Introduction to Quantum Mechanic

A) Radiation

B) Light is made of particles. The need for a quantification

1) Black-body radiation (1860-1901)
2) Atomic Spectroscopy (1888-)
3) Photoelectric Effect (1887-1905)

C) Wave–particle duality

1) Compton Effect (1923).
2) Electron Diffraction Davisson and Germer (1925).
3) Young's Double Slit Experiment

D) Louis de Broglie relation for a photon from relativity

E) A new mathematical tool: Wavefunctions and operators

F) Measurable physical quantities and associated operators - Correspondence principle

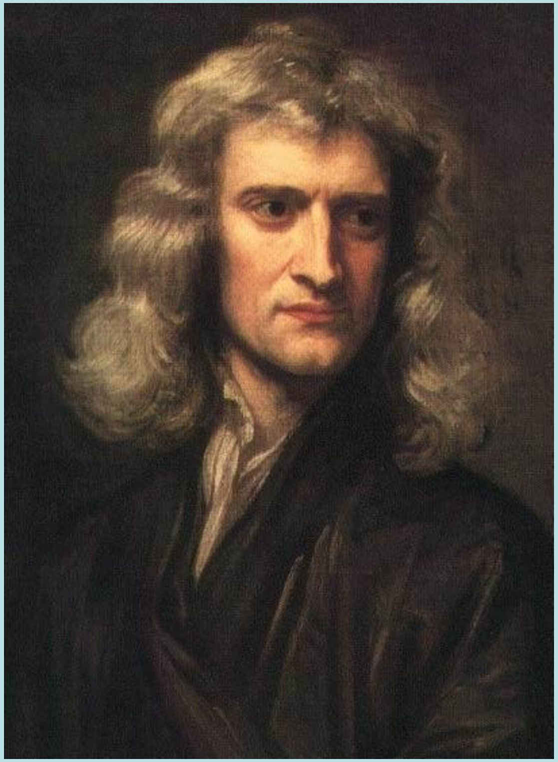
G) The Schrödinger Equation (1926)

H) The Uncertainty principle

When you find this image,  you may skip this part

This is less important

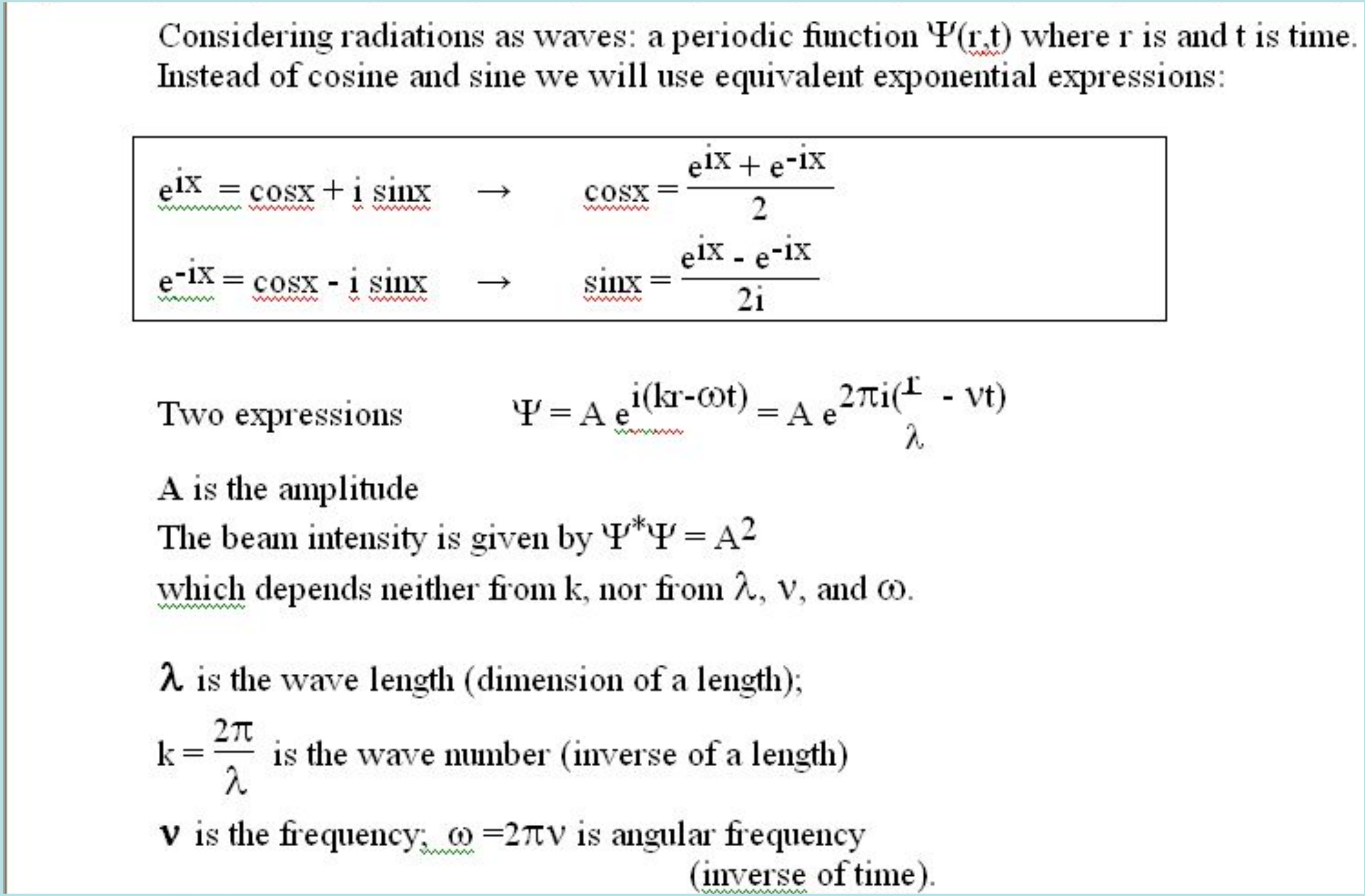
The idea of duality is rooted in a debate over the nature of light and matter dating back to the 1600s, when competing theories of light were proposed by Huygens and Newton.



Christiaan Huygens
Dutch 1629-1695
light consists of waves

Sir Isaac Newton
1643 1727
light consists of particles

Radiations, terminology



Considering radiations as waves: a periodic function $\Psi(r,t)$ where r is and t is time. Instead of cosine and sine we will use equivalent exponential expressions:

$$e^{ix} = \cos x + i \sin x \quad \rightarrow \quad \cos x = \frac{e^{ix} + e^{-ix}}{2}$$

$$e^{-ix} = \cos x - i \sin x \quad \rightarrow \quad \sin x = \frac{e^{ix} - e^{-ix}}{2i}$$

Two expressions $\Psi = A\, e^{i(kr-\omega t)} = A\, e^{2\pi i(\frac{r}{\lambda} - \nu t)}$

A is the amplitude

The beam intensity is given by $\Psi^*\Psi = A^2$

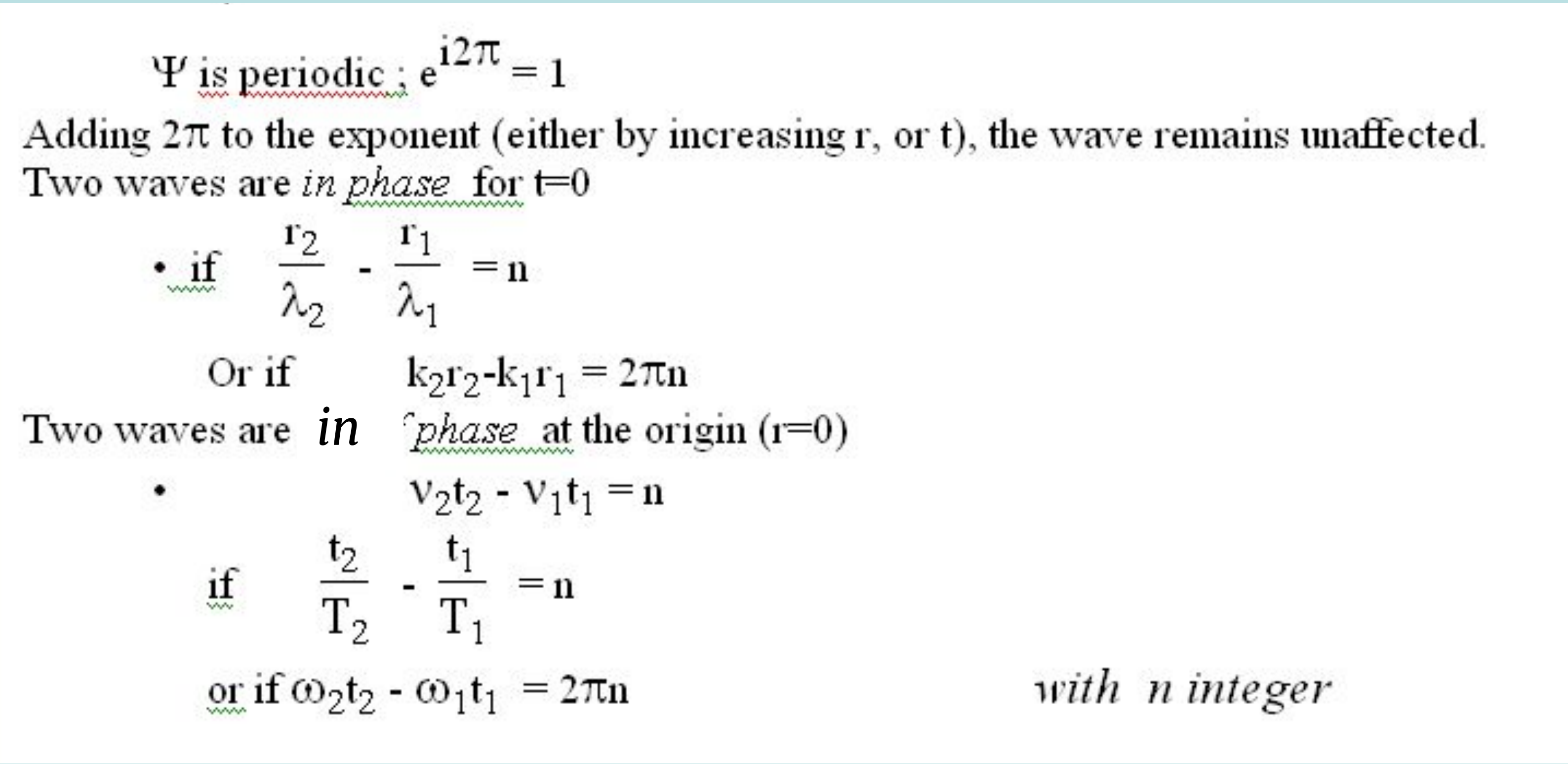
which depends neither from k, nor from λ, ν, and ω.

λ is the wave length (dimension of a length);

$k = \frac{2\pi}{\lambda}$ is the wave number (inverse of a length)

ν is the frequency; $\omega = 2\pi\nu$ is angular frequency (inverse of time).

Interferences



Ψ is periodic ; $e^{i2\pi} = 1$

Adding 2π to the exponent (either by increasing r, or t), the wave remains unaffected.

Two waves are *in phase* for t=0

- if $\frac{r_2}{\lambda_2} - \frac{r_1}{\lambda_1} = n$

Or if $k_2r_2 - k_1r_1 = 2\pi n$

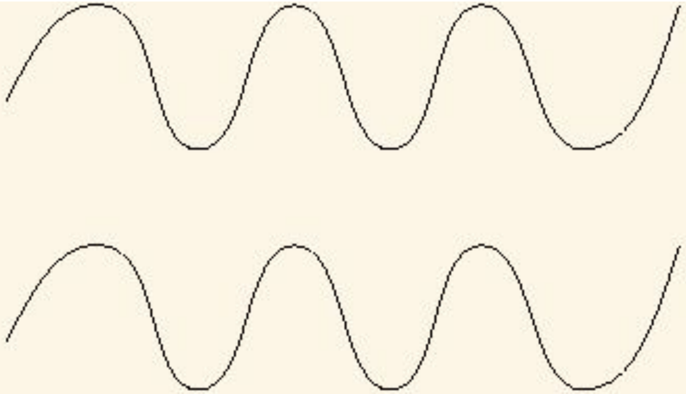
Two waves are *in* *phase* at the origin (r=0)

- $\nu_2 t_2 - \nu_1 t_1 = n$

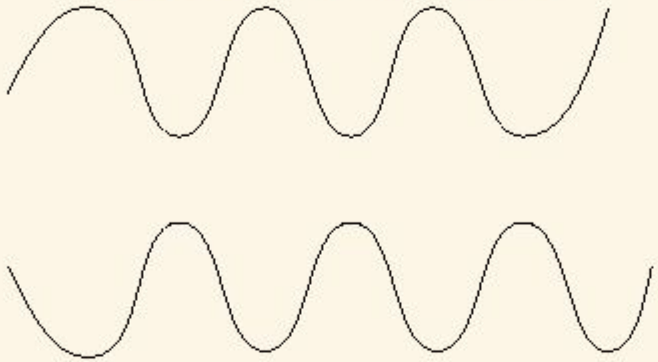
if $\frac{t_2}{T_2} - \frac{t_1}{T_1} = n$

or if $\omega_2 t_2 - \omega_1 t_1 = 2\pi n$ *with n integer*

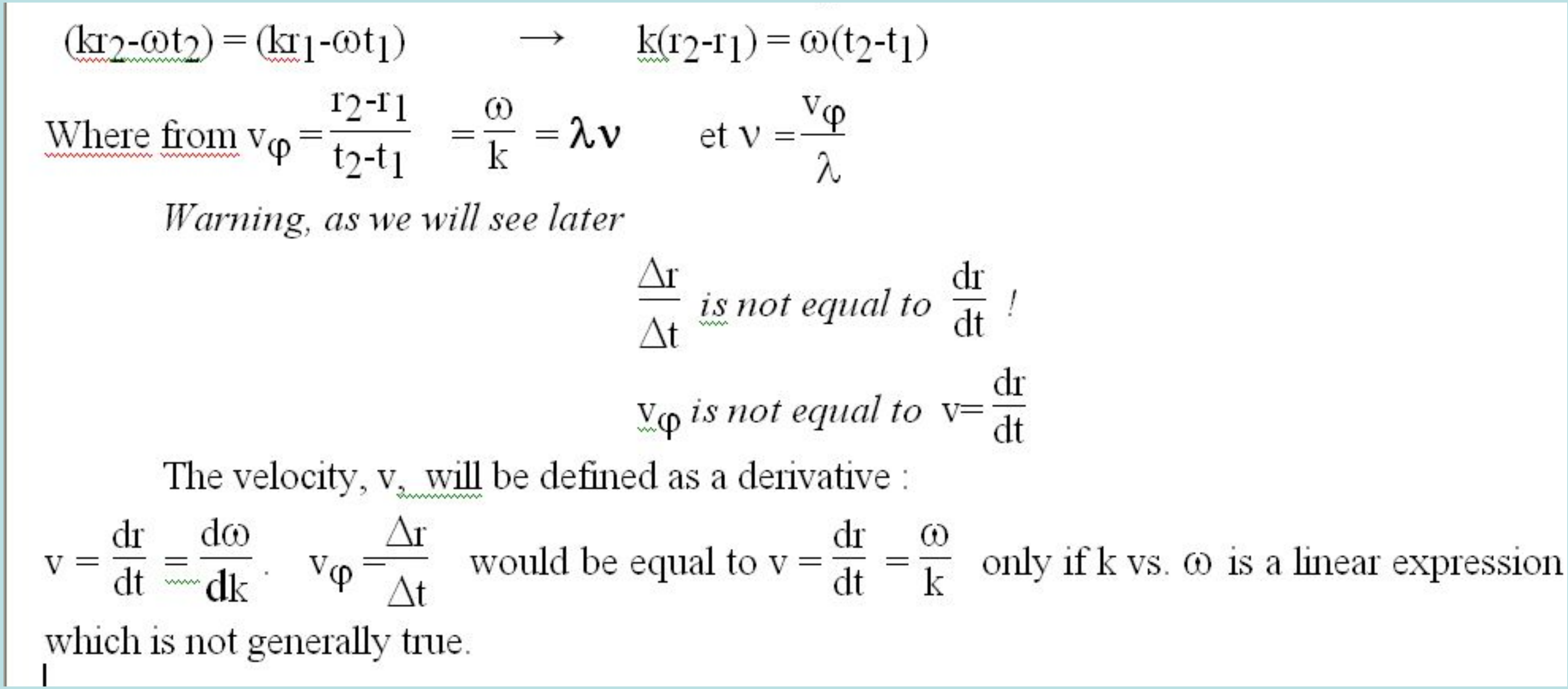
Constructive Interferences



Destructive Interferences



Phase speed or velocity



$(kr_2-\omega t_2) = (kr_1-\omega t_1) \quad \longrightarrow \quad k(r_2-r_1) = \omega(t_2-t_1)$

Where from $v_\varphi = \frac{r_2-r_1}{t_2-t_1} = \frac{\omega}{k} = \lambda\nu$ et $\nu = \frac{v_\varphi}{\lambda}$

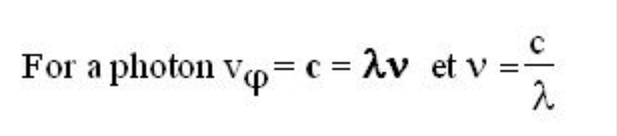
Warning, as we will see later

$\frac{\Delta r}{\Delta t}$ *is not equal to* $\frac{dr}{dt}$ *!*

v_φ *is not equal to* $v=\frac{dr}{dt}$

The velocity, v, will be defined as a derivative :

$v = \frac{dr}{dt} = \frac{d\omega}{dk}$. $v_\varphi = \frac{\Delta r}{\Delta t}$ would be equal to $v = \frac{dr}{dt} = \frac{\omega}{k}$ only if k vs. ω is a linear expression which is not generally true.



