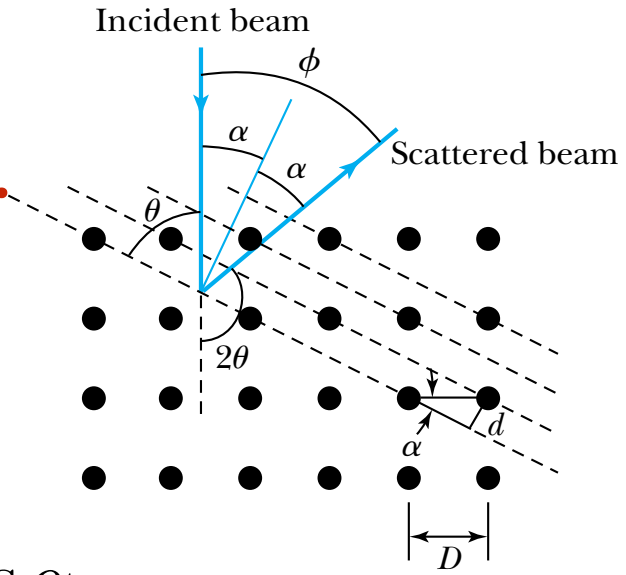


Bragg's Law with condition 2

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

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

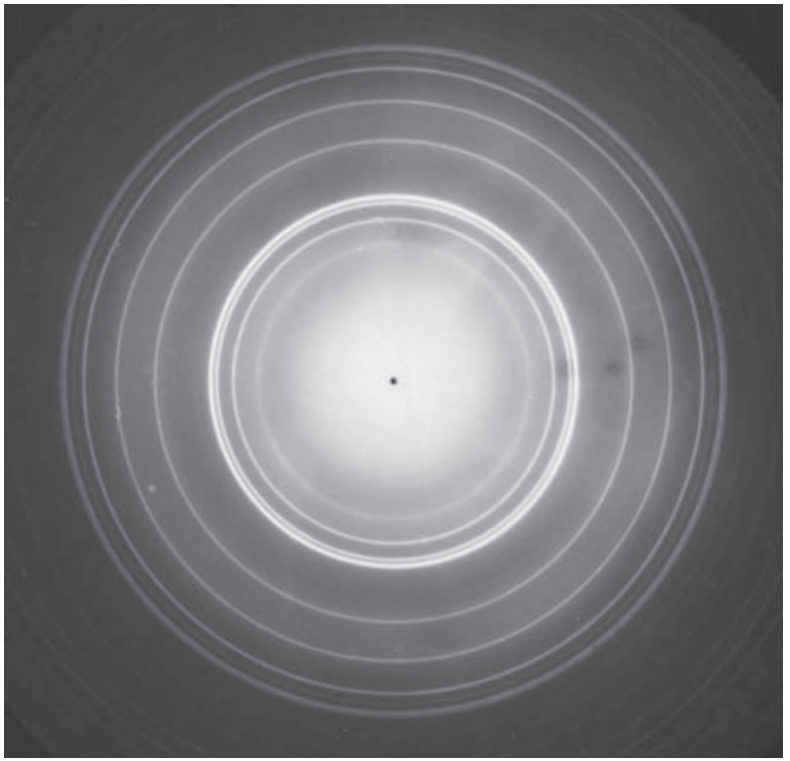
For nickel the interatomic distance is D=0.215 nm. If the peak found by Davisson and Germer at 50° was n=1, then the electron wavelength should be

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



Courtesy of David Follstaedt, Sandia National Laboratory

(a)



Omikron/Photo Researchers, Inc.

(b)

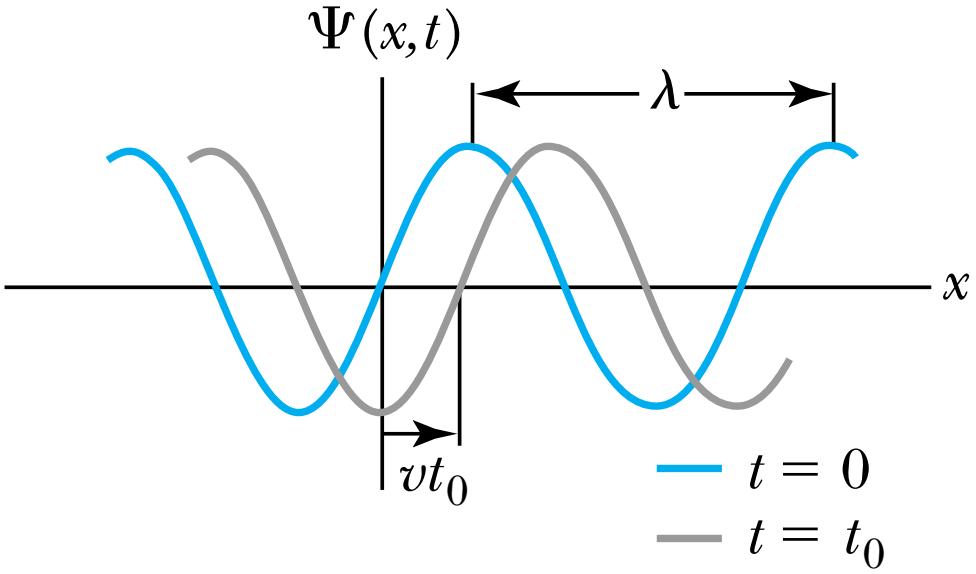

CRAFTS
FOR

Wave motion

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.



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

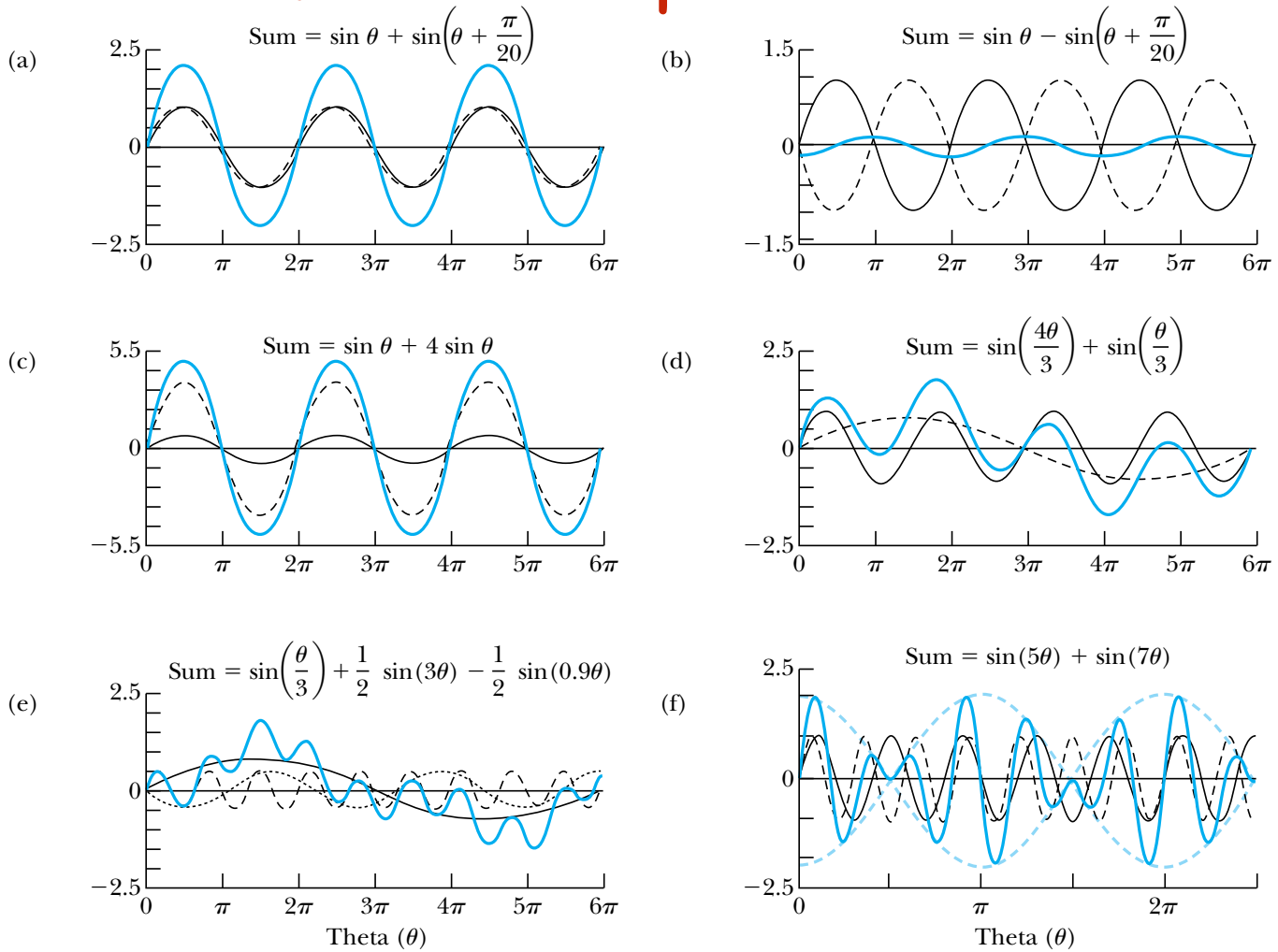
$$\Psi(x,t) = A\sin\left[kx - \omega t + \phi\right]$$

