Spectroscopy:

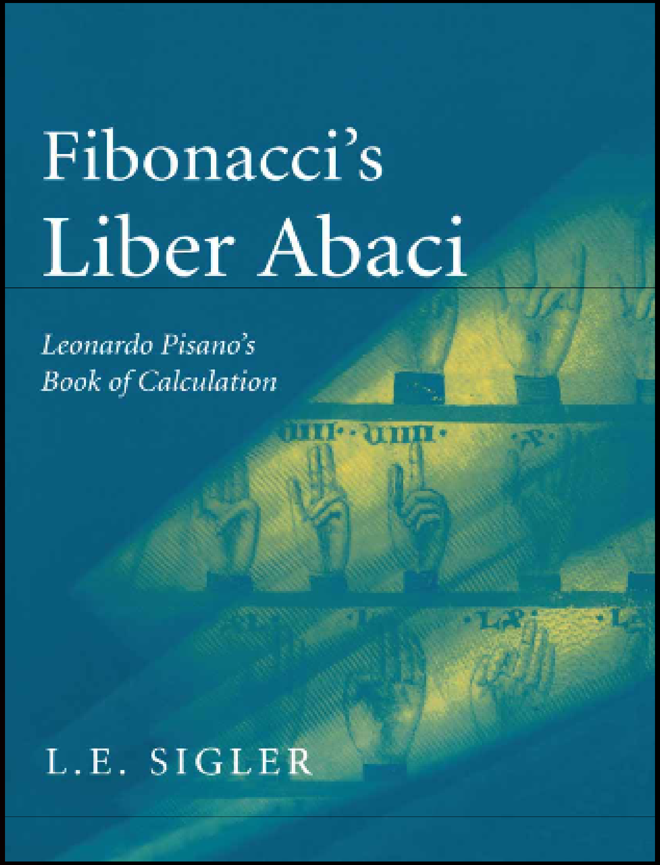
an Historic Journey

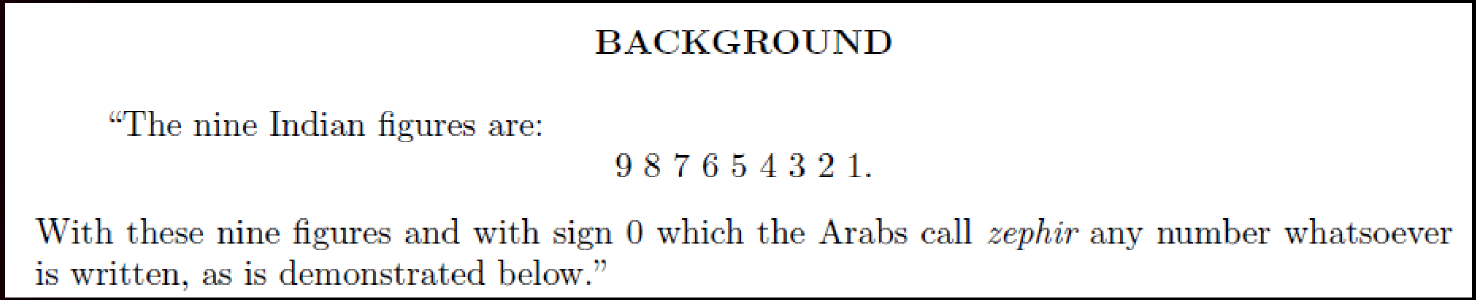
(pre-history)

1202

Fibonacci

(c. 1170 – c. 1250)





BACKGROUND

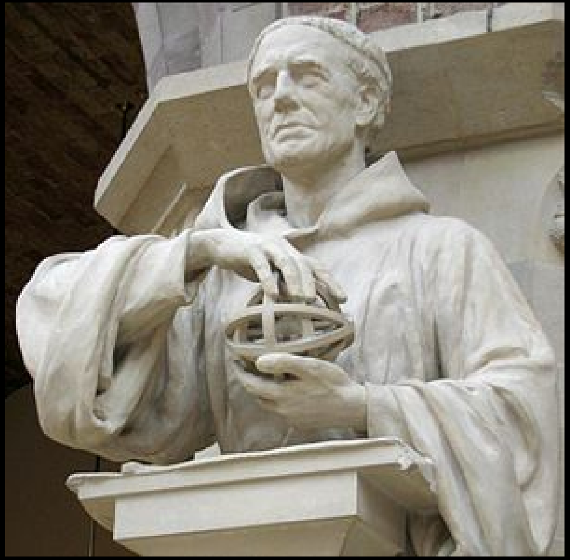
"The nine Indian figures are:

9 8 7 6 5 4 3 2 1.