For a photon $v_\varphi = c = \lambda\nu$ et $\nu = \frac{c}{\lambda}$

Introducing new variables

- At the moment, let consider this just a formal change, introducing

$$p = \frac{h}{\lambda} \text{ and } E = h\nu$$

and

$$\hbar = \frac{h}{2\pi}$$

we obtain

$$\Psi = A\, e^{i(kr-\omega t)} = A\, e^{2\pi i(\frac{r}{\lambda} - \nu t)} = A\, e^{\frac{i}{\hbar}(pr-Et)}$$

Introducing new variables

$$\Psi = A\, e^{i(kr-\omega t)} = A\, e^{2\pi i(\frac{r}{\lambda} - \nu t)} = A\, e^{\frac{i}{\hbar}(pr-Et)}$$

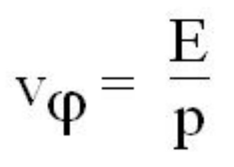
At the moment, h is a simple constant

Later on, h will have a dimension and the p and E will be physical quantities

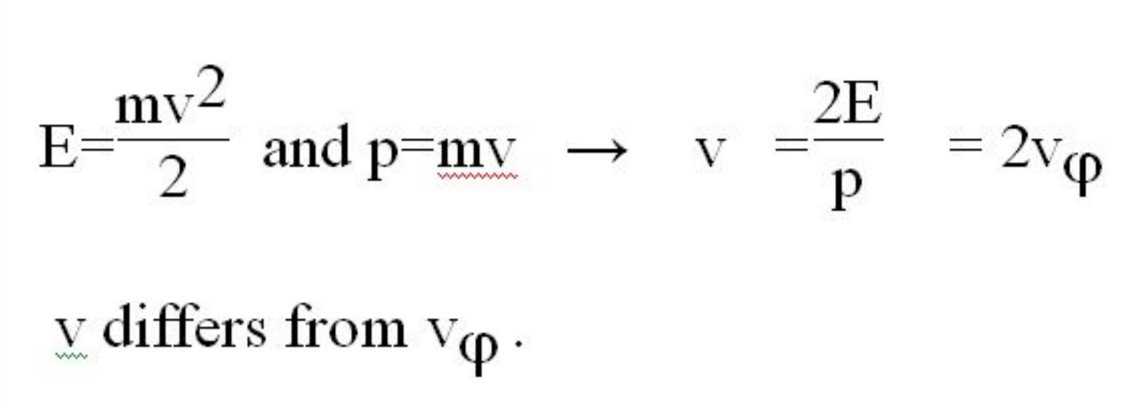
Then

$$p = \hbar\ k = \frac{h}{\lambda} \quad ; \quad E = \hbar\ \omega = h\nu = \frac{h}{T} \quad \text{et} \quad v_\varphi = \frac{E}{p}$$

2 different velocities, v and v_ϕ



$$v_\varphi = \frac{E}{p}$$



$$E = \frac{mv^2}{2} \text{ and } p = mv \rightarrow v = \frac{2E}{p} = 2v_\varphi$$

v differs from v_φ .

If h is the Planck constant J.s

Then

$$p = \hbar\, k = \frac{h}{\lambda} \quad ; \quad E = \hbar\, \omega = h\nu = \frac{h}{T} \quad \text{et} \quad v_{\varphi} = \frac{E}{p}$$

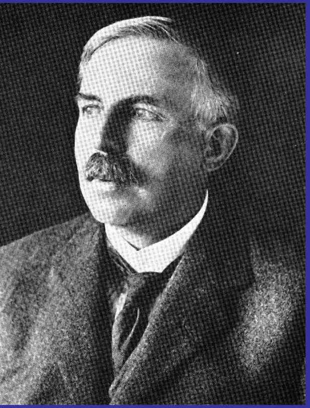
Louis de BROGLIE
French
(1892-1987)

Max Planck (1901)
Göttingen

Soon after the electron discovery in 1887

- J. J. Thomson (1887) Some negative part could be extracted from the atoms

- Robert Millikan (1910) showed that it was quantified.

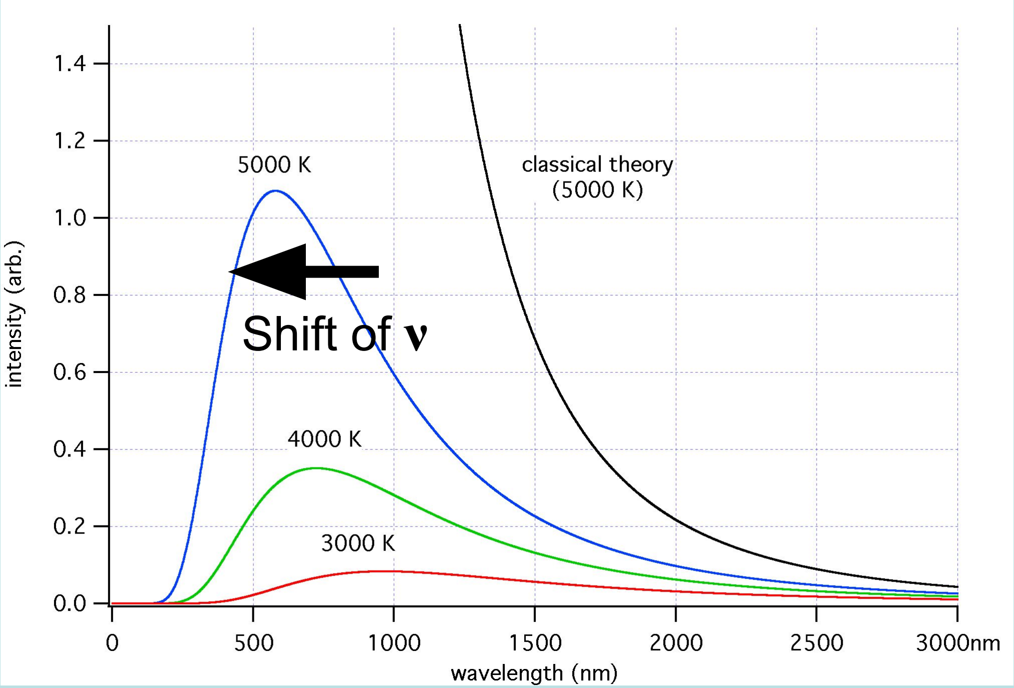


-Rutherford (1911) showed that the negative part was diffuse while the positive part was concentrated.

black-body radiation

Gustav Kirchhoff (1860). The light emitted by a black body is called **black-body radiation**

At room temperature, black bodies emit IR light, but as the temperature increases past a few hundred degrees Celsius, black bodies start to emit at visible wavelengths, from red, through orange, yellow, and white before ending up at blue, beyond which the emission includes increasing amounts of UV



RED

Small ν

WHITE

Large ν

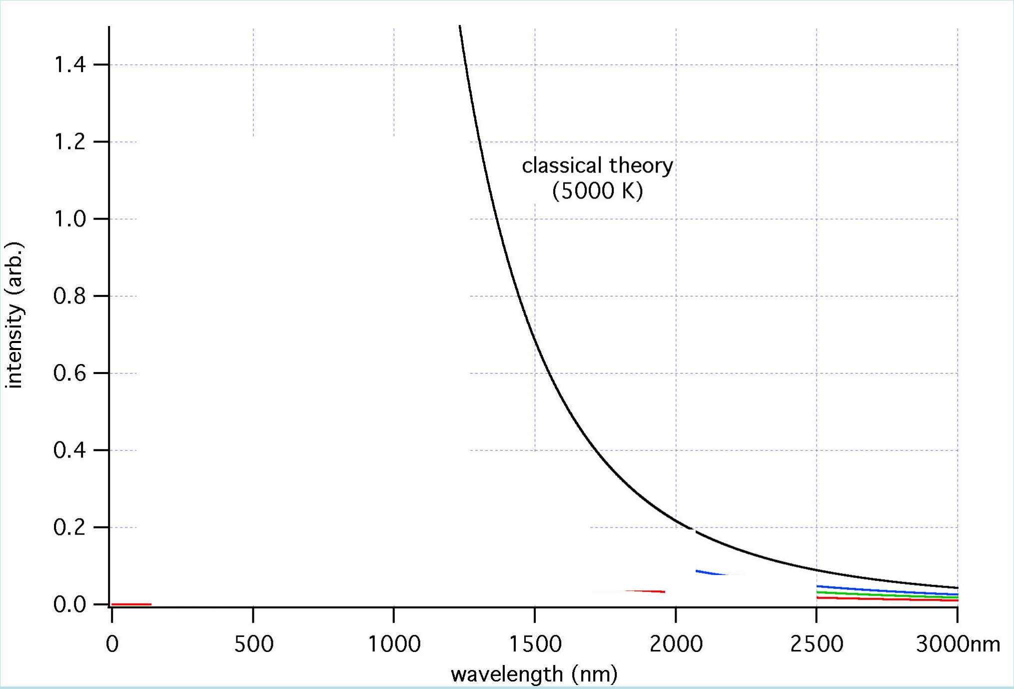
black-body radiation

Classical Theory

Fragmentation of the surface.

One large area (Small λ Large ν) → smaller pieces (Large λ Small ν)

Vibrations associated to the size, N^2 or N^3



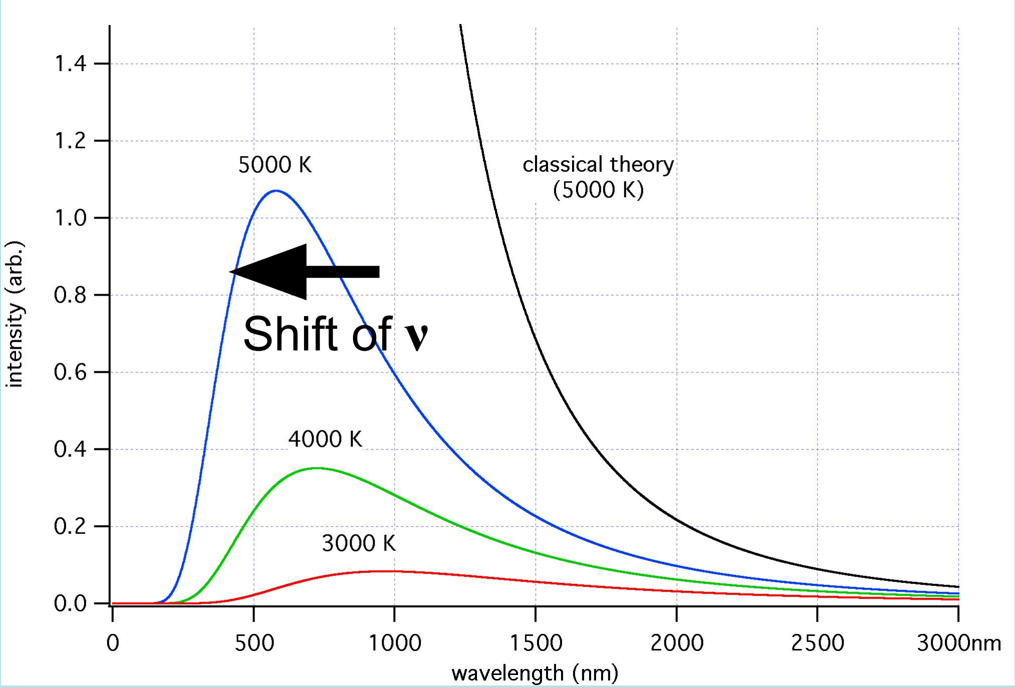
Kirchhoff

black-body radiation

Radiation is emitted when a solid after receiving energy goes back to the most stable state (ground state). The energy associated with the radiation is the difference in energy between these 2 states. When T increases, the a**verage** $\mathbf{E^*_{Mean}}$ is higher and intensity increases.

$\mathbf{E^*_{Mean} - E = kT}$.

k is Boltzmann constant (k= 1.38 10^{-23} Joules K^{-1}).



RED
Small ν

WHITE
Large ν

Why a decrease for small λ ?
Quantification

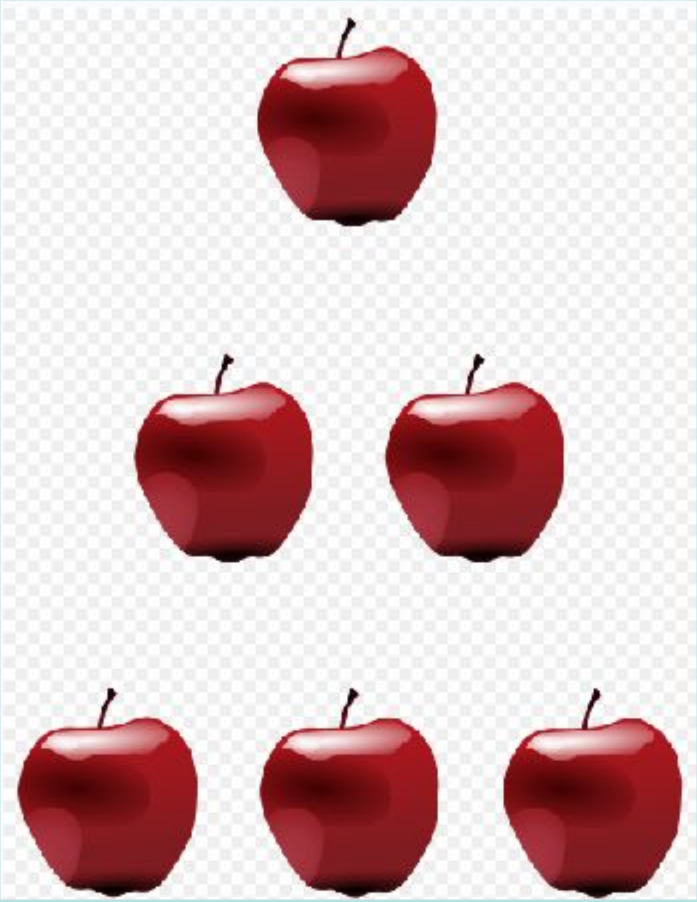
black-body radiation

Max Planck (1901)
Göttingen

Numbering rungs of ladder introduces quantum numbers (here equally spaced)