Phase constant

Wave motion

南開大學

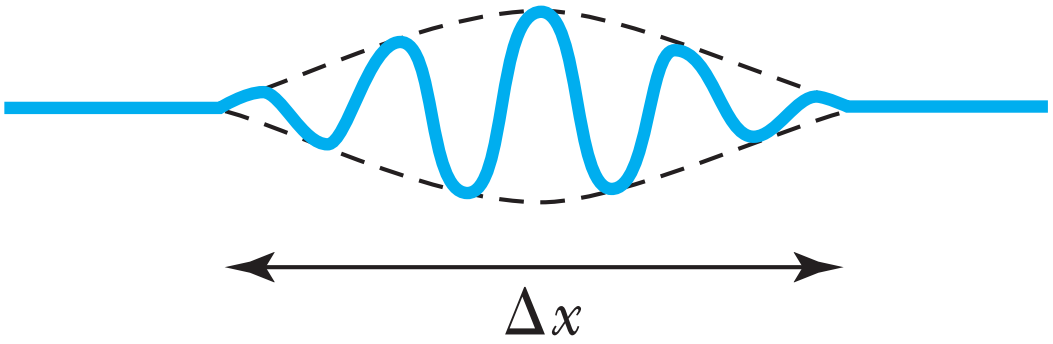
According to the principle of superposition, we add the displacements of all waves present.



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 $\Delta\omega/2$.

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

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

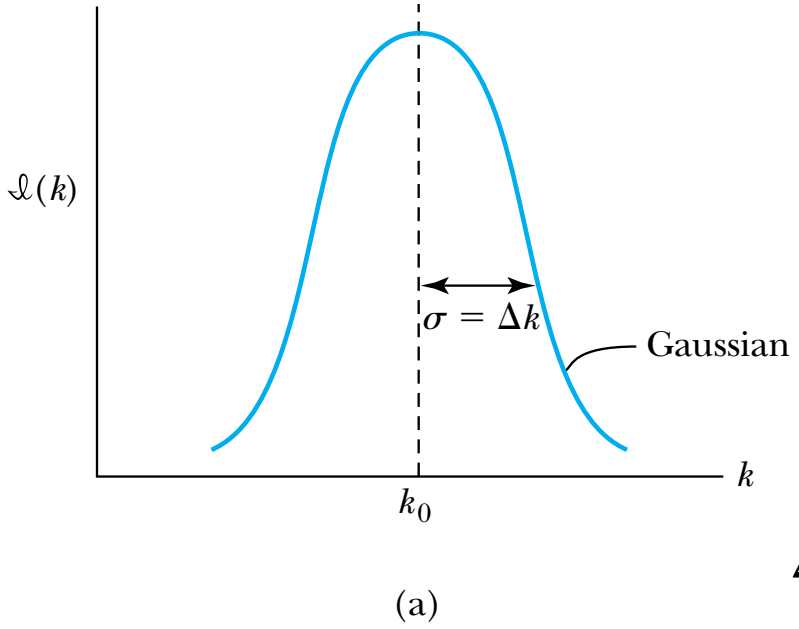
If we are to treat particles as matter waves, we have to be able to describe the particle in terms of waves.

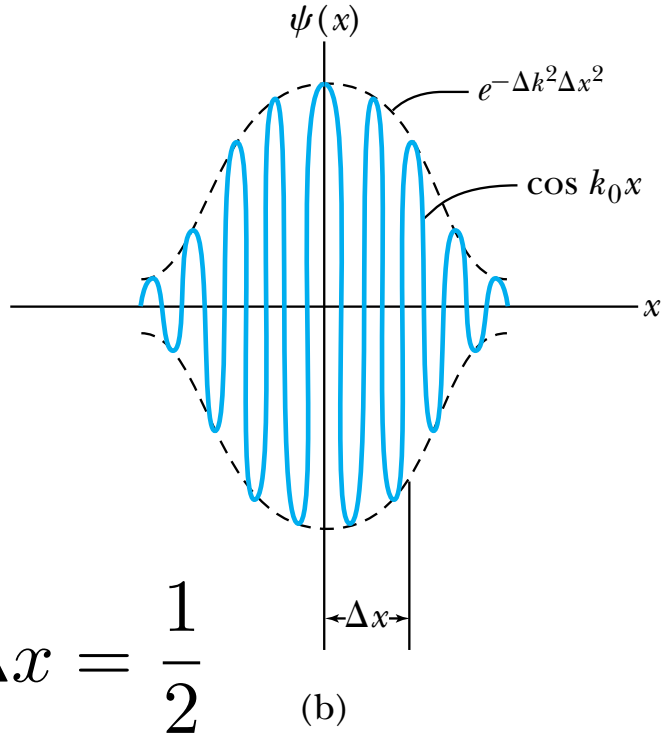
An important aspect of a particle is its localization in space.

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

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

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





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


35
Br
eaking
56
Ba
d

Uncertainty Principle

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.

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.

Uncertainty Principle

南開大學

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



南開大學

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



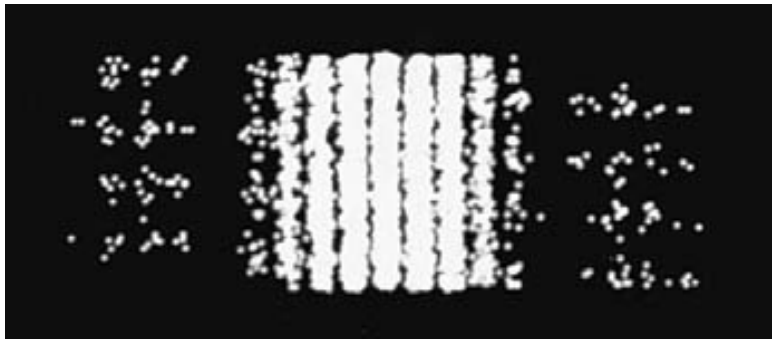
(a) 20 counts



(b) 100 counts



(c) 500 counts



(d) ~4000 counts

Simulation and photos courtesy of Julian V. Noble.

Probability and Wave Functions

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

We used a function Ψ(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

Probability and Wave Functions

In general, $\Psi(x, y, z, t)$ 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

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



南開大學

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 ψ(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.