With these nine figures and with sign 0 which the Arabs call *zephir* any number whatsoever is written, as is demonstrated below."

Roger Bacon

(1214(?) - 1294)



Opus Majus 1267

Part V – Optics

Part VI – Experimental Sciences

Explanation of the rainbow

Newton

(1643 - 1727)

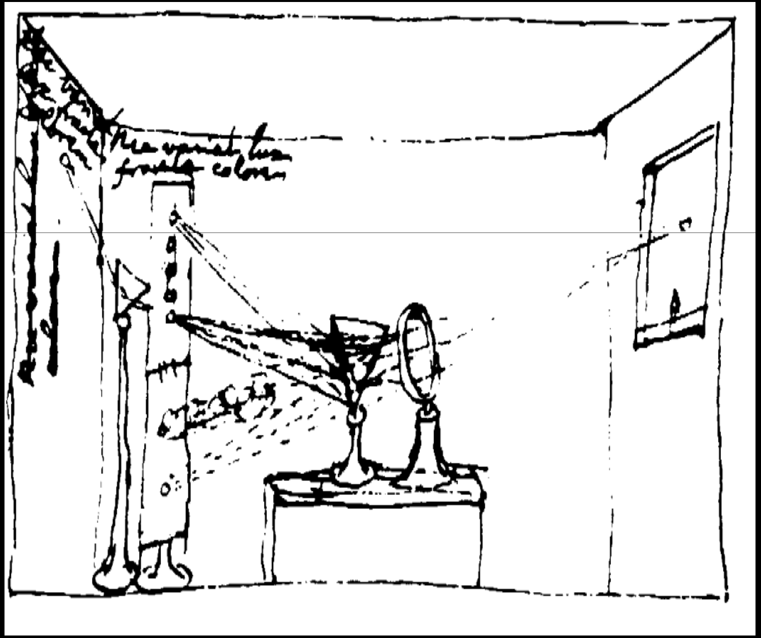
1671

Coined the term spectrum

Newton sketch of it´s experiment:

A hole
A collimator lens
A dispersion prism
A target to display it

A second prism to
recreate white light



Beyond the visible

Herschel

(1738 -1822)

Using a thermometer maximum heating effect occurs beyond the red (IR radiation).

(1800)

Beyond the visible

Ritter

(1776 -1810)

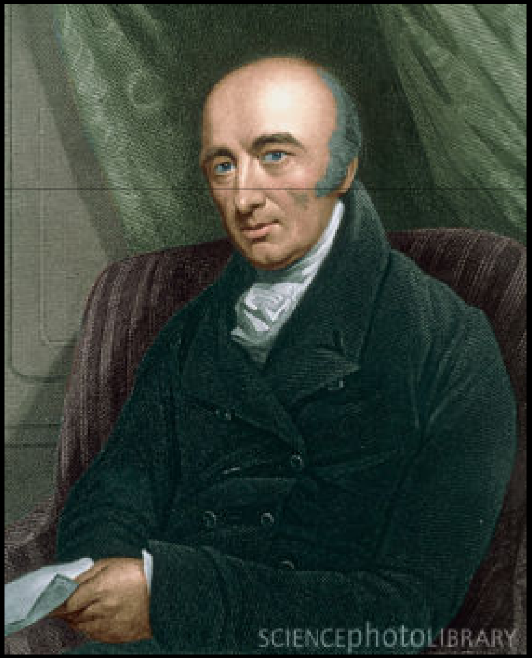
Detected the blackening of AgCl when placed on the side of the violet area of the spectra (UV radiation).