Quantum numbers

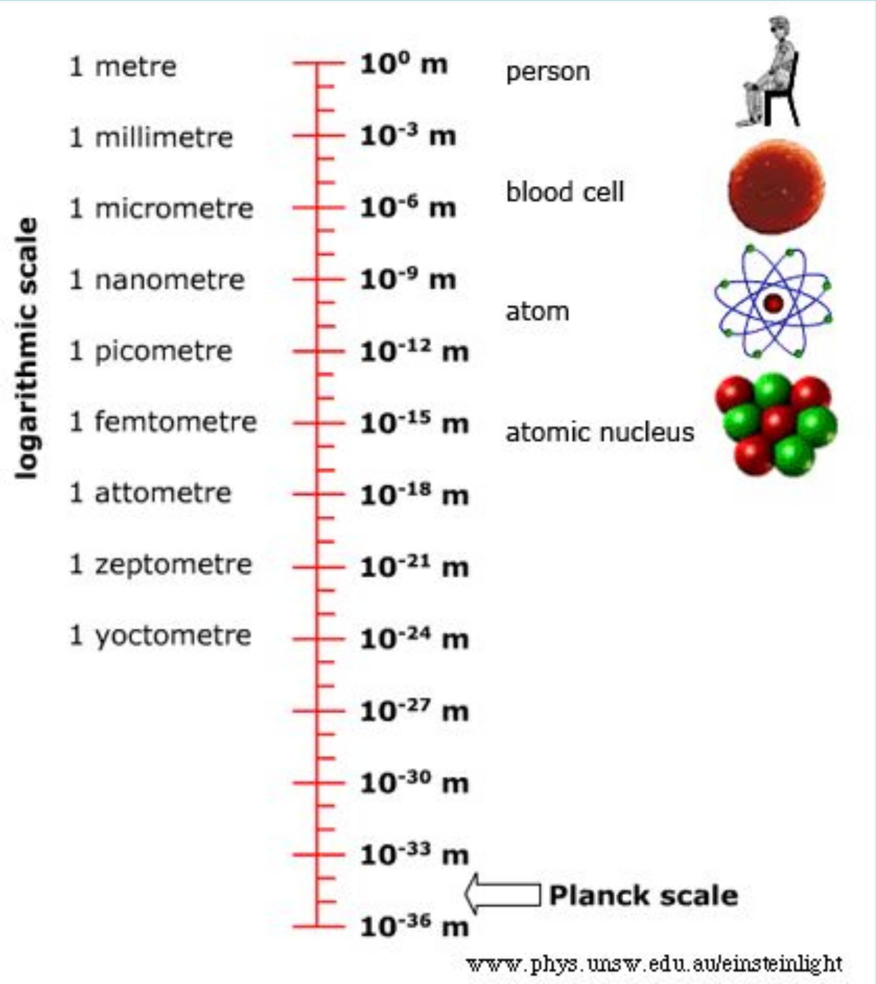
In mathematics, a natural number (also called counting number) has two main purposes: they can be used for counting ("there are 6 apples on the table"), and they can be used for ordering ("this is the 3rd largest city in the country").



Why a decrease for small λ ?
Quantification

black-body radiation

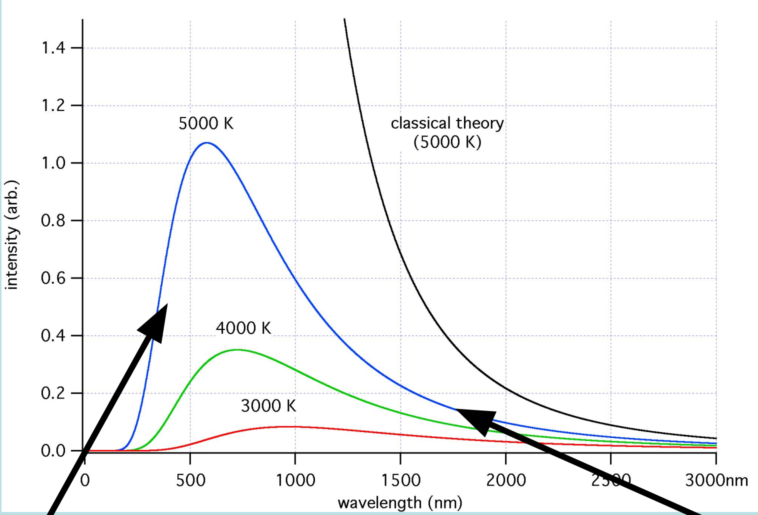
Max Planck (1901)
Göttingen



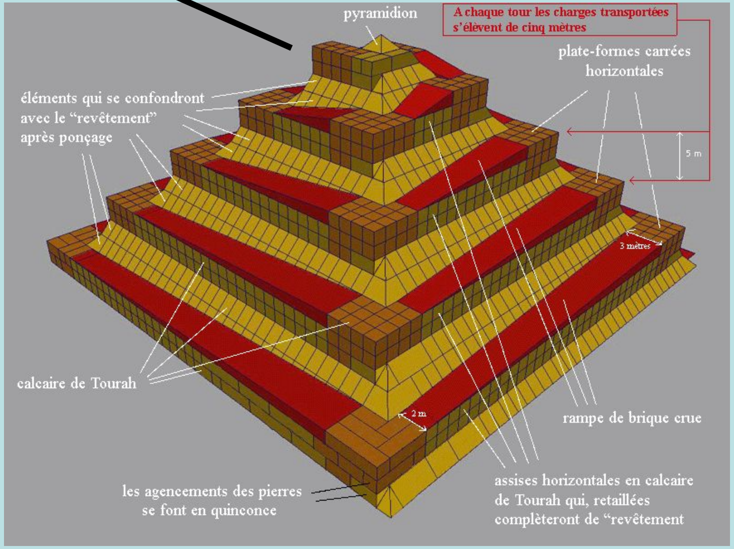
www.phys.unsw.edu.au/einsteinlight

black-body radiation, quantification

Max Planck

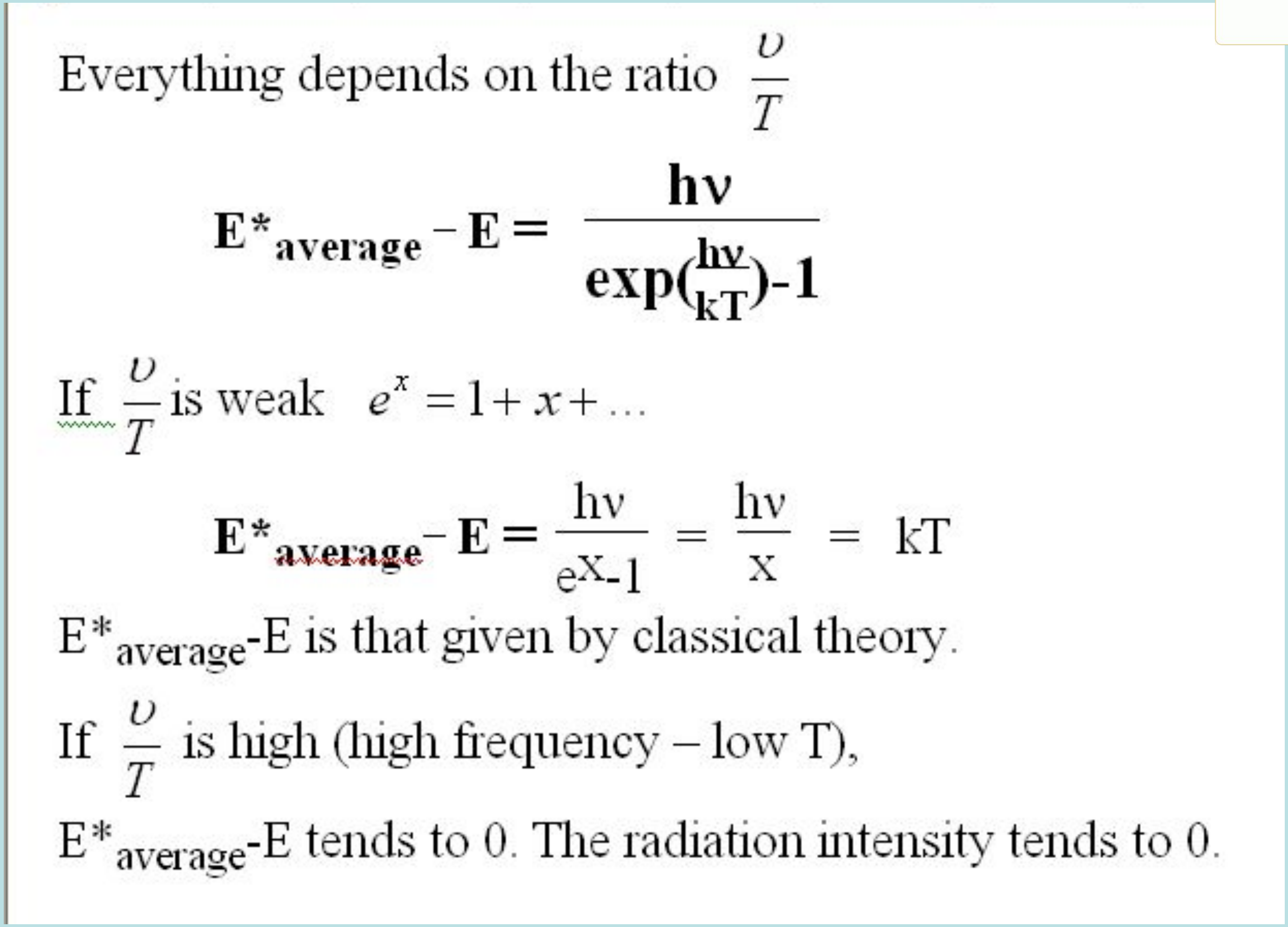


Steps too hard to climb
Pyramid nowadays



Easy slope, ramp
Pyramid under construction

Max Planck



Everything depends on the ratio $\frac{\upsilon}{T}$

$$\mathbf{E^*_{average} - E = \frac{h\nu}{\exp(\frac{h\nu}{kT})-1}}$$

If $\frac{\upsilon}{T}$ is weak $e^x = 1 + x + \dots$

$$\mathbf{E^*_{average}} - \mathbf{E} = \frac{h\nu}{e^x-1} = \frac{h\nu}{x} = kT$$

$E^*_{average}$-E is that given by classical theory.

If $\frac{\upsilon}{T}$ is high (high frequency – low T),

$E^*_{average}$-E tends to 0. The radiation intensity tends to 0.

Atomic Spectroscopy

Absorption or Emission

$$\frac{1}{\lambda_{\text{vac}}} = R_{\text{H}}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

Johannes Rydberg 1888
Swedish

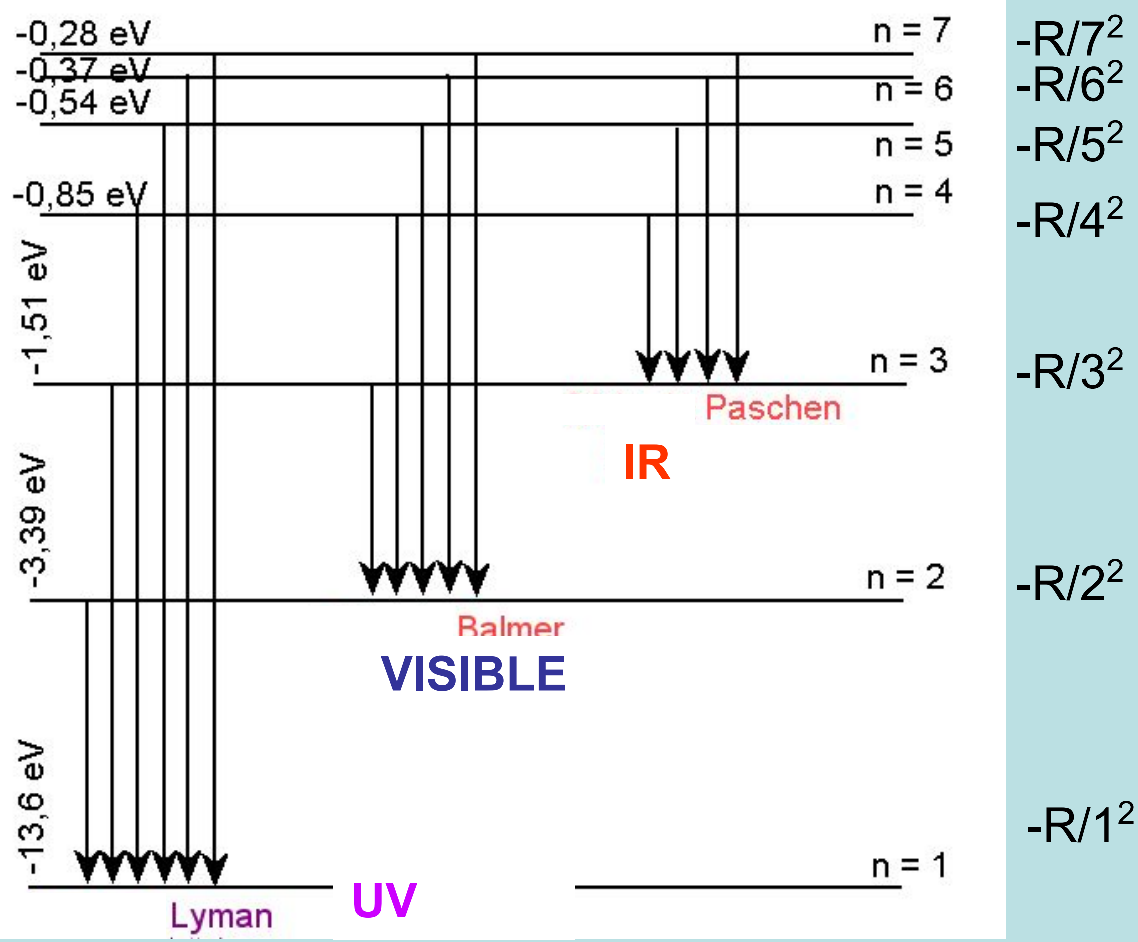
$n_1 \to n_2$	name	Converges to (nm)
$1 \to \infty$	Lyman	91
$2 \to \infty$	Balmer	365
$3 \to \infty$	Pashen	821
$4 \to \infty$	Brackett	1459
$5 \to \infty$	Pfund	2280
$6 \to \infty$	Humphreys	3283

Atomic Spectroscopy

Absorption or Emission

Johannes Rydberg 1888
Swedish

$$\frac{1}{\lambda_{\mathrm{vac}}} = R_{\mathrm{H}}\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right)$$



Emission

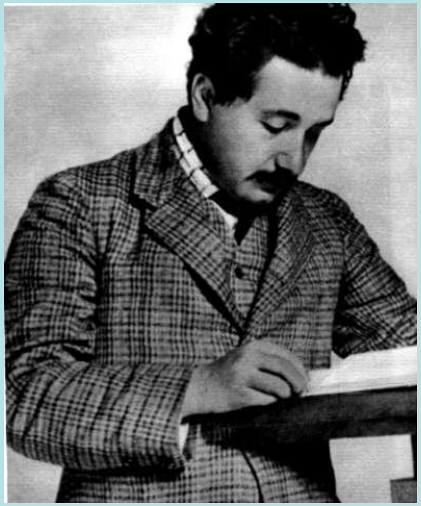
Quantum numbers n, levels are not equally spaced

R = 13.6 eV

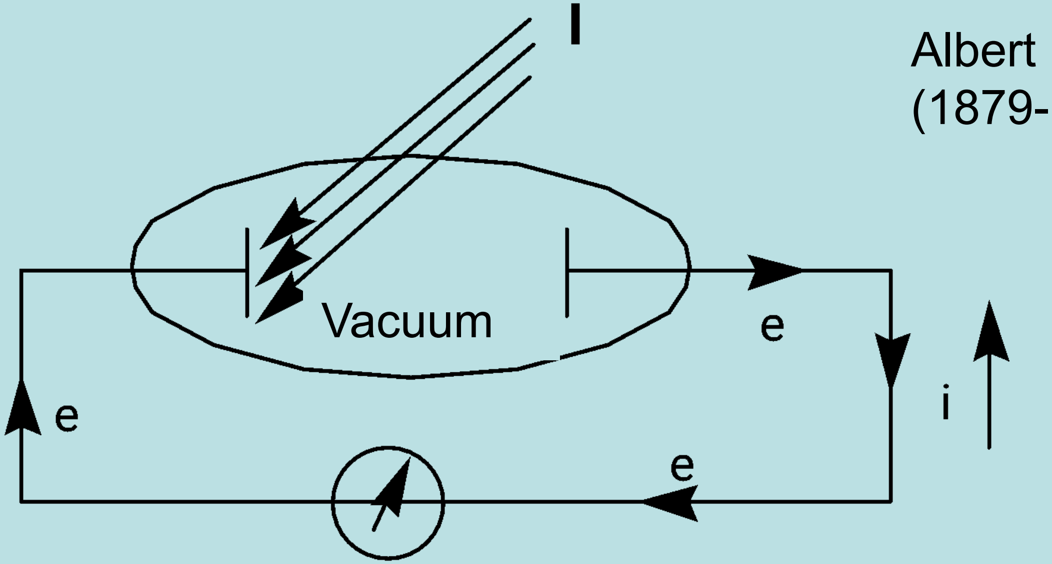
Photoelectric Effect (1887-1905)