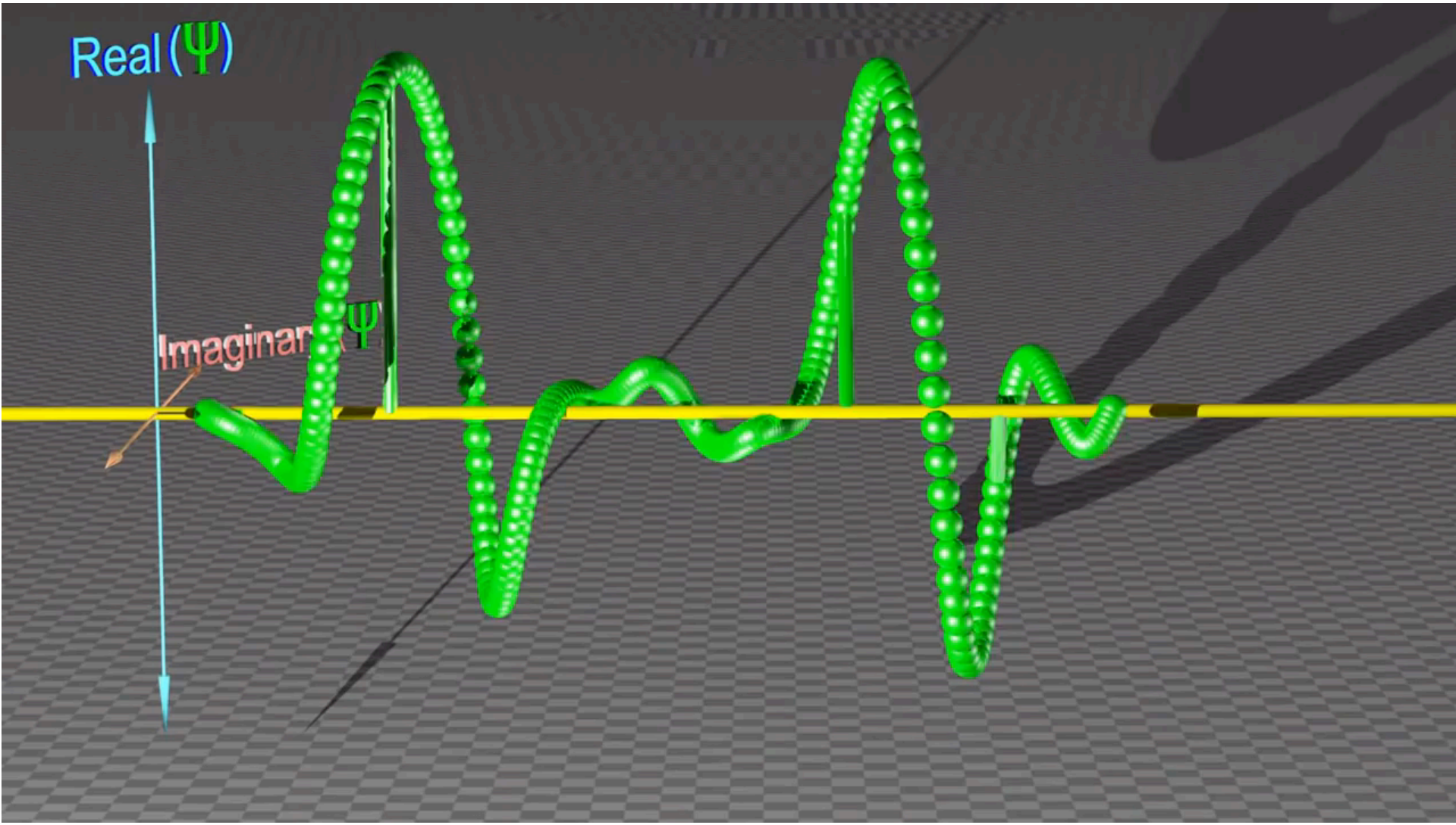
$$i\hbar\frac{1}{f(t)}\frac{\partial f(t)}{\partial t} = B$$

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)

Operator

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

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

Postulate 3:

An observable is represented by a linear and hermitian operator that is written as A in quantum mechanics

Operator

An operator, A, is a mathematical instruction, which when applied to a mathematical object, say ψ, gives another mathematical object ϕ of the same nature. It is symbolically written as $\hat{A}\psi = \phi$

A simple operator, for instance, may contain the instruction for just taking the derivative of a function. Suppose we call this operator D. Then, for a given function ψ(x):

$$\hat{D}\psi(x) = \frac{d\psi}{dx} = \phi(x).$$

Or, in shorthand notation, we just write

$$\hat{D}\psi(x) = \phi(x)$$

Another operator could be the instruction to obtain a new function ϕ(x) by multiplying a given function φ(x) by its independent variable x, that is

$$\phi(x) = x\psi(x)$$

In other words, the independent variable x can also be looked upon as an operator.

$$\phi(x) = \hat{x}\psi(x) = x\psi(x)$$

inear operators: If, for the given scalars α and β and unctions φ(x) and ϕ(x), the operator A satisfies the elation

$$\hat{A}(\alpha\psi(x) + \beta\phi(x)) = \alpha\hat{A}\psi(x) + \beta\hat{A}\phi(x)$$

Operator

If the action of an operator A on a function ϕ(x) is to multiply that function by some constant a:

$$\hat{A}\phi(x) = a\,\phi(x)$$

we say that the constant a is an eigenvalue of the operator A, and we call ϕ(x) an eigenfunction of A.

An operator can have more than one eigenvalues.

The set of all possible eigenvalues of an operator constitutes the so-called eigenvalue spectrum (or, simply spectrum) of the operator.

Given an operator A, let us define an operator A† by

$$\int_{-\infty}^{+\infty} \phi^*(\vec{r}) \left(\hat{A}\psi(\vec{r})\right) d^3x = \int_{-\infty}^{+\infty} \left(\hat{A}^\dagger \phi(\vec{r})\right)^* \psi(\vec{r})\, d^3x.$$

The operator A† is called the operator hermitian conjugate (adjoint) to the operator A.

If an operator A is equal to its hermitian conjugate operator, that is,

$$\hat{A}^\dagger = \hat{A},$$

it is called a hermitian operator. On the other hand, if

$$\hat{A}^\dagger = -\hat{A},$$

then the operator A is called anti-hermitian.

Operator

We may ask why do we use hermitian operators to represent dynamical variables in quantum mechanics.

As we shall see later, in quantum mechanics, it is postulated that if we measure a dynamical variable A of a system in a given quantum state ψ, the result will be one of the eigenvalues of the operator A that represents the dynamical variable.

Since the results of measurement are real numbers (in appropriate units), the eigenvalues of operator A must be real.

The eigenvalues of a hermitian operator are real.

Consider a hermitian operator A and its eigenvalue equation

$$\hat{A}\psi_n(\vec{r}) = \lambda_n \psi_n(\vec{r}), \quad \vec{r} = (x, y, z).$$

As stated earlier, λ_n are in general complex. Now, since A is hermitian, we have

$$\int_{-\infty}^{+\infty} \psi_n^* (\hat{A}\psi_n) d^3x = \int_{-\infty}^{+\infty} (\hat{A}\psi_n)^* \psi_n \, d^3x.$$

Using the eigenvalue equation for A, we have

$$(\lambda_n - \lambda_n^*) \int_{-\infty}^{+\infty} \psi_n^* \psi_n \, d^3x = 0$$

For the non-trivial solutions to the eigenvalue equation,

$$\int_{-\infty}^{+\infty} \psi_n^* \psi_n \, d^3x \neq 0$$

and we get:

$$\lambda_n = \lambda_n^*$$

Operator

The eigenfunctions of a hermitian operator, corresponding to distinct eigenvalues, are orthogonal.

The eigenvalues of an anti-hermitian operator are either purely imaginary or equal to zero.