(1801)

The solar Spectrum

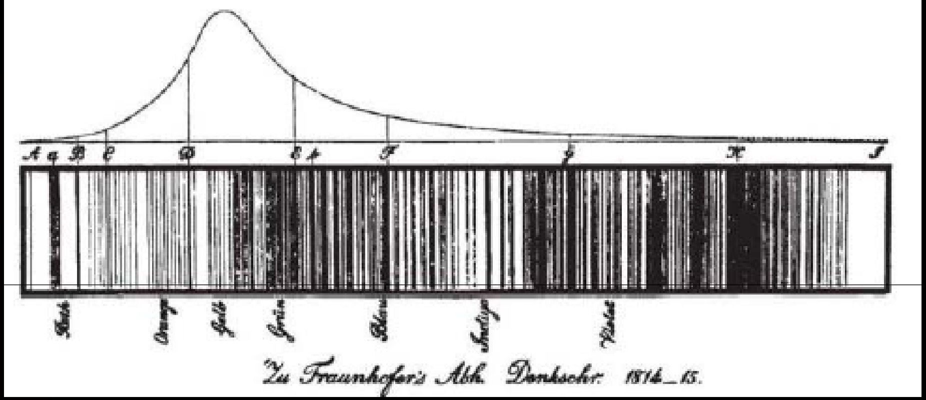
William H. Wollaston

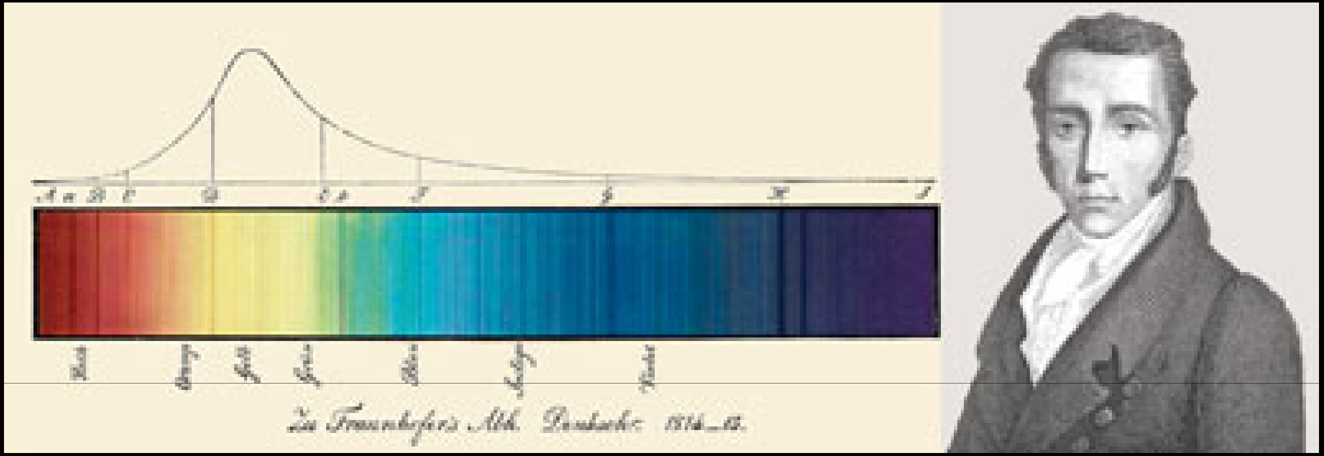
(1766 -1828)



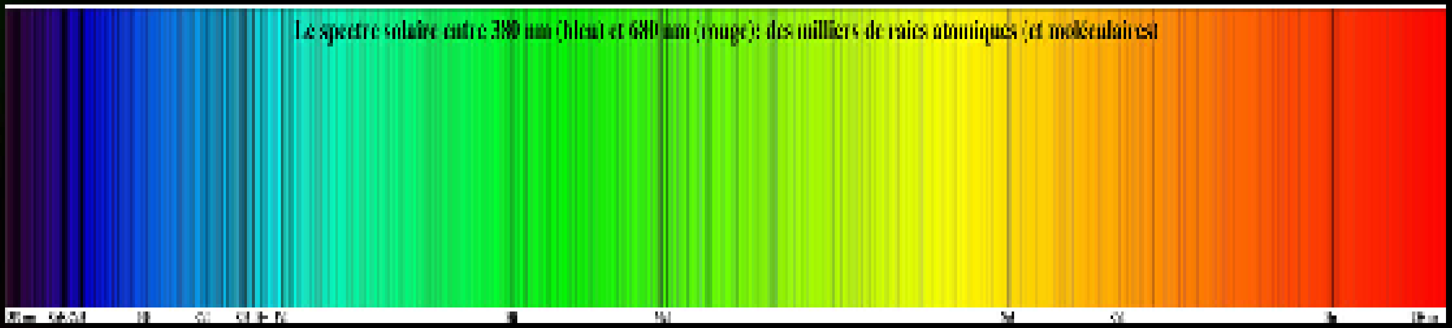
Detected dark lines in solar spectrum (1802)