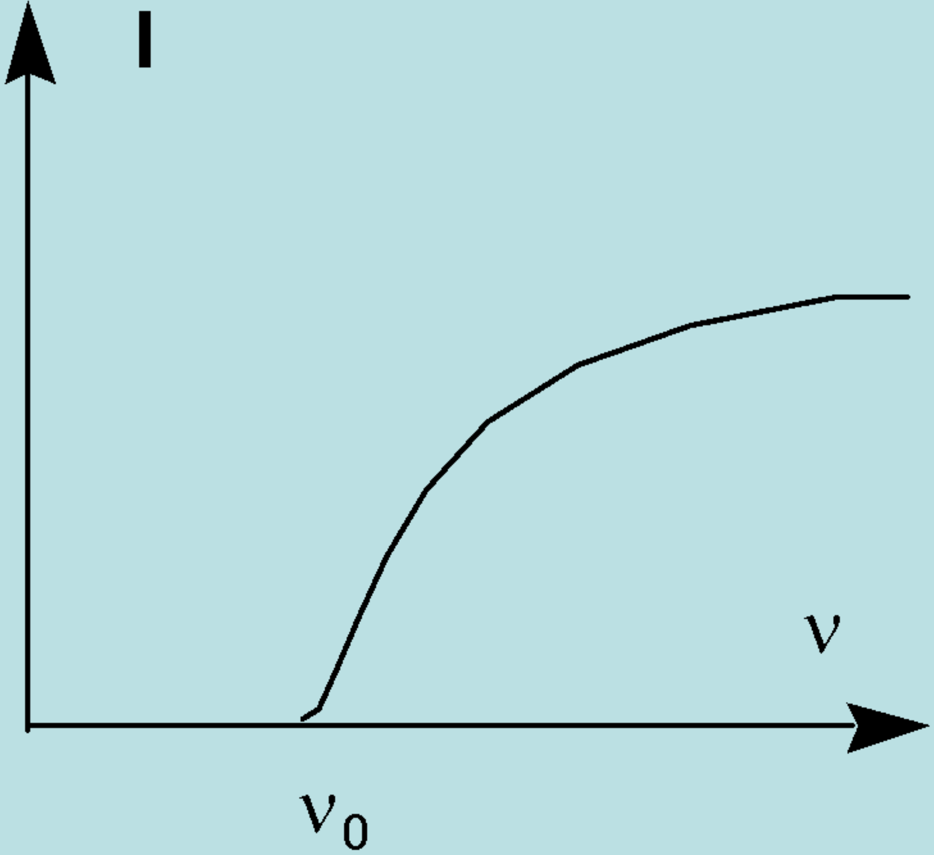
discovered by Hertz in 1887 and explained in 1905 by Einstein.

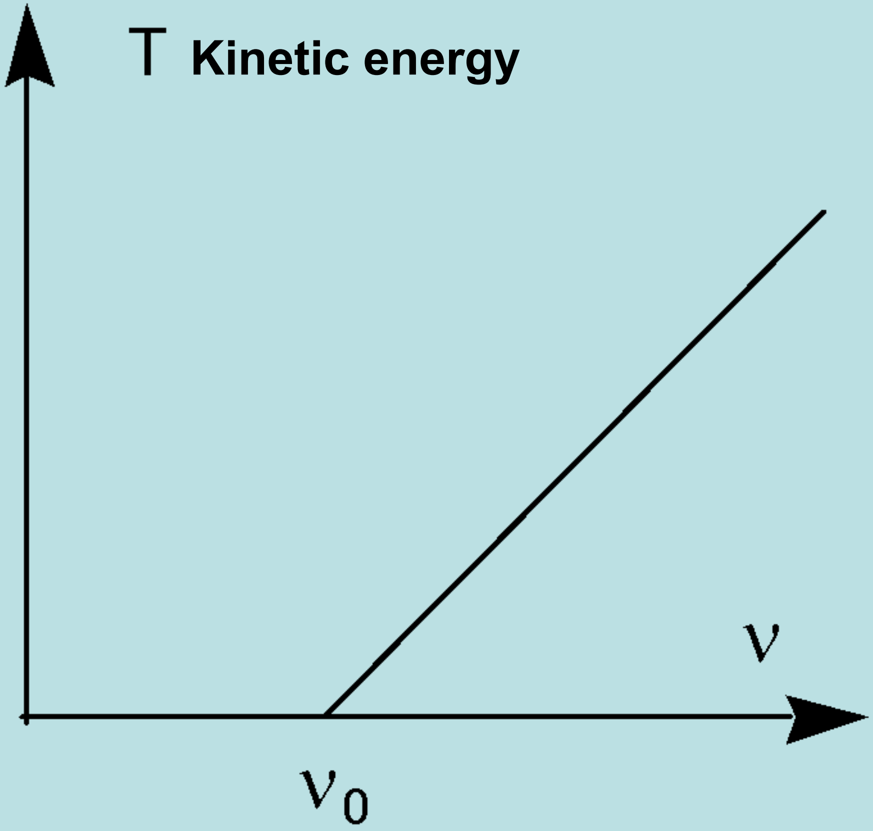
Heinrich HERTZ
(1857-1894)

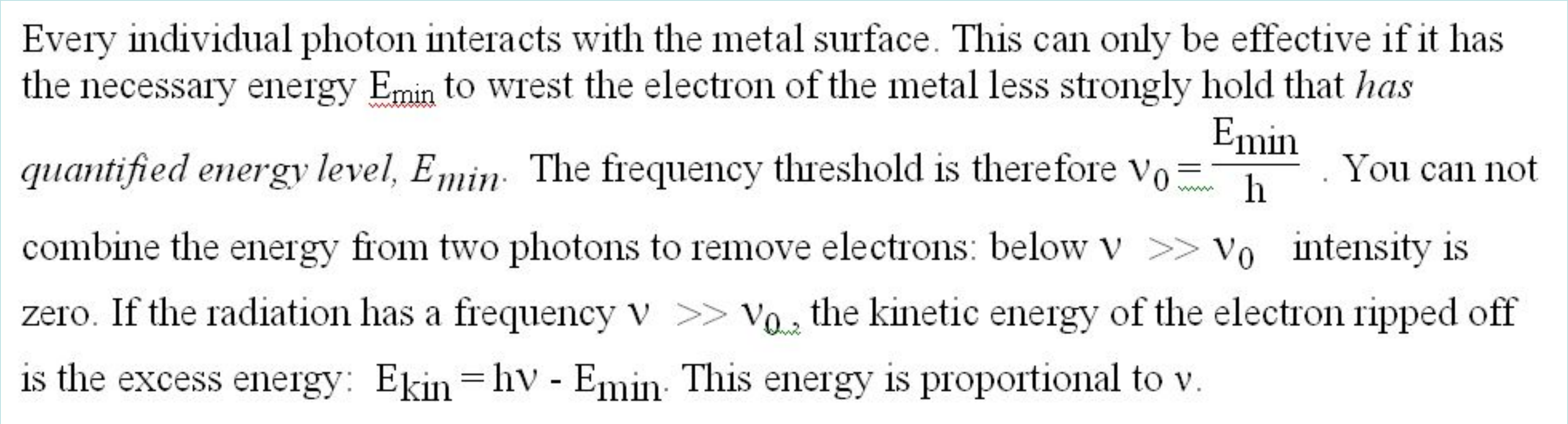


Albert EINSTEIN
(1879-1955)





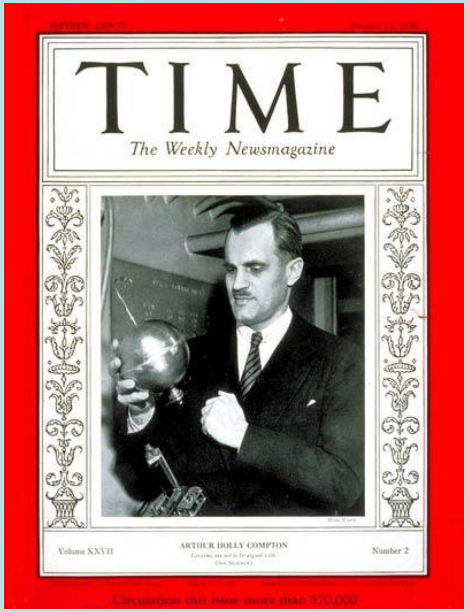




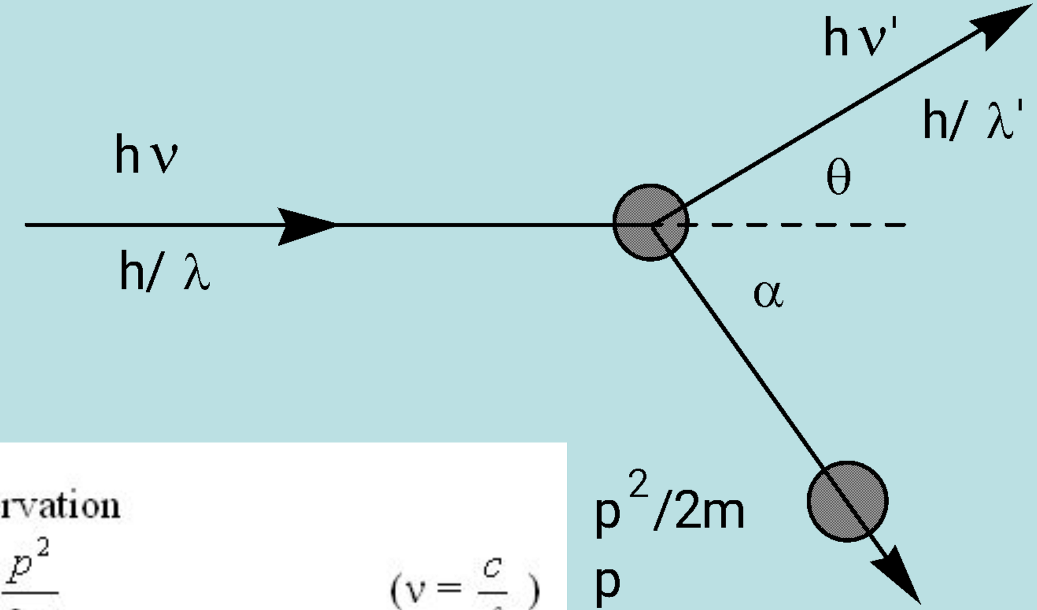
Every individual photon interacts with the metal surface. This can only be effective if it has the necessary energy E_{min} to wrest the electron of the metal less strongly hold that *has quantified energy level, E_{min}*. The frequency threshold is therefore $\nu_0 = \frac{E_{min}}{h}$. You can not combine the energy from two photons to remove electrons: below $\nu >> \nu_0$ intensity is zero. If the radiation has a frequency $\nu >> \nu_0$., the kinetic energy of the electron ripped off is the excess energy: $E_{kin} = h\nu - E_{min}$. This energy is proportional to ν.

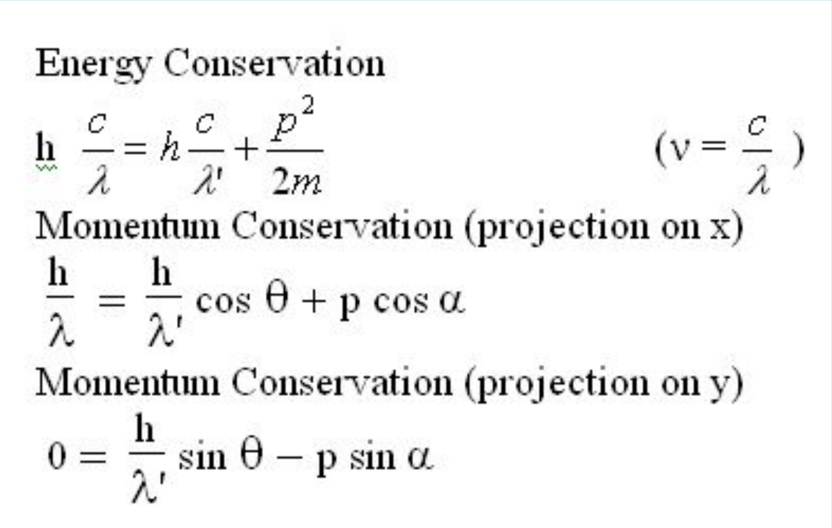
Compton effect 1923

playing billiards assuming λ=h/p



Arthur Holly Compton
American
1892-1962





Energy Conservation

$$h\frac{c}{\lambda} = h\frac{c}{\lambda'} + \frac{p^2}{2m} \qquad (\nu = \frac{c}{\lambda})$$

Momentum Conservation (projection on x)

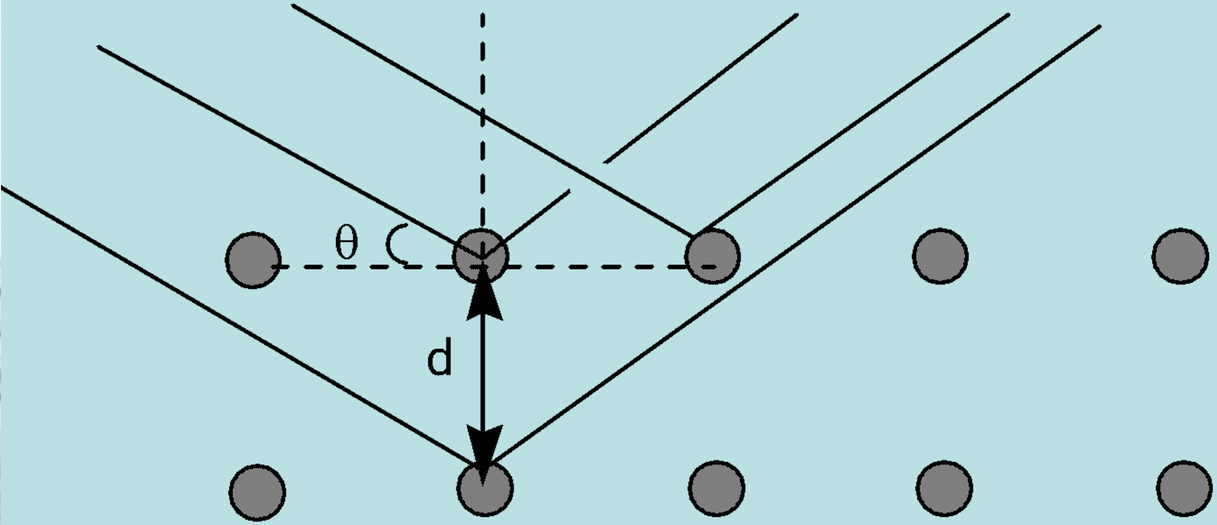
$$\frac{h}{\lambda} = \frac{h}{\lambda'}\cos\theta + p\cos\alpha$$

Momentum Conservation (projection on y)

$$0 = \frac{h}{\lambda'}\sin\theta - p\sin\alpha$$

Davisson and Germer 1925

Clinton Davisson
Lester Germer
In 1927



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

Diffraction is similarly observed using a mono-energetic electron beam

Bragg law is verified assuming $\lambda = h/p$

Wave-particle Equivalence.