Dynamical variables in classical mechanics	*Corresponding operators in quantum mechanics*
Coordinates: $\begin{cases} \vec{r} \\ x, \quad y, \quad z \end{cases}$ Momentum: $\begin{cases} \vec{p} \\ p_x, \quad p_y, \quad p_z \end{cases}$	$\begin{cases} \hat{\vec{r}} \\ x, \quad y, \quad z \end{cases}$ $\begin{cases} -i\hbar\vec{\nabla} \\ -i\hbar\frac{\partial}{\partial x}, \quad -i\hbar\frac{\partial}{\partial y}, \quad -i\hbar\frac{\partial}{\partial z} \end{cases}$
Angular momentum: $\begin{cases} \vec{L} \\ L_x = yp_z - zp_y \\ L_y = zp_x - xp_z \\ L_z = xp_y - yp_x \end{cases}$	$\begin{cases} \hat{\vec{r}} \times \hat{\vec{p}} \\ -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right) \\ -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right) \\ -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) \end{cases}$
Energy: $H = \frac{\vec{p}^2}{2m} + V(\vec{r})$	$-\frac{\hbar^2}{2m}\vec{\nabla}^2 + \hat{V}(\vec{r})$

TISE in one dimension

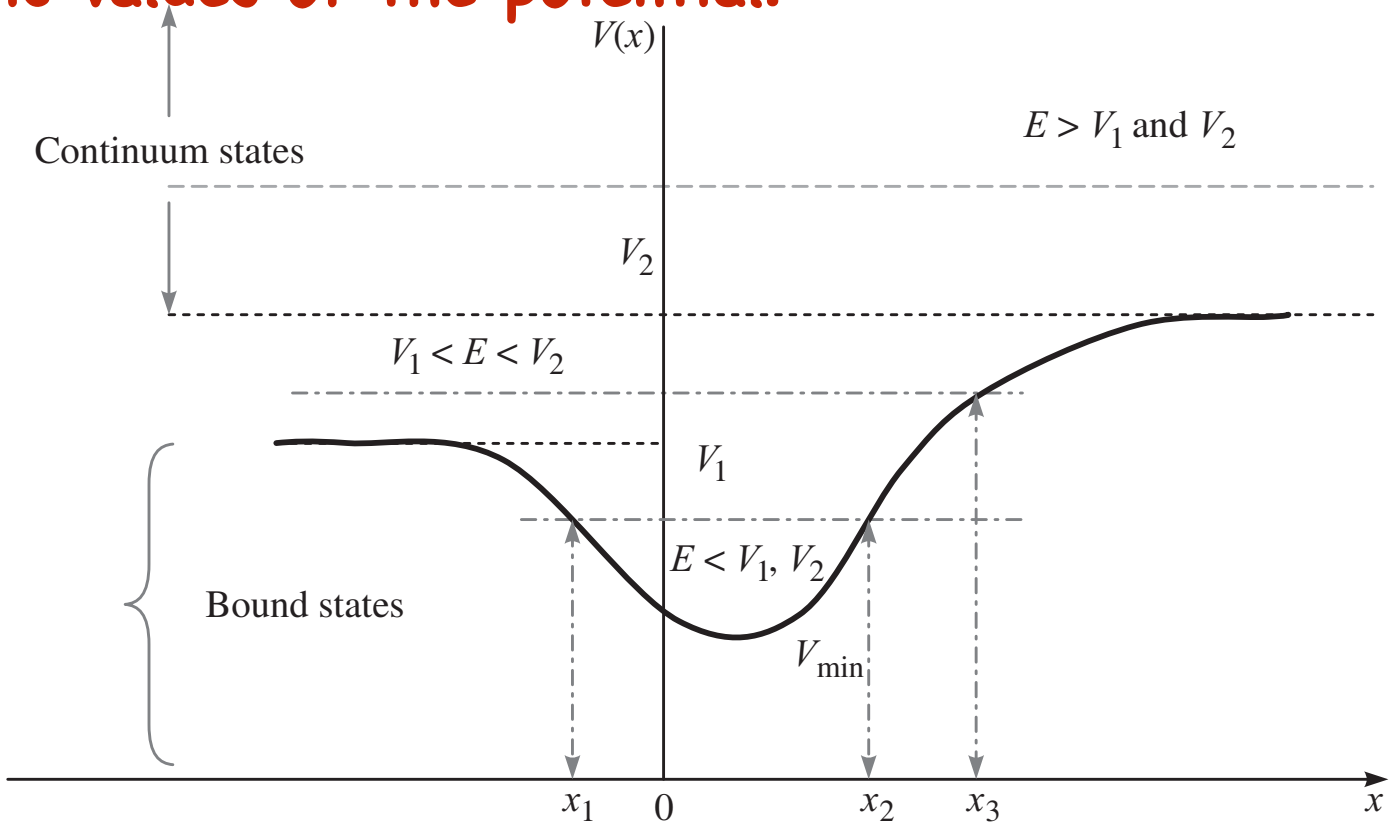
The TISE in one spatial dimension takes the form:

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

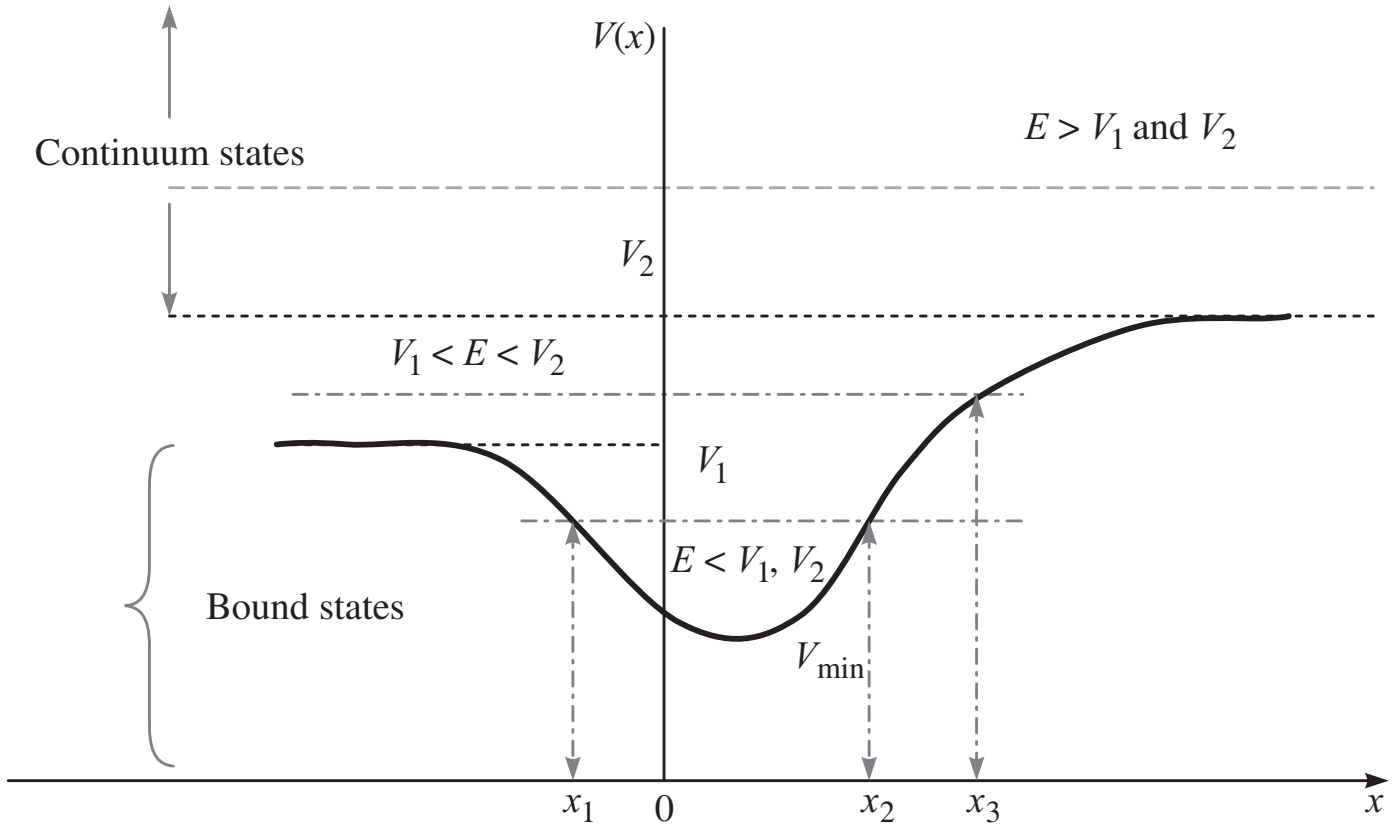
where $x \in (-\infty,+\infty)$ is the independent variable. The nature and the properties of the solutions to this equation depend on the interrelationship between the total energy, E, of the particle and the potential V (x).