- **Compton Effect (1923).**
- **Electron Diffraction Davisson and Germer (1925)**
- **Young's Double Slit Experiment**

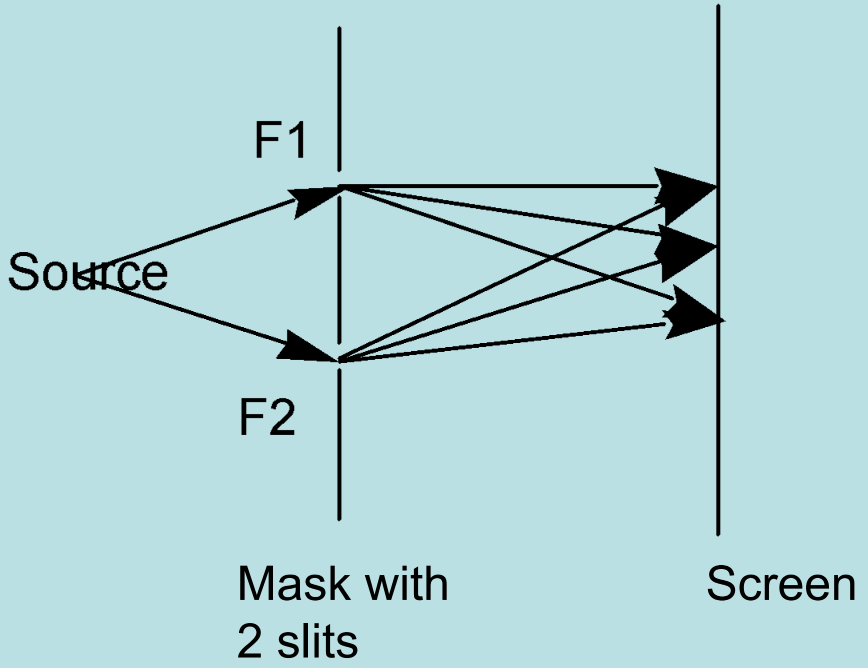
Wave–particle duality

In physics and chemistry, **wave–particle duality** is the concept that all matter and energy exhibits both wave-like and particle-like properties. A central concept of quantum mechanics, duality, addresses the inadequacy of classical concepts like "particle" and "wave" in fully describing the behavior of small-scale objects. Various interpretations of quantum mechanics attempt to explain this apparent paradox.

Thomas Young 1773 – 1829

English, was born into a family of Quakers.
At age 2, he could read.
At 7, he learned Latin, Greek and maths.
At 12, he spoke Hebrew, Persian and could handle optical instruments.
At 14, he spoke Arabic, French, Italian and Spanish, and soon the Chaldean Syriac. "…
He is a PhD to 20 years "gentleman, accomplished flute player and minstrel (troubadour). He is reported dancing above a rope."
He worked for an insurance company, continuing research into the structure of the retina, astigmatism ...
He is the rival Champollion to decipher hieroglyphics.
He is the first to read the names of Ptolemy and Cleopatra which led him to propose a first alphabet of hieroglyphic scriptures (12 characters).

Young's Double Slit Experiment



Young's Double Slit Experiment

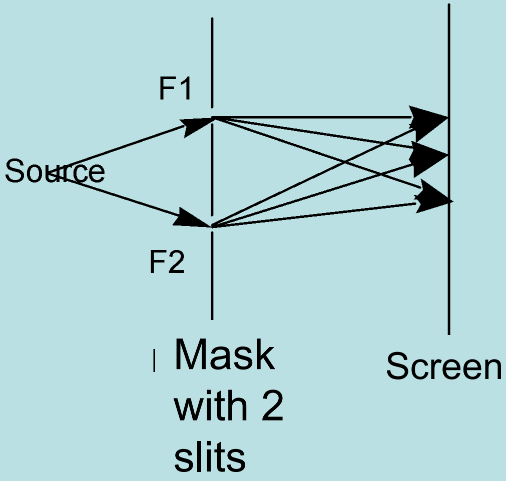
This is a typical experiment showing the wave nature of light and interferences.

What happens when we decrease the light intensity ?
If radiation = particles, individual photons reach one spot and there will be no interferences
If radiation ≠ particles there will be no spots on the screen

The result is ambiguous
There are spots
The superposition of all the impacts make interferences

Young's Double Slit Experiment

Assuming a single electron each time
What means interference with itself ?
What is its trajectory?
If it goes through F1, it should ignore the presence of F2



F1

Source

F2

Mask with 2 slits

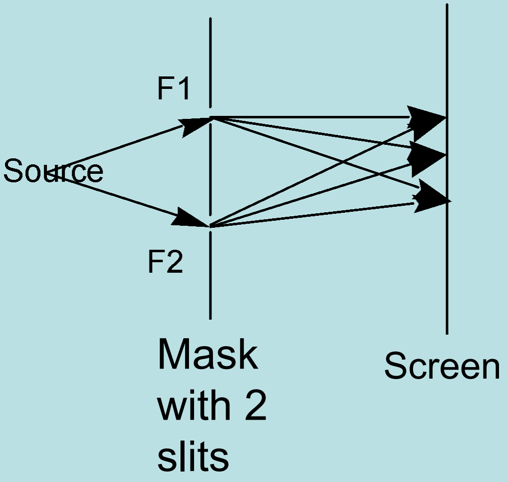
Screen

Young's Double Slit Experiment

There is no possibility of knowing through which split the photon went!
If we measure the crossing through F1, we have to place a screen behind.
Then it does not go to the final screen.
We know that it goes through F1 but we do not know where it would go after.
These two questions are not compatible

Two important differences with classical physics:

- measurement is not independent from observer
- trajectories are not defined; hν goes through F1 and F2 both! or through them with equal probabilities!



Macroscopic world:
A basket of cherries
Many of them (identical)
We can see them and taste others
Taking one has negligible effect
Cherries are both red and good

Microscopic world:
A single cherry
Either we look at it without eating
It is red
Or we eat it, it is good
You can not try both at the same time
The cherry could not be good and red at the same time

Slot machine “one-arm bandit”

After introducing a coin, you have 0 coin or X coins.

A measure of the profit has been made: profit = X

de Broglie relation from relativity

Popular expressions of relativity:
m_0 is the mass at rest, m in motion

$$m = \frac{m_0}{\sqrt{1-\frac{v^2}{c^2}}} \quad \text{and} \quad E = m\,c^2$$

E like to express E(m) as E(p) with p=mv

$$E^2 = m^2 c^4 \left(1-\frac{v^2}{c^2}\right) + p^2c^2 = \boxed{m_0^2 c^4 + p^2c^2}$$

$$= \sqrt{m_0^2 c^4 + p^2c^2} = m_0 c^2 \left(1 + \frac{p^2}{m_0^2c^2}\right)^{1/2} = E_i + \frac{p^2}{2m_0} + \dots$$

$E_i + T + E_{relativistic} + \dots$

de Broglie relation from relativity

$$E^2 = m_0^2\, c^4 + p^2 c^2$$

Application to a photon (m_0=0)

$$\boxed{E = h\nu}$$

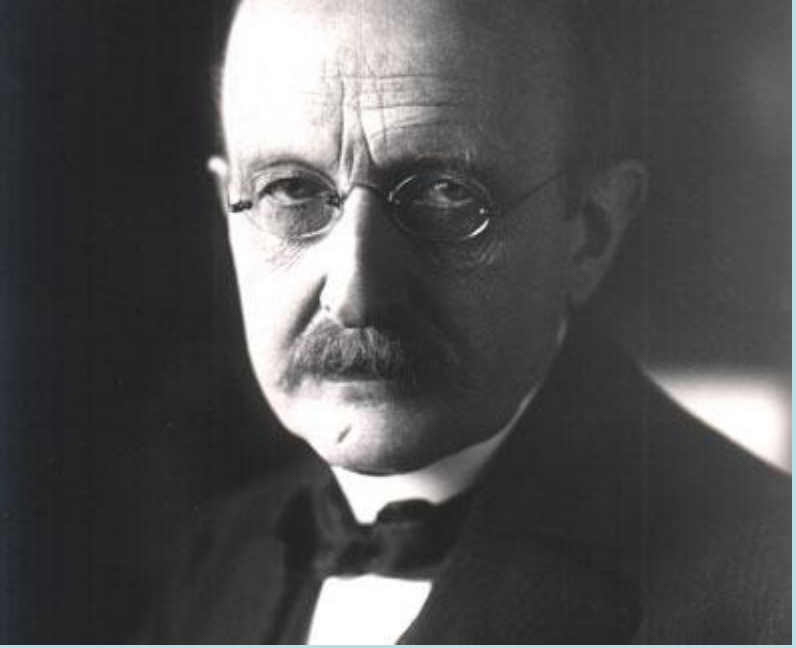
To **remember**

$$E = pc \;\longrightarrow\; pc = h\nu$$

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

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

To **remember**



Max Planck

Useful to remember to relate energy and wavelength

$$\lambda = \frac{hc}{E} \rightarrow \lambda\,(\text{Å}) = \frac{\mathbf{12410}}{\mathbf{E(eV)}}$$

A New mathematical tool:
Wave functions and Operators

Each particle may be described by a wave function $\Psi(x,y,z,t)$, real or complex, having a single value when position (x,y,z) and time (t) are defined.

If it is not time-dependent, it is called stationary.

The expression $\Psi=Ae^{i(pr-Et)}$ does not represent one molecule but a flow of particles: a plane wave

Wave functions describing one particle

To represent a single particle $\mathbf{\Psi}(x,y,z)$ that does not evolve in time, $\mathbf{\Psi}(x,y,z)$ must be finite (0 at ∞).

In QM, a particle is not localized but has a probability to be in a given volume:
dP= $\mathbf{\Psi}^* \mathbf{\Psi}$ dV is the probability of finding the particle in the volume dV.
Around one point in space, the density of probability is dP/dV= $\mathbf{\Psi}^* \mathbf{\Psi}$
$\mathbf{\Psi}$ has the dimension of $L^{-1/3}$
Integration in the whole space should give one
$\mathbf{\Psi}$ is said to be normalized.

$$\int_{total\_space} \Psi^* \Psi dV = 1$$

Operators associated to physical quantities

We cannot use functions (otherwise we would end with classical mechanics)

Any physical quantity is associated with an operator.
An operator O is “the recipe to transform Ψ into Ψ' ”
We write: O $\Psi = \Psi'$
If O $\Psi = o\Psi$ (o is a number, meaning that O does not modify Ψ, just a scaling factor), we say that Ψ is an eigenfunction of O and o is the eigenvalue.
We have solved the wave equation O $\Psi = o\Psi$ by finding simultaneously Ψ and o that satisfy the equation.
o is the measure of O for the particle in the state described by Ψ.

O is a Vending machine (cans)

Introducing a coin, you get one can.

No measure of the gain is made unless you sell the can (return to coins)

Slot machine (one-arm bandit)

Introducing a coin, you have 0 coin or X coins.

A measure of the profit has been made: profit = X

Examples of operators in mathematics : P parity

$$\boxed{Pf(x) = f(-x)}$$

Even function : no change after $x \rightarrow -x$
Odd function : f changes sign after $x \rightarrow -x$
$y=x^2$ is even
$y=x^3$ is odd
$y= x^2 + x^3$ has no parity: $P(x^2 + x^3) = x^2 - x^3$

Examples of operators in mathematics : A

$$\boxed{A = \frac{d^2}{dx^2} - x^2}$$

Apply to the wave function $y = e^{-x^2/2}$

$$A = \frac{d^2y}{dx^2} - x^2y = \frac{d^2e^{-x^2/2}}{dx^2} + x^2\, e^{-x^2/2}$$

$$A\, y = \frac{d(-x\, e^{-x^2/2}\,)}{dx} - x^2\, e^{-x^2/2} = -\ e^{-x^2/2} + x^2\, e^{-x^2/2} - x^2\, e^{-x^2/2}$$

$$A\, y = -\ e^{-x^2/2} = -y$$

y is an eigenvector; the eigenvalue is -1

Linearity

The operators are linear:

$O\,(a\Psi_1 + b\Psi_1) = O\,(a\Psi_1\,) + O(\,b\Psi_1)$

Normalization

An eigenfunction remains an eigenfunction when multiplied by a constant

$O(\lambda\Psi)= o(\lambda\Psi)$ thus it is always possible to normalize a finite function

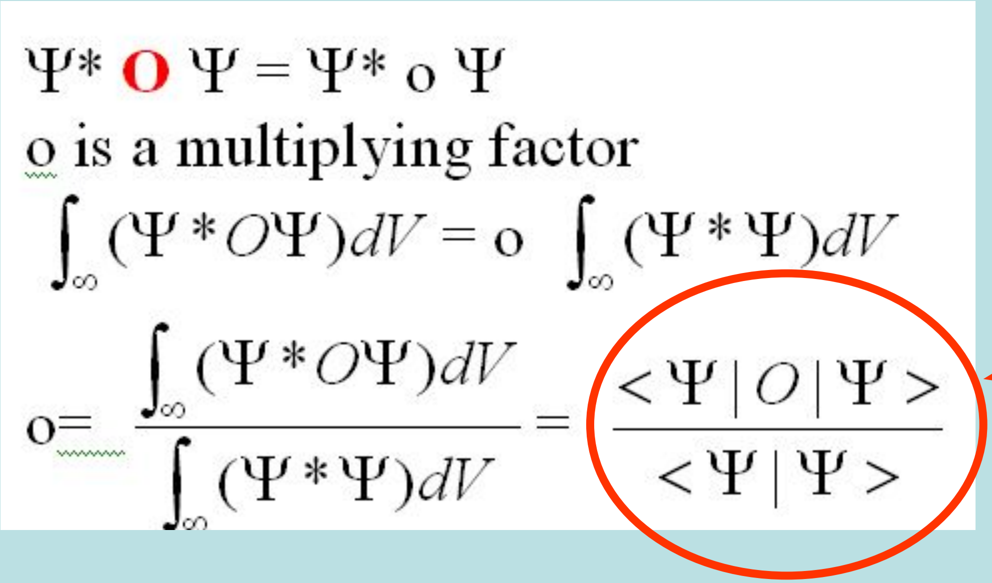
$$\int_{total\_space} \Psi^{*}\Psi\, dV = N \quad \text{taking} \quad \Psi' = \frac{1}{\sqrt{N}}\Psi \quad \text{gives} \quad \int_{total\_space} \Psi'^{*}\, \Psi'\, dV = 1$$

Dirac notations $\langle\Psi|\Psi\rangle$

Mean value

- If Ψ_1 and Ψ_2 are associated with the same eigenvalue o: $O(a\Psi_1 + b\Psi_2) = o(a\Psi_1 + b\Psi_2)$
- If not $O(a\Psi_1 + b\Psi_2) = o_1(a\Psi_1) + o_2(b\Psi_2)$

we define $\bar{o} = (a^2 o_1 + b^2 o_2)/(a^2 + b^2)$



$$\Psi^* \, O \, \Psi = \Psi^* \, o \, \Psi$$

o is a multiplying factor

$$\int_\infty (\Psi^* O \Psi) dV = o \int_\infty (\Psi^* \Psi) dV$$

$$o = \frac{\int_\infty (\Psi^* O \Psi) dV}{\int_\infty (\Psi^* \Psi) dV} = \frac{< \Psi | O | \Psi >}{< \Psi | \Psi >}$$

Dirac notations

Sum, product and commutation of operators

$(A+B)\Psi = A\Psi + B\Psi$

$(AB)\Psi = A(B\Psi)$

eigenvalues

wavefunctions

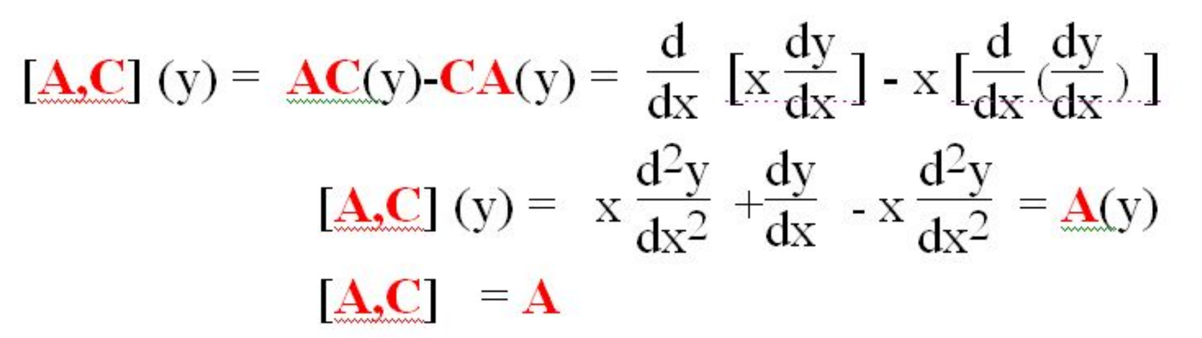
operators

	$y_1 = e^{4x}$	$y_2 = x^2$	$y_3 = 1/x$
d/dx	4	--	--
x3	3	3	3
x d/dx	--	2	-1

Sum, product and commutation of operators

[A,C]=AC-CA≠0

[A,B]=AB-BA=0
[B,C]=BC-CB=0



$$[\mathbf{A},\mathbf{C}]\,(y) = \mathbf{AC}(y)-\mathbf{CA}(y) = \frac{d}{dx}\left[x\,\frac{dy}{dx}\right] - x\left[\frac{d}{dx}\left(\frac{dy}{dx}\right)\right]$$

$$[\mathbf{A},\mathbf{C}]\,(y) = x\,\frac{d^2y}{dx^2} + \frac{dy}{dx} - x\,\frac{d^2y}{dx^2} = \mathbf{A}(y)$$

$$[\mathbf{A},\mathbf{C}] = \mathbf{A}$$

	$y_1=e^{4x}$	$y_2=x^2$	$y_3=1/x$
A = d/dx	4	--	--
B = x3	3	3	3
C= x d/dx	--	2	-1

not compatible operators

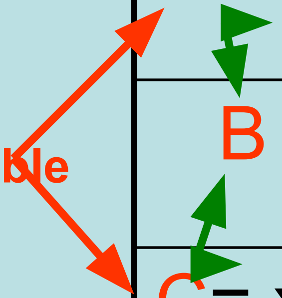
Compatibility, incompatibility of operators

$[A,C]=AC-CA\neq 0$

$[A,B]=AB-BA=0$
$[B,C]=BC-CB=0$

When operators commute, the physical quantities may be simultaneously defined (compatibility)

When operators do not commute, the physical quantities can not be simultaneously defined (incompatibility)

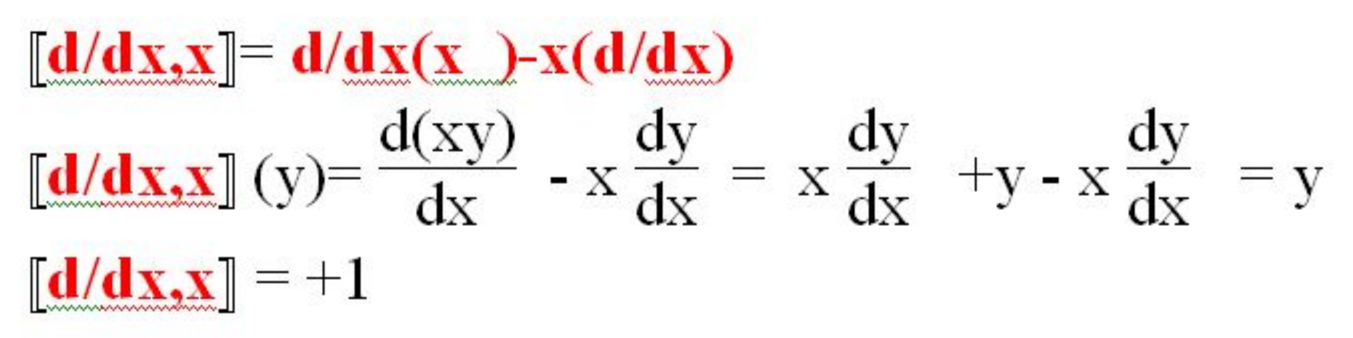


compatible operators

not compatible operators

	$y_1=e^{4x}$	$y_2=x^2$	$y_3=1/x$
A = d/dx	4	--	--
B = x3	3	3	3
C= x d/dx	--	2	-1

x and d/dx do not commute, are incompatible

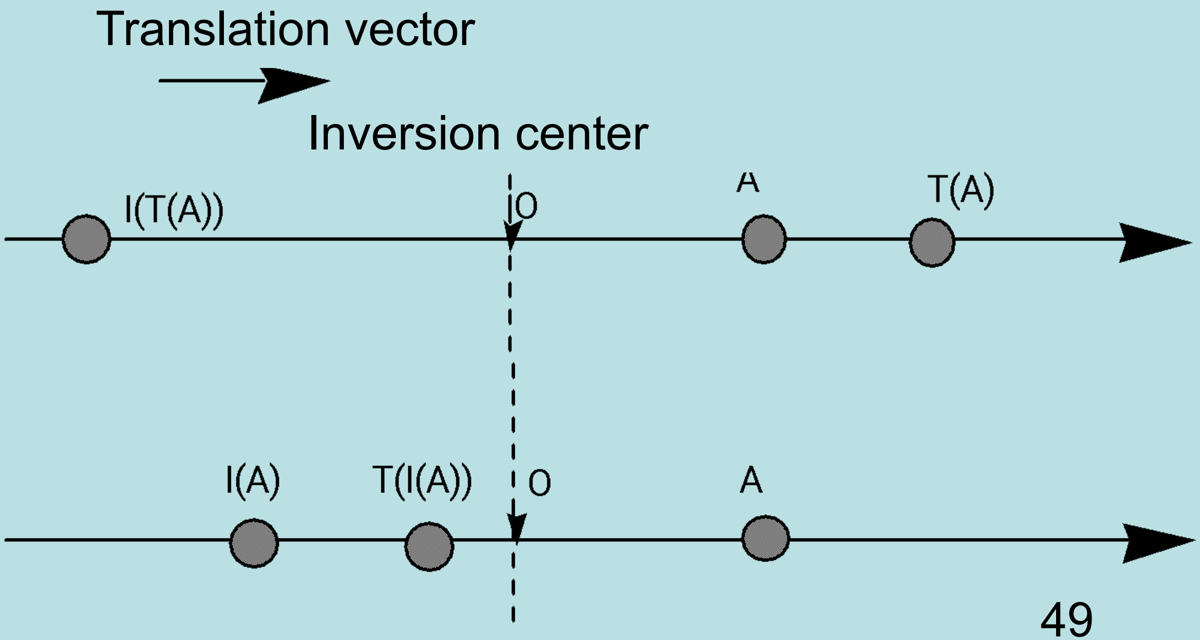


$$[d/dx, x] = d/dx(x\ \ ) - x(d/dx)$$

$$[d/dx, x]\,(y) = \frac{d(xy)}{dx} - x\frac{dy}{dx} = x\frac{dy}{dx} + y - x\frac{dy}{dx} = y$$

$$[d/dx, x] = +1$$

Translation and inversion do not commute, are incompatible

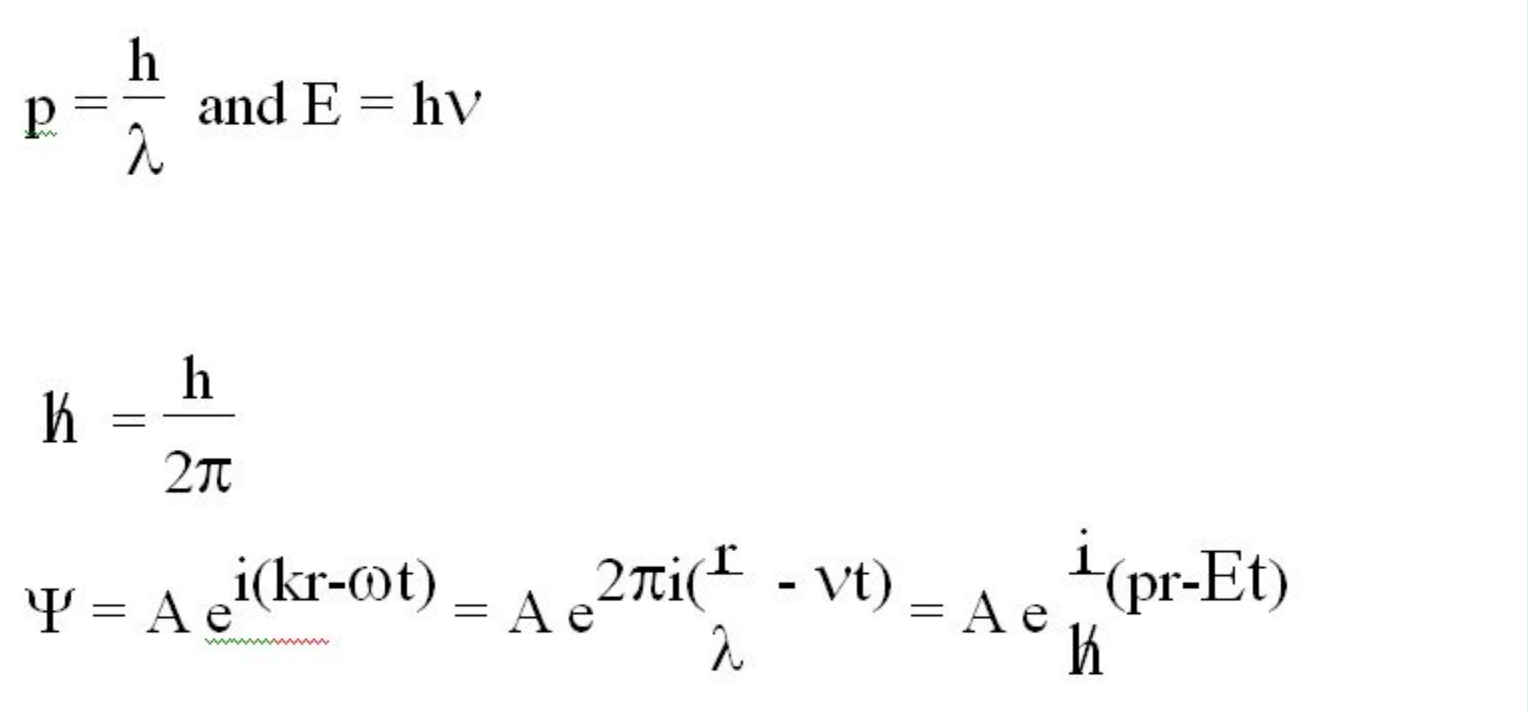


Introducing new variables

Now it is time to give a physical meaning.

p is the momentum, E is the Energy

H=6.62 10^{-34} J.s



$$p = \frac{h}{\lambda} \text{ and } E = h\nu$$

$$\hbar = \frac{h}{2\pi}$$

$$\Psi = A\,e^{i(kr-\omega t)} = A\,e^{2\pi i(\frac{r}{\lambda} - \nu t)} = A\,e^{\frac{i}{\hbar}(pr-Et)}$$

Plane waves

$$\Psi = A\, e^{i(kr-\omega t)} = A\, e^{2\pi i(\frac{r}{\lambda} - \nu t)} = A\, e^{\frac{i}{\hbar}(pr-Et)}$$

This represents a (monochromatic) beam, a continuous flow of particles with the same velocity (monokinetic).

k, λ, ω, ν, p and E are perfectly defined

R (position) and t (time) are not defined.

$\Psi\Psi^* = A^2$=constant everywhere; there is no localization.

If E=constant, this is a stationary state, independent of t which is not defined.

Correspondence principle 1913/1920

Niels Henrik David Bohr
Danish
1885-1962

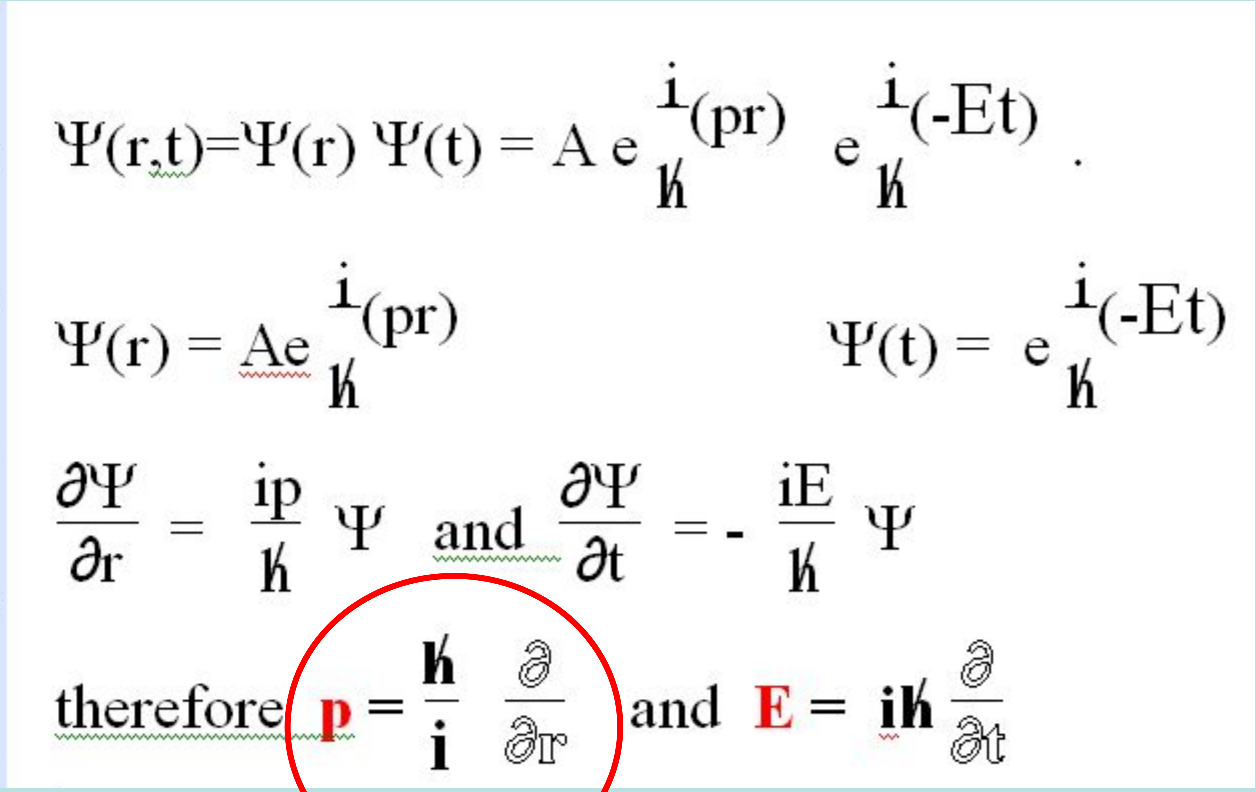
For every physical quantity one can define an operator. The definition uses formulae from classical physics replacing quantities involved by the corresponding operators

QM is then built from classical physics in spite of demonstrating its limits

Operators p and H

We use the expression of the plane wave which allows defining exactly p and E.