Consider an arbitrary form of the potential V (x), which is general enough to allow for the illustration of all the desired features. Without any loss of generality, the potential has been assumed to remain finite at spatial infinities: $\lim_{x\to-\infty}V(x)=V_1 \quad \lim_{x\to+\infty}V(x)=V_2$

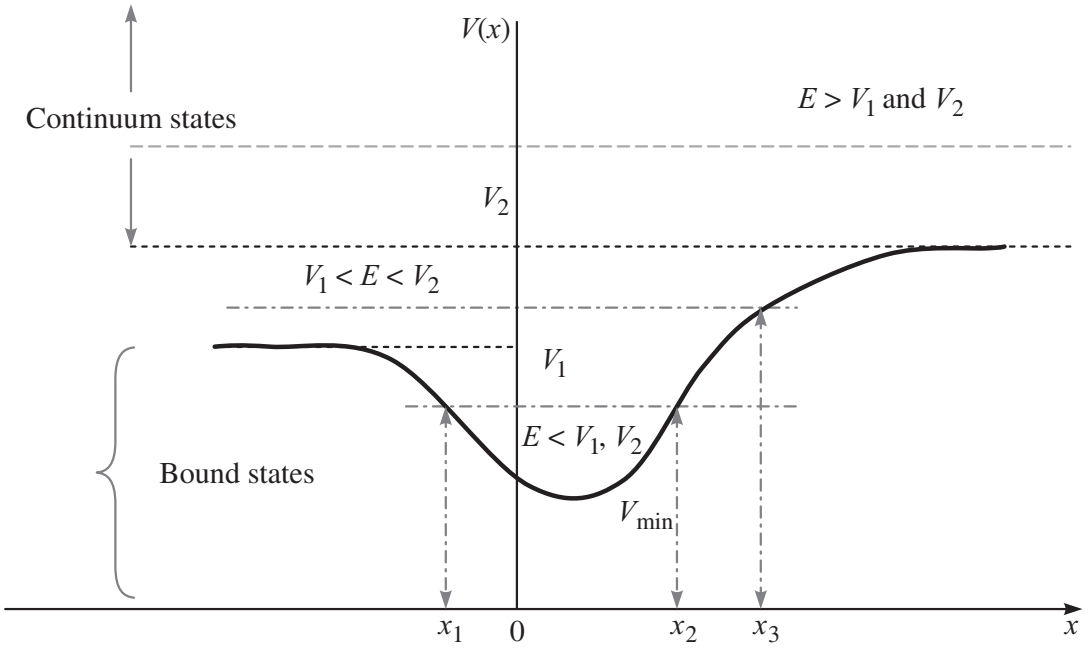
and it has a minimum V_{min} at some point. The character of the energy states of the particle is completely determined by the energy E of the particle in comparison with the asymptotic values of the potential.



Bound states: Bound states occur whenever the particle is confined (or bound) at all energies to move within a finite and limited region of space.



Scattering states: If the total energy of the particle is either greater than V_1 and less than V_2 or greater than both V_1 and V_2, the particle's motion is not confined to a finite region of space and the states of the particle, corresponding to these ranges of the total energy, are called scattering states.



TISE in one dimension

Important properties of bound state energy levels and the wave functions in one dimension:

1. The bound state energy levels of a system in one spatial dimension are discrete and nondegenerate.

2. In general, the nth bound state wave function, $\varphi_n(x)$, in one spatial dimension has n nodes (that is, $\varphi_n(x)$ vanishes n times), if n = 0 corresponds to the ground state and (n – 1) nodes if n = 1 corresponds to the ground state.

The Free Particle Solution

A free particle represents a typical example of a stationary state that corresponds to an unbounded motion (scattering state) both along the positive and the negative x directions. In this case, the external potential is absent, that is, V (x) = 0, and the TISE reads

$$-\frac{\hbar^2}{2m}\frac{d^2\phi(x)}{dx^2} = E\phi(x) \quad \Rightarrow \quad \frac{d^2\phi(x)}{dx^2} + k^2\phi(x) = 0,$$

where

$$k^2 = \frac{2mE}{\hbar^2}, E > 0.$$

This equation has two linearly independent solutions:

$$\phi_{(+)}(x) = e^{ikx}, \quad \phi_{(-)}(x) = e^{-ikx}.$$

The Free Particle Solution

The general stationary state solution is the linear superposition given by

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

where $A_{(+)}$ and $A_{(-)}$ are arbitrary, in general complex, constants. If we use the de Broglie formula, the solution can be written as

$$\psi(x,t) = A_{(+)}\, e^{\frac{i}{\hbar}(px-Et)} + A_{(-)}\, e^{-\frac{i}{\hbar}(px+Et)}.$$

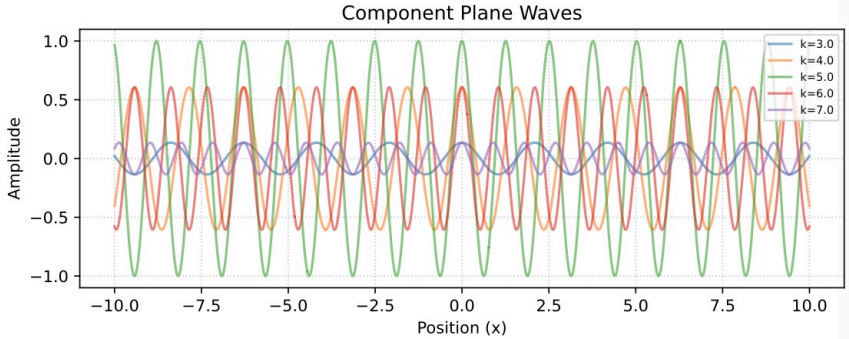
The first term in the above equation represents a particle traveling to the right (positive x direction) and the second term represents a particle traveling to the left.

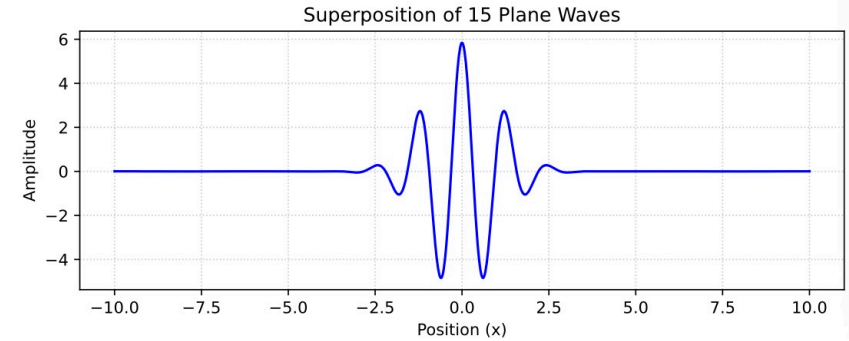
The Free Particle Solution

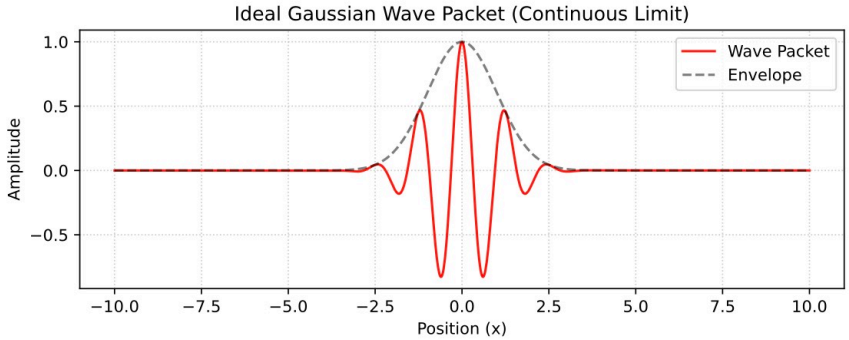
Three problems about the solution of free particle:

1. Firstly, the probability densities corresponding to either solutions are constant that is, they depend neither on x nor on t.
2. The second difficulty is in an apparent discrepancy between the speed of the wave and the speed of the particle it is supposed to represent. $v_p = \frac{\omega}{k} = \frac{E}{\hbar k} = \frac{\hbar k}{2m}$. $v = \frac{p}{m} = \frac{\hbar k}{m} = 2v_p$.
3. The third difficulty is that the free particle wave function cannot be normalized:

$$\int_{-\infty}^{+\infty} |\psi(x,t)|^2 \, dx = |A_{\pm}|^2 \int_{-\infty}^{+\infty} dx \;\rightarrow\; \infty.$$


Component Plane Waves
k=3.0
k=4.0
k=5.0
k=6.0
k=7.0
Amplitude
Position (x)

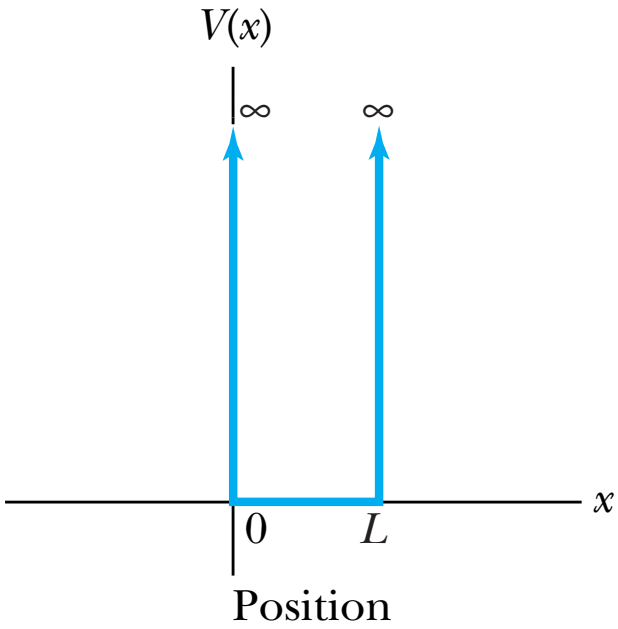

Superposition of 15 Plane Waves
Amplitude
Position (x)


Ideal Gaussian Wave Packet (Continuous Limit)
Wave Packet
Envelope
Amplitude
Position (x)

Infinite Square-Well Potential

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,

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

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

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

Infinite Square-Well Potential

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

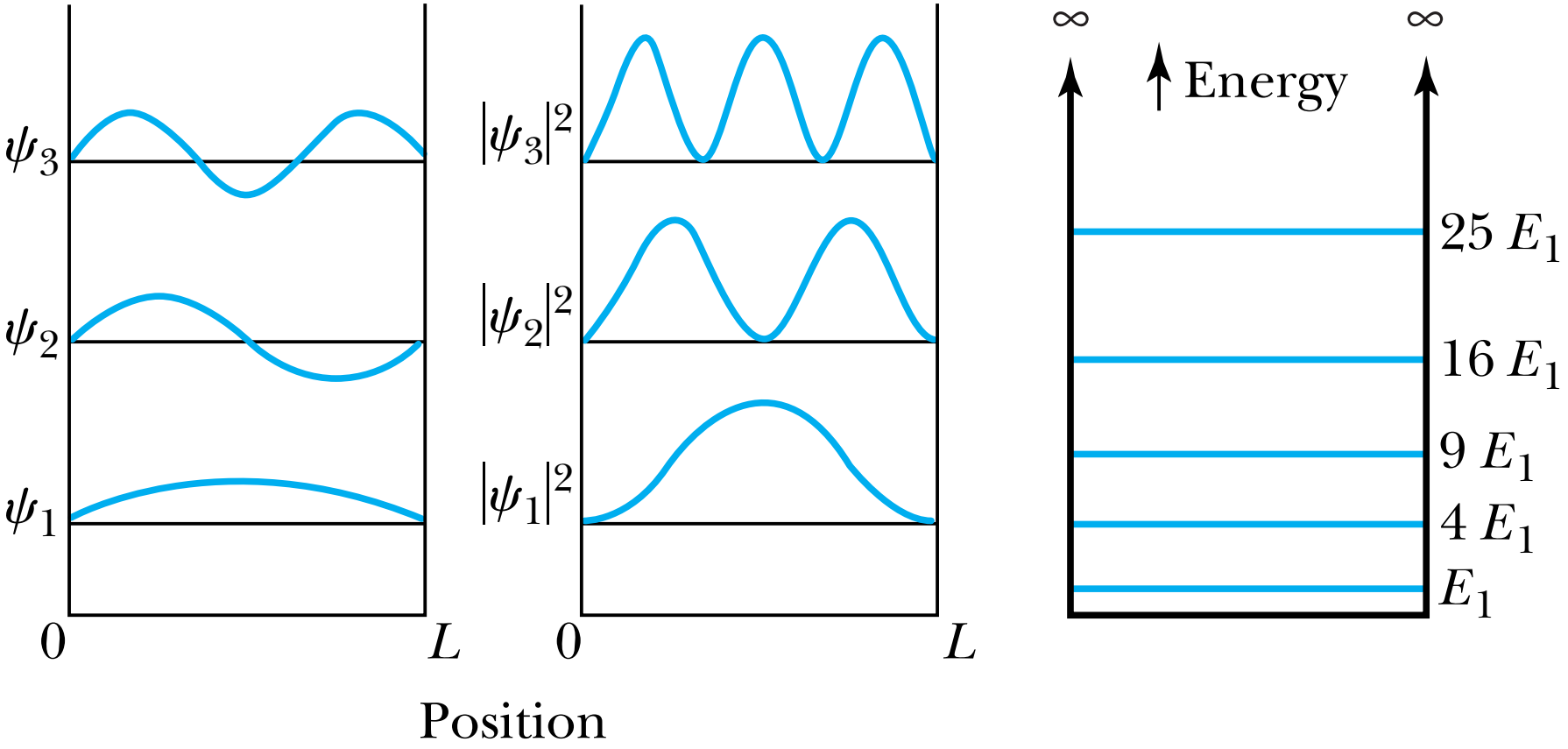
$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right), \quad n = 1, 2, 3, \ldots$$