Momentum and Energy Operators



$$\Psi(r,t)=\Psi(r)\,\Psi(t) = A\,e^{\frac{i}{\hbar}(pr)}\;e^{\frac{i}{\hbar}(-Et)}\ .$$

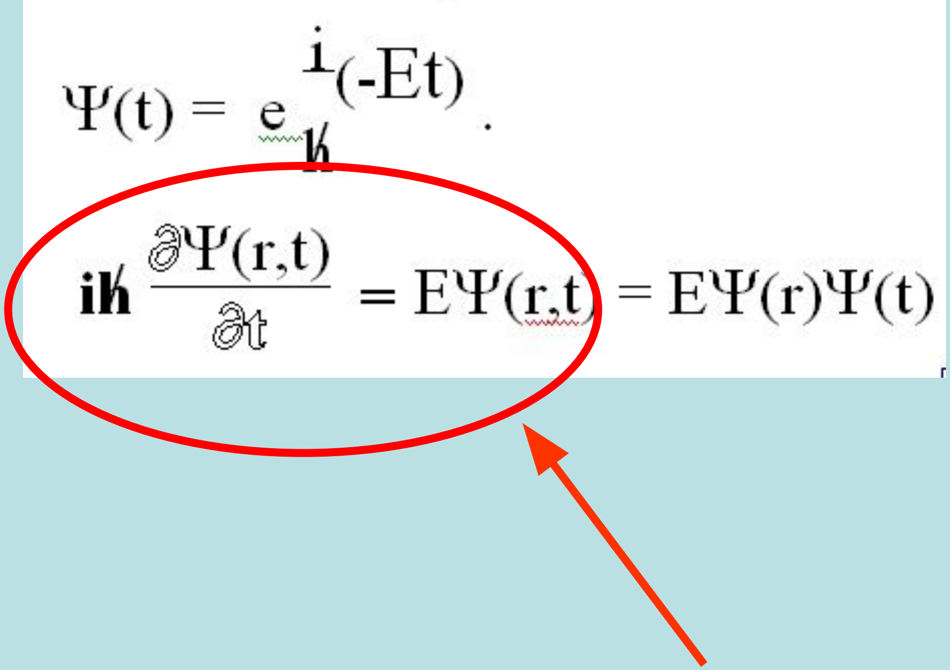
$$\Psi(r) = Ae^{\frac{i}{\hbar}(pr)} \qquad\qquad \Psi(t) = e^{\frac{i}{\hbar}(-Et)}$$

$$\frac{\partial\Psi}{\partial r} = \frac{ip}{\hbar}\Psi \quad \text{and} \quad \frac{\partial\Psi}{\partial t} = -\frac{iE}{\hbar}\Psi$$

$$\text{therefore}\quad \boxed{\mathbf{p} = \frac{\hbar}{i}\frac{\partial}{\partial r}} \quad \text{and} \quad \mathbf{E} = i\hbar\frac{\partial}{\partial t}$$

Remember during this chapter

Stationary state E=constant



$$\Psi(t) = e^{\frac{i}{\hbar}(-Et)} .$$

$$i\hbar \frac{\partial \Psi(r,t)}{\partial t} = E\Psi(r,t) = E\Psi(r)\Psi(t)$$

Remember for 3 slides after

Kinetic energy

Classical $T = \frac{p^2}{2m}$ quantum operator $\mathbb{P}^2 = \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$

In 3D :

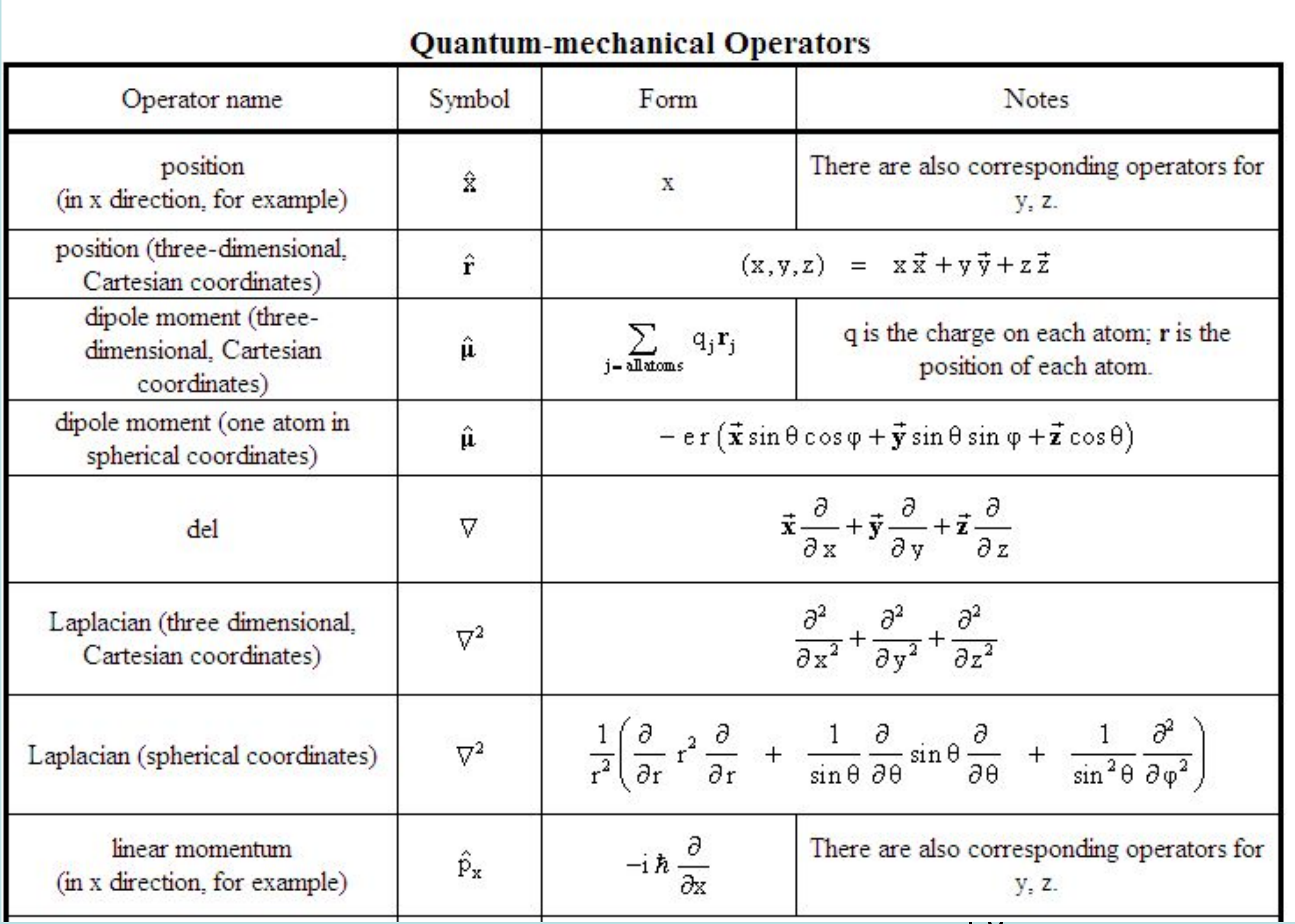
$$\mathbb{T} = \frac{-\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) = \frac{-\hbar^2}{2m}\,\Delta$$

Calling $\Delta = \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)$ the laplacian

Pierre Simon, Marquis de Laplace
(1749 -1827)

Correspondence principle angular momentum

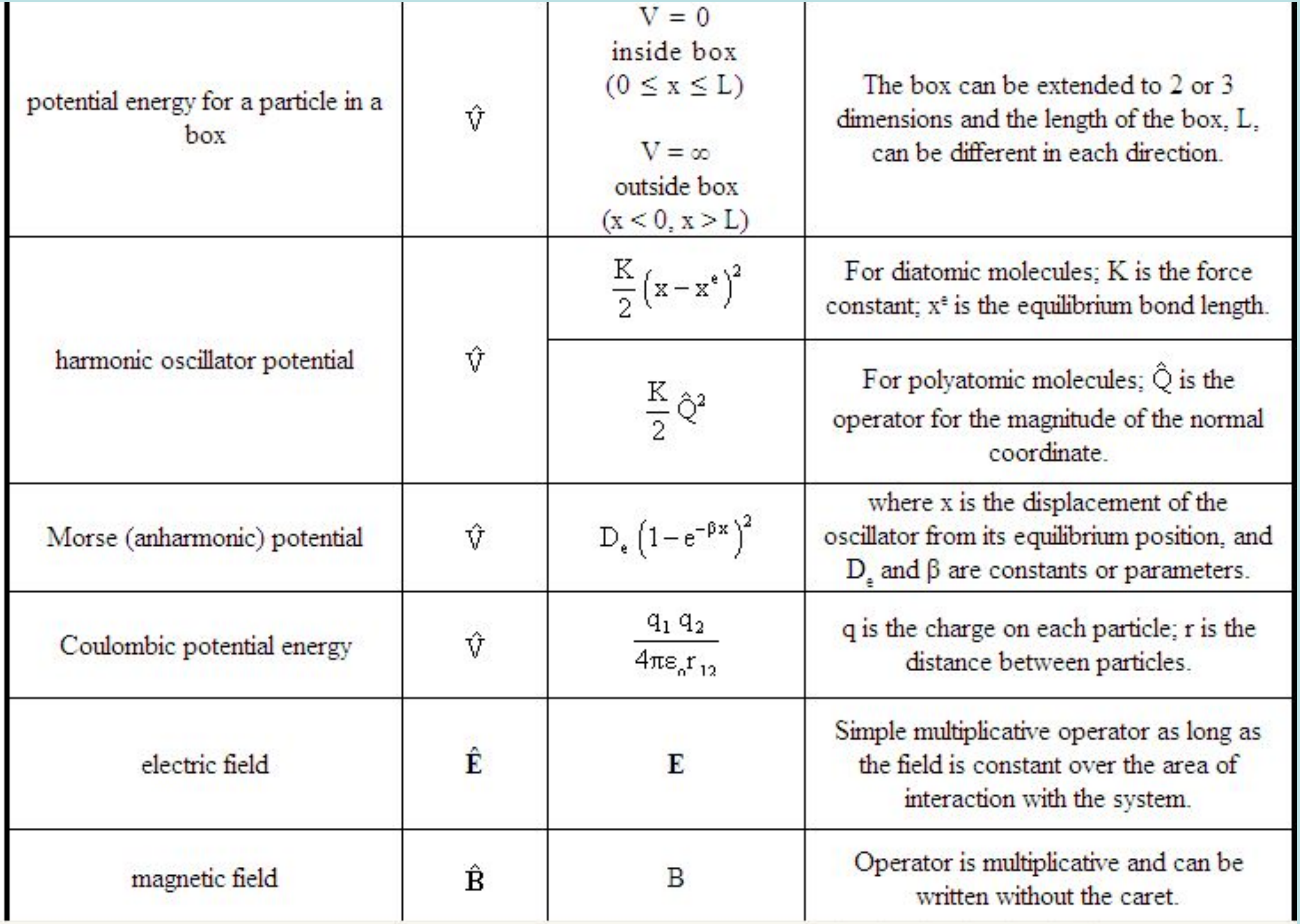
Classical expression	Quantum expression
$l_Z = xp_y - yp_x$	$\mathbb{L}_{\mathbb{Z}} = -i\hbar\,(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x})$



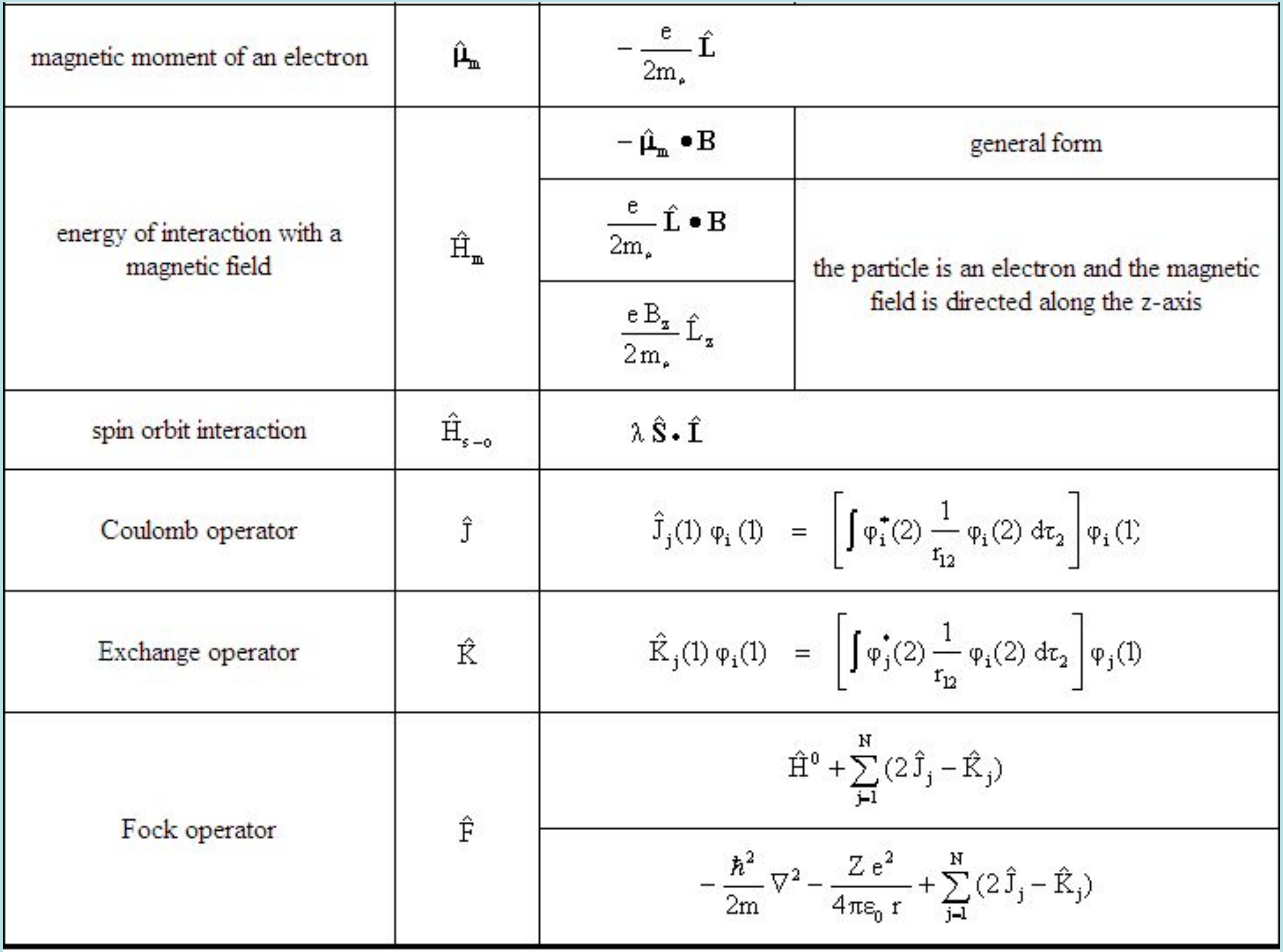
Quantum-mechanical Operators

Operator name	Symbol	Form	Notes
position (in x direction, for example)	$\hat{x}$	x	There are also corresponding operators for y, z.
position (three-dimensional, Cartesian coordinates)	$\hat{\mathbf{r}}$	$(x,y,z) = x\vec{x} + y\vec{y} + z\vec{z}$	
dipole moment (three-dimensional, Cartesian coordinates)	$\hat{\boldsymbol{\mu}}$	$\sum_{j=\text{all atoms}} q_j \mathbf{r}_j$	q is the charge on each atom; **r** is the position of each atom.
dipole moment (one atom in spherical coordinates)	$\hat{\boldsymbol{\mu}}$	$-e\,r\left(\vec{\mathbf{x}}\sin\theta\cos\varphi + \vec{\mathbf{y}}\sin\theta\sin\varphi + \vec{\mathbf{z}}\cos\theta\right)$	
del	∇	$\vec{\mathbf{x}}\frac{\partial}{\partial x} + \vec{\mathbf{y}}\frac{\partial}{\partial y} + \vec{\mathbf{z}}\frac{\partial}{\partial z}$	
Laplacian (three dimensional, Cartesian coordinates)	∇^2	$\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$	
Laplacian (spherical coordinates)	∇^2	$\frac{1}{r^2}\left(\frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right)$	
linear momentum (in x direction, for example)	$\hat{p}_x$	$-i\hbar\frac{\partial}{\partial x}$	There are also corresponding operators for y, z.

linear momentum (3 dimensions)	$\hat{\mathbf{p}}$	$-i\hbar\nabla$	
z-component of angular momentum	$\hat{M}_z$	$-i\hbar\dfrac{\partial}{\partial\varphi}$	
the square of total angular momentum	$\hat{M}^2$	$-\hbar^2\left[\dfrac{1}{\sin\theta}\dfrac{\partial}{\partial\theta}\sin\theta\dfrac{\partial}{\partial\theta} + \dfrac{1}{\sin^2\theta}\dfrac{\partial^2}{\partial\varphi^2}\right]$	
electronic angular momentum	$\hat{\mathbf{L}}$	$\vec{\mathbf{x}}\,\hat{L}_x + \vec{\mathbf{y}}\,\hat{L}_y + \vec{\mathbf{z}}\,\hat{L}_z$	Operator has the same form as the angular momentum operator, $\hat{M}$
total energy (Hamiltonian)	$\hat{H}$	$\hat{T} + \hat{V}$	The potential energy (V) depends on the specific system being modeled. Additional energy terms can be added (e.g., interactions with electric or magnetic fields.)
kinetic energy for a single particle (Cartesian coordinates)	$\hat{T}_x$	$\left(\dfrac{-\hbar^2}{2m}\right)\dfrac{\partial^2}{\partial x^2}$	one-dimensional expression
	$\hat{T}$	$\left(\dfrac{-\hbar^2}{2m}\right)\nabla^2$	generalized expression
kinetic energy for a single particle (spherical coordinates)	$\hat{T}$	$\dfrac{-\hbar^2}{2\mu r^2}\left[\dfrac{\partial}{\partial r}r^2\dfrac{\partial}{\partial r} + \dfrac{1}{\sin\theta}\dfrac{\partial}{\partial\theta}\sin\theta\dfrac{\partial}{\partial\theta} + \dfrac{1}{\sin^2\theta}\dfrac{\partial^2}{\partial\varphi^2}\right]$	



potential energy for a particle in a box	$\hat{V}$	$V = 0$ inside box $(0 \leq x \leq L)$ $V = \infty$ outside box $(x < 0, x > L)$	The box can be extended to 2 or 3 dimensions and the length of the box, L, can be different in each direction.
harmonic oscillator potential	$\hat{V}$	$\frac{K}{2}\left(x - x^e\right)^2$	For diatomic molecules; K is the force constant; x^e is the equilibrium bond length.
		$\frac{K}{2}\hat{Q}^2$	For polyatomic molecules; $\hat{Q}$ is the operator for the magnitude of the normal coordinate.
Morse (anharmonic) potential	$\hat{V}$	$D_e\left(1 - e^{-\beta x}\right)^2$	where x is the displacement of the oscillator from its equilibrium position, and D_e and β are constants or parameters.
Coulombic potential energy	$\hat{V}$	$\frac{q_1 q_2}{4\pi\varepsilon_0 r_{12}}$	q is the charge on each particle; r is the distance between particles.
electric field	$\hat{\mathbf{E}}$	$\mathbf{E}$	Simple multiplicative operator as long as the field is constant over the area of interaction with the system.
magnetic field	$\hat{\mathbf{B}}$	B	Operator is multiplicative and can be written without the caret.



magnetic moment of an electron	$\hat{\mu}_m$	$-\frac{e}{2m_e}\hat{\mathbf{L}}$	
energy of interaction with a magnetic field	$\hat{H}_m$	$-\hat{\mu}_m \bullet \mathbf{B}$	general form
		$\frac{e}{2m_e}\hat{\mathbf{L}} \bullet \mathbf{B}$	the particle is an electron and the magnetic field is directed along the z-axis
		$\frac{e B_z}{2 m_e}\hat{L}_z$	
spin orbit interaction	$\hat{H}_{s-o}$	$\lambda \hat{\mathbf{S}} \bullet \hat{\mathbf{l}}$	
Coulomb operator	$\hat{J}$	$\hat{J}_j(1)\,\varphi_i(1) = \left[\int \varphi_i^*(2)\,\frac{1}{r_{12}}\,\varphi_i(2)\,d\tau_2\right]\varphi_i(1)$	
Exchange operator	$\hat{K}$	$\hat{K}_j(1)\,\varphi_i(1) = \left[\int \varphi_j^*(2)\,\frac{1}{r_{12}}\,\varphi_i(2)\,d\tau_2\right]\varphi_j(1)$	
Fock operator	$\hat{F}$	$\hat{H}^0 + \sum_{j=1}^{N}(2\hat{J}_j - \hat{K}_j)$	
		$-\frac{\hbar^2}{2m}\nabla^2 - \frac{Z e^2}{4\pi\varepsilon_0 r} + \sum_{j=1}^{N}(2\hat{J}_j - \hat{K}_j)$	

Time-dependent Schrödinger Equation

Without potential E = T
With potential E = T + V

$$i\hbar\frac{\partial\Psi(r,t)}{\partial t} = -\frac{\hbar^2}{2m}\,\Delta\Psi(r,t)$$

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

Erwin Rudolf Josef Alexander **Schrödinger**
Austrian
1887 –1961

Schrödinger Equation for stationary states

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

$$\Psi(r,t) = \Psi(r).\Psi(t) = A\exp\left(\frac{-iEt}{\hbar}\right)\Psi(r)$$

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

$$\underbrace{-\frac{\hbar^2}{2m}\Delta\Psi(r)}_{\text{Kinetic energy}} + \underbrace{V(r)\Psi(r)}_{\text{Potential energy}} = \underbrace{E\,\Psi(r)}_{\text{Total energy}}$$

Schrödinger Equation for stationary states

$$-\frac{\hbar^2}{2m}\Delta\Psi(r) + V(r)\Psi(r) = E\,\Psi(r)$$

Remember

$$\mathbb{H}\,\Psi(x,y,z) = E\Psi(x,y,z) \quad \text{with} \quad \mathbb{H} = -\frac{\hbar^2}{2m}\Delta + \mathbb{V}$$

H is the hamiltonian

Half penny bridge in Dublin

Sir **William Rowan Hamilton**
Irish 1805-1865

Chemistry is nothing but an application of Schrödinger Equation (Dirac)

$\langle \Psi | \Psi \rangle$ $\langle \Psi | O | \Psi \rangle$

Dirac notations

Paul Adrien Dirac 1902 – 1984
Dirac’s mother was British and his father was Swiss

Uncertainty principle

the **Heisenberg uncertainty principle** states that locating a particle in a small region of space makes the momentum of the particle uncertain; and conversely, that measuring the momentum of a particle precisely makes the position uncertain

We already have seen incompatible operators

Werner Heisenberg
German
1901-1976

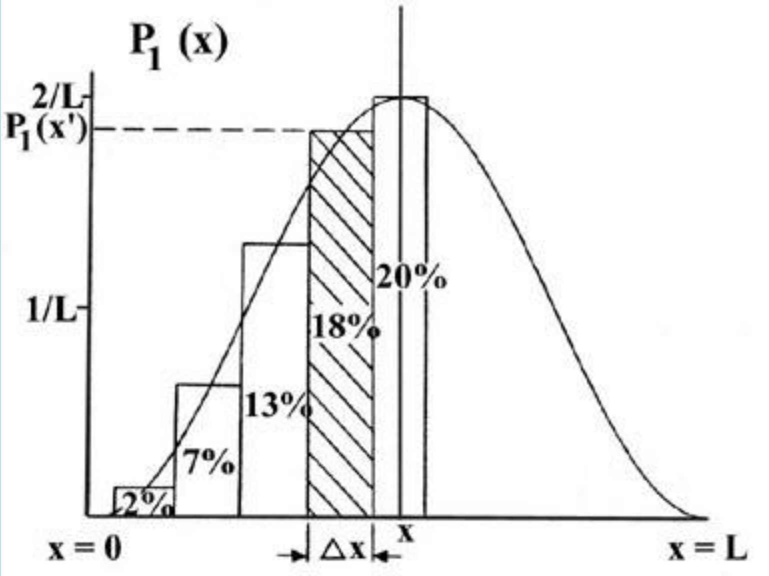
It is not surprising to find that quantum mechanics does not predict the position of an electron exactly. Rather, it provides only a ***probability*** as to where the electron will be found.

We shall illustrate the probability aspect in terms of the system of an electron confined to motion along a line of length *L*. Quantum mechanical probabilities are expressed in terms of a distribution function.

For a plane wave, p is defined and the position is not.

With a superposition of plane waves, we introduce an uncertainty on p and we localize. Since, the sum of 2 wavefucntions is neither an eigenfunction for p nor x, we have average values.

With a Gaussian function, the localization below is 1/2π



p and x do not commute and are incompatible

For a plane wave, p is known and x is not ($\Psi^*\Psi=A^2$ everywhere)

Let’s superpose two waves… $\lambda_1 = \lambda + \frac{\Delta\lambda}{2}$ et $\lambda_2 = \lambda - \frac{\Delta\lambda}{2}$.

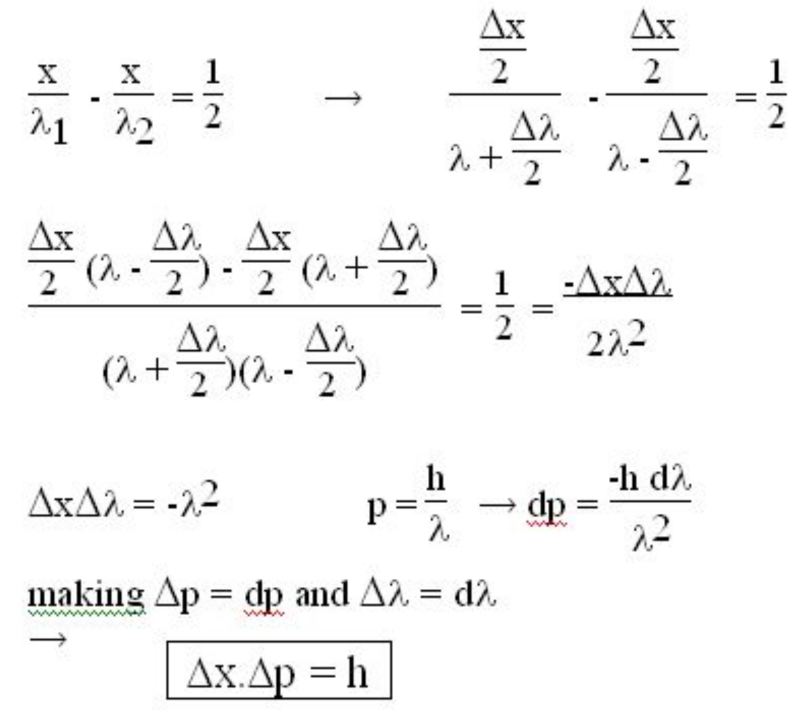
this introduces a delocalization for p and may be localize x

At the origin x=0 and at t=0 we want to increase the total amplitude, so the two waves Ψ_1 and Ψ_2 are taken in phase

At ± Δx/2 we want to impose them out of phase

The position is therefore known for x ± Δx/2

the waves will have wavelengths



$$\frac{x}{\lambda_1} - \frac{x}{\lambda_2} = \frac{1}{2} \quad \rightarrow \quad \frac{\frac{\Delta x}{2}}{\lambda + \frac{\Delta\lambda}{2}} - \frac{\frac{\Delta x}{2}}{\lambda - \frac{\Delta\lambda}{2}} = \frac{1}{2}$$

$$\frac{\frac{\Delta x}{2}(\lambda - \frac{\Delta\lambda}{2}) - \frac{\Delta x}{2}(\lambda + \frac{\Delta\lambda}{2})}{(\lambda + \frac{\Delta\lambda}{2})(\lambda - \frac{\Delta\lambda}{2})} = \frac{1}{2} = \frac{-\Delta x\Delta\lambda}{2\lambda^2}$$

$$\Delta x\Delta\lambda = -\lambda^2 \qquad p = \frac{h}{\lambda} \rightarrow dp = \frac{-h\,d\lambda}{\lambda^2}$$

making $\Delta p = dp$ and $\Delta\lambda = d\lambda$

→

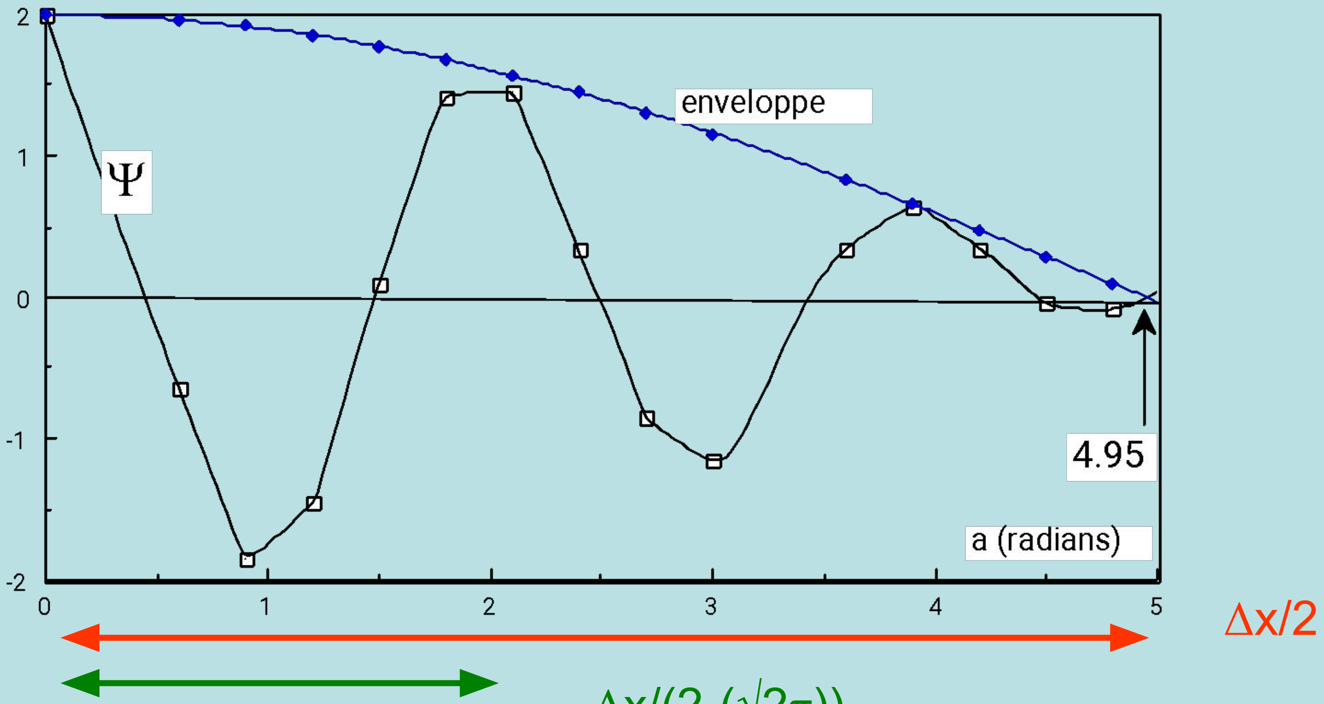
$$\boxed{\Delta x.\Delta p = h}$$

Superposition of two waves

$$\Psi = \cos(2\pi(\frac{x}{0.9} - \nu t)) + \cos(2\pi(\frac{x}{1.1} - \nu t)) = 2\cos(\frac{\pi x}{9.9})\cos(2\pi(\frac{x}{0.99} - \nu t))$$

$$\frac{\Delta x}{2} = 4.95 \qquad \Delta\lambda = 1.1\text{-}0.9 = 0.2$$

$$\Delta x . \Delta\lambda = 0.99 \text{ close to } \lambda^2 = 1$$



$\Delta x/2$

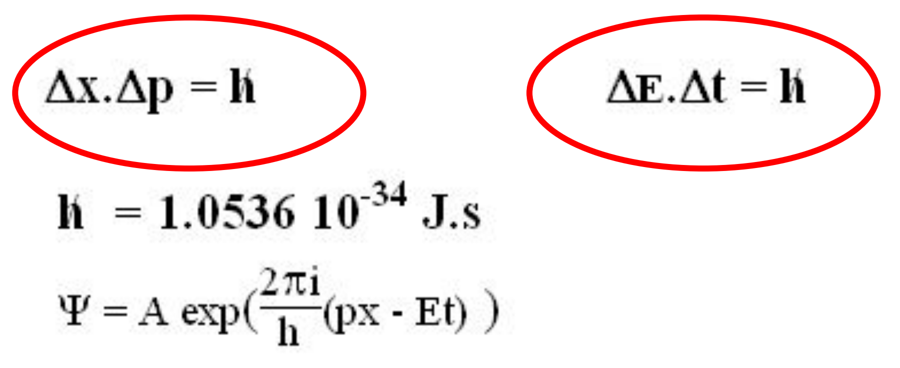
$\Delta x/(2_x(\sqrt{2\pi}))$

Factor $1/2\pi$ a more realistic localization

Uncertainty principle

Werner Heisenberg
German
1901-1976

A more accurate calculation localizes more (1/2π the width of a gaussian) therefore one gets



$$\Delta x . \Delta p = \hbar \qquad \Delta E . \Delta t = \hbar$$

$$\hbar = 1.0536\ 10^{-34}\ \mathrm{J.s}$$

$$\Psi = A \exp(\frac{2\pi i}{h}(px - Et))$$

x and p or E and t play symmetric roles in the plane wave expression; Therefore, there are two main uncertainty principles