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

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

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

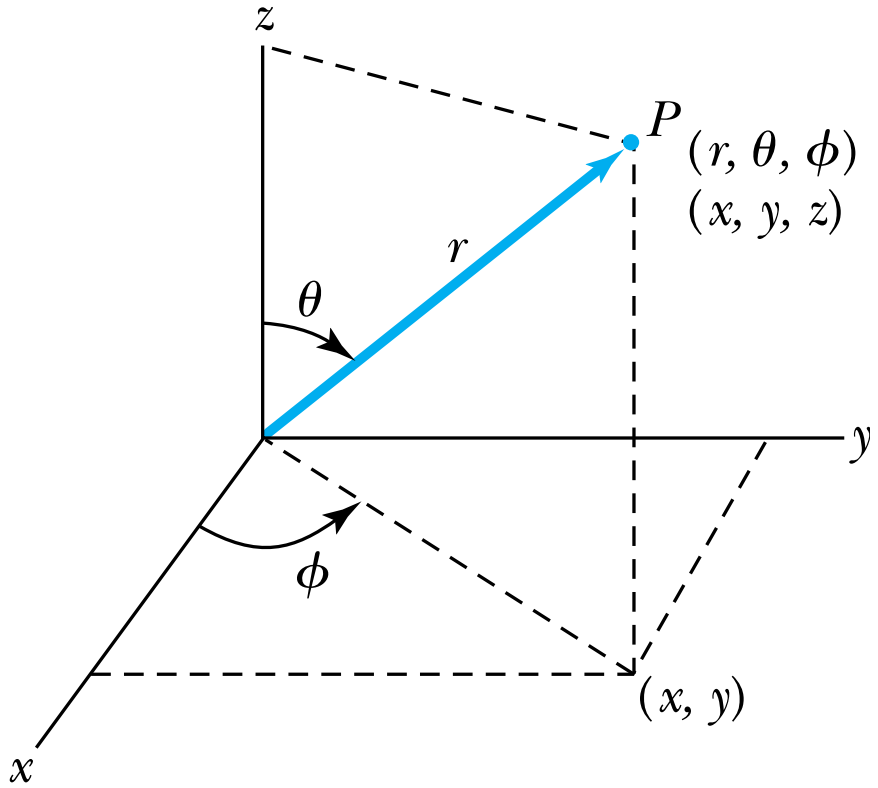
We rewrite the three-dimensional time-independent Schrödinger Equation

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

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

The Schrödinger Equation for H

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 for H



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

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

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

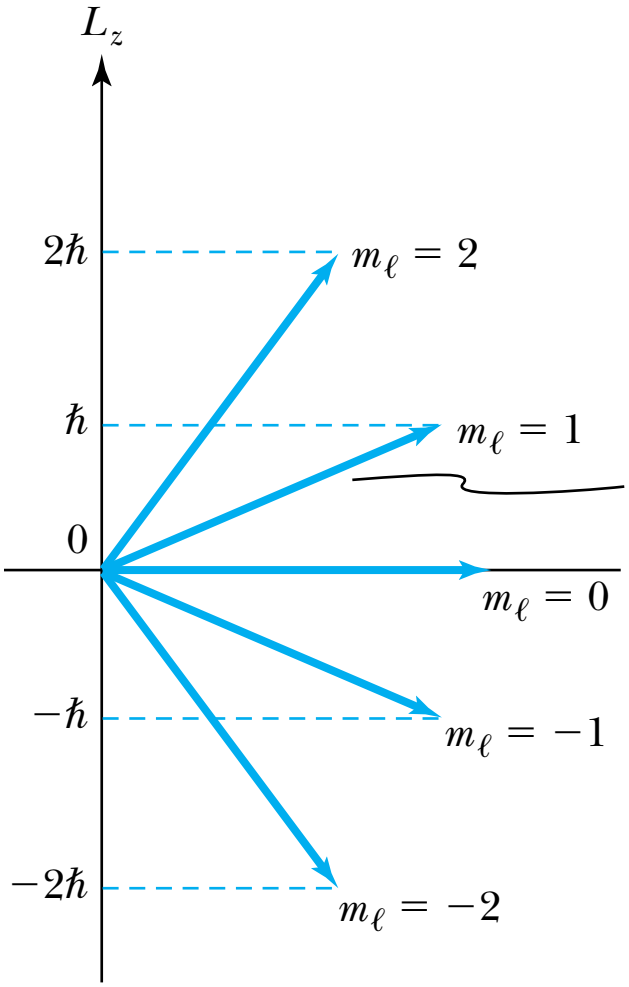
Principal Quantum Number n

Orbital Angular Momentum Quantum Number l

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

Magnetic Quantum Number m_l

$$L_z = m_l \hbar$$



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

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

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

Quantized energy of hydrogen

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

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	$\frac{1}{(a_0)^{3/2}} \frac{4}{81\sqrt{30}} \frac{r^2}{{a_0}^2} e^{-r/3a_0}$

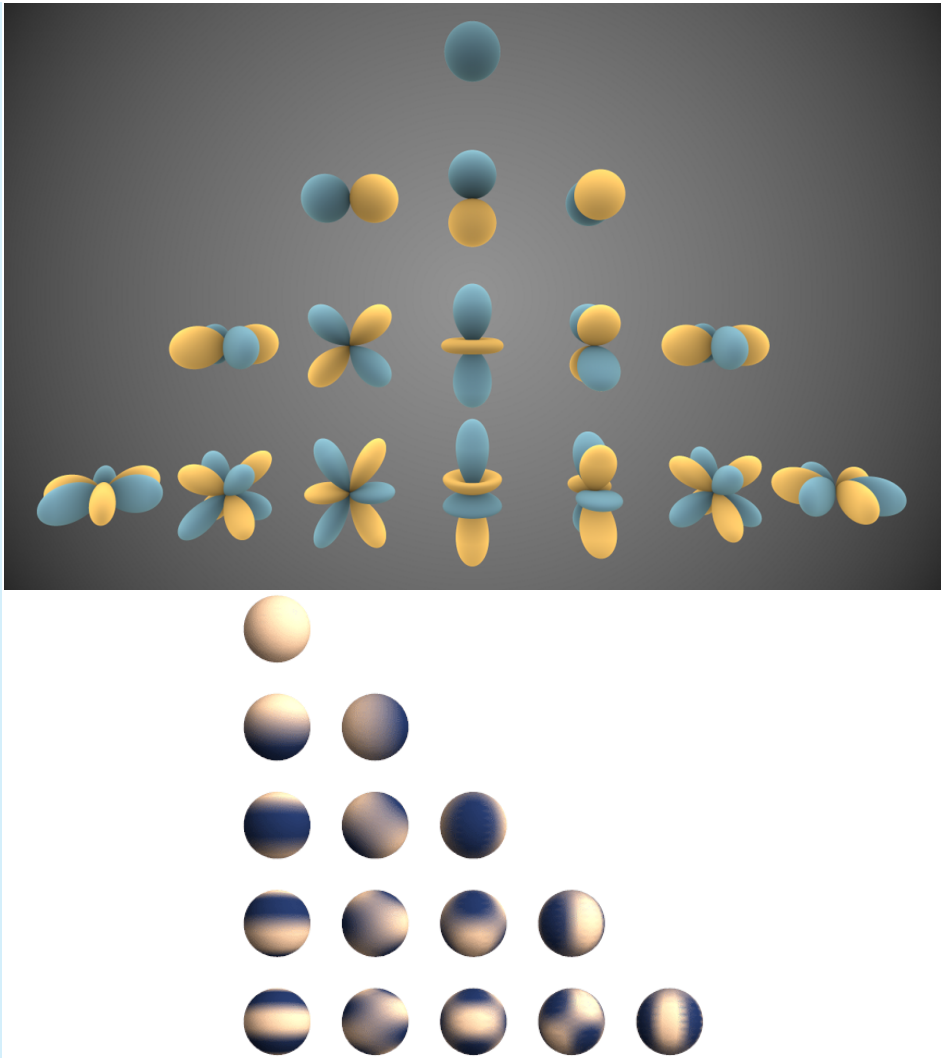
Laguerre polynomials

The Schrödinger Equation for H

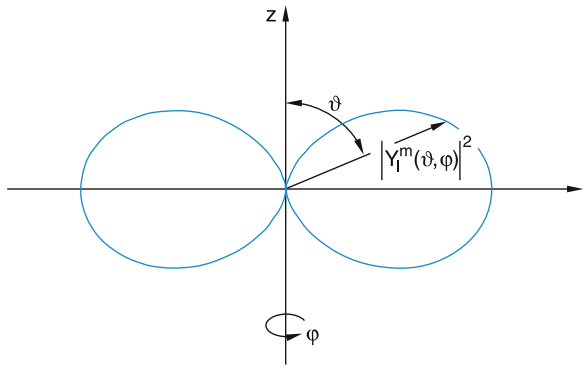
Normalized Spherical Harmonics

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

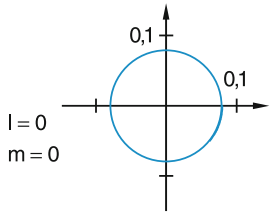
ℓ	m_ℓ	$Y_{\ell m_\ell}$
0	0	$\frac{1}{2\sqrt{\pi}}$
1	0	$\frac{1}{2}\sqrt{\frac{3}{\pi}}\cos\theta$
1	±1	$\mp\frac{1}{2}\sqrt{\frac{3}{2\pi}}\sin\theta\, e^{\pm i\phi}$
2	0	$\frac{1}{4}\sqrt{\frac{5}{\pi}}(3\cos^2\theta - 1)$
2	±1	$\mp\frac{1}{2}\sqrt{\frac{15}{2\pi}}\sin\theta\cos\theta\, e^{\pm i\phi}$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

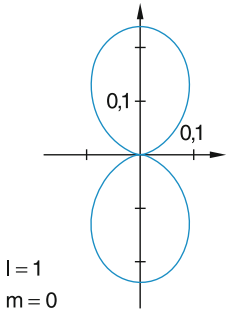


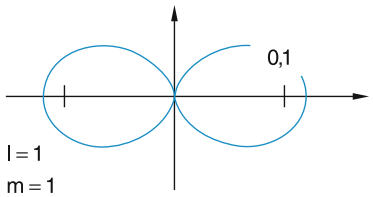
The wave function of hydrogen

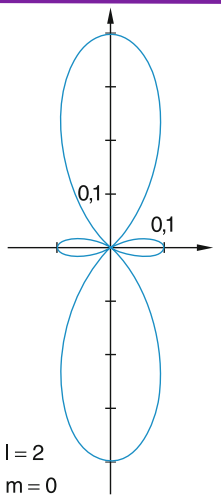


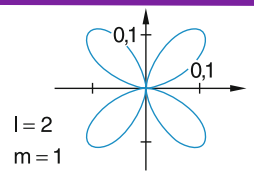
$$\left|Y_l^m(\vartheta,\varphi)\right|^2$$

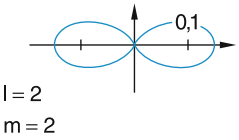


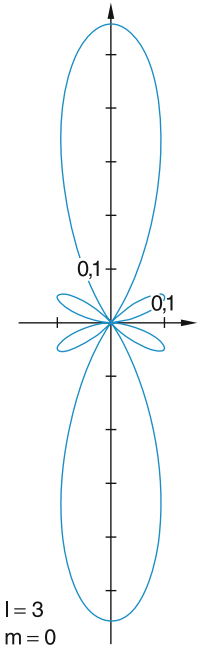


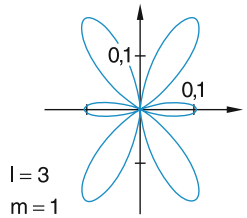


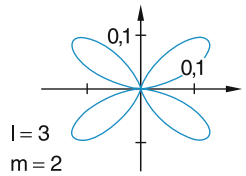


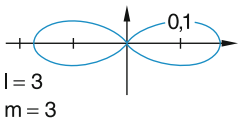




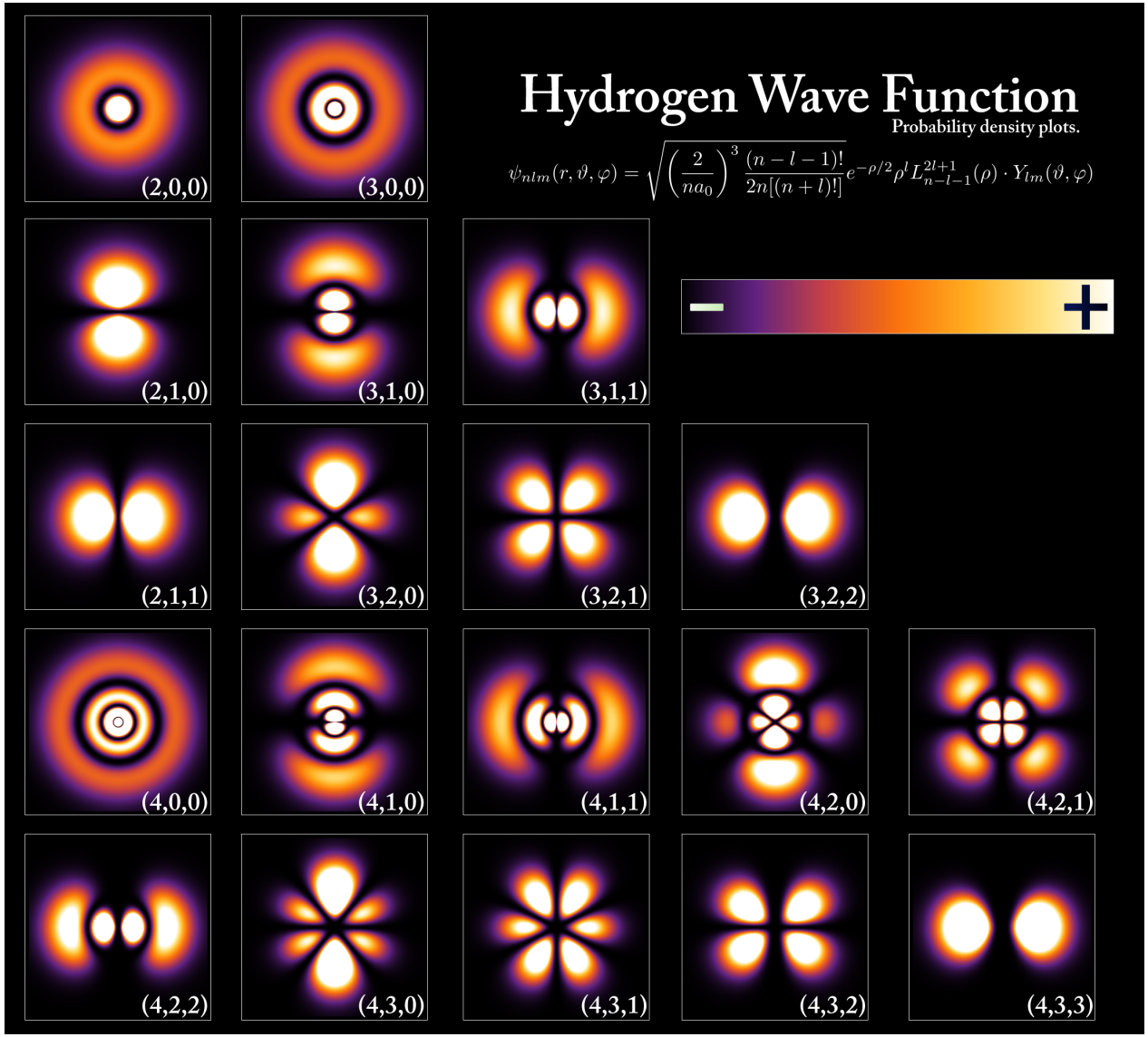








The wave function of hydrogen



Expectation Values

For the statistical description of properties of a many particle system one has to define average values, which depend on the distribution of these properties over the particles of the system. The mean velocity in a system of particles with velocity distribution f (v) is defined by

$$\bar{v} = \int_{v=0}^{\infty} v f(v)\,\mathrm{d}v.$$

The mean square velocity

$$\overline{v^2} = \int_{v=0}^{\infty} v^2 f(v)\,\mathrm{d}v$$

Expectation Values

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,

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

Expectation Values

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)

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

The Physics of Atoms and Quanta

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

Exercise class

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

1.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

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

2. 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.

2. 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,

$$eV_0 = h\nu - \phi = 3.10 - 2.93 = 0.17 \text{ eV}$$
$$V_0 = 0.17 \text{ V}$$

3. (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.

3. (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)

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

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

(b)

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

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

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

4. 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

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

5. 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).

5. 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

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

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

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