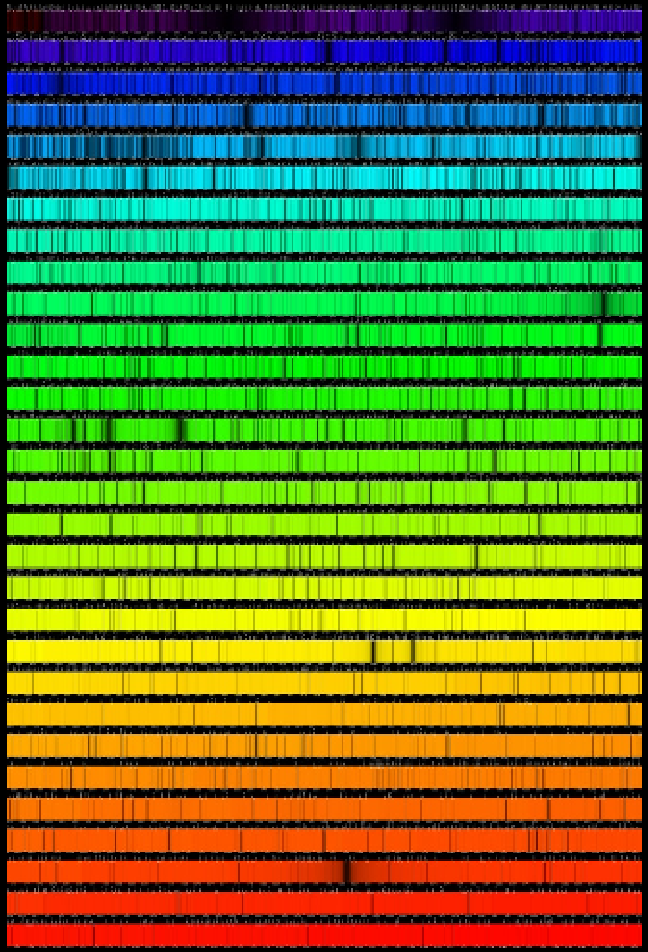
The solar Spectrum





Fraunhofer mesures with precision the position of 574 of the dark lines . (1814)


Le spectre solaire entre 380 nm (bleu) et 680 nm (rouge): des milliers de raies atomiques (et moléculaires)



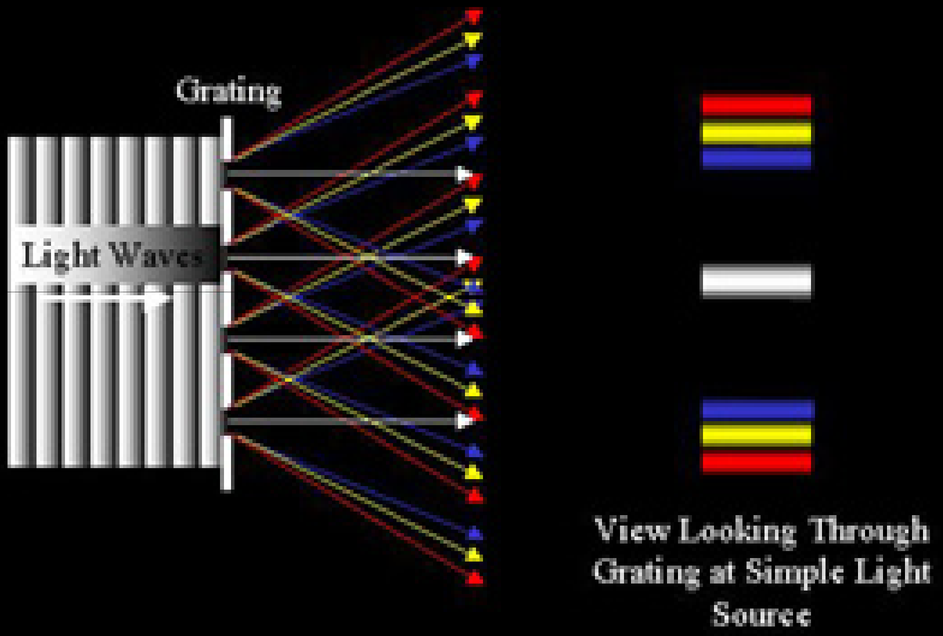
Fraunhofer’s spectroscope

(1787-1826)

Fraunhofer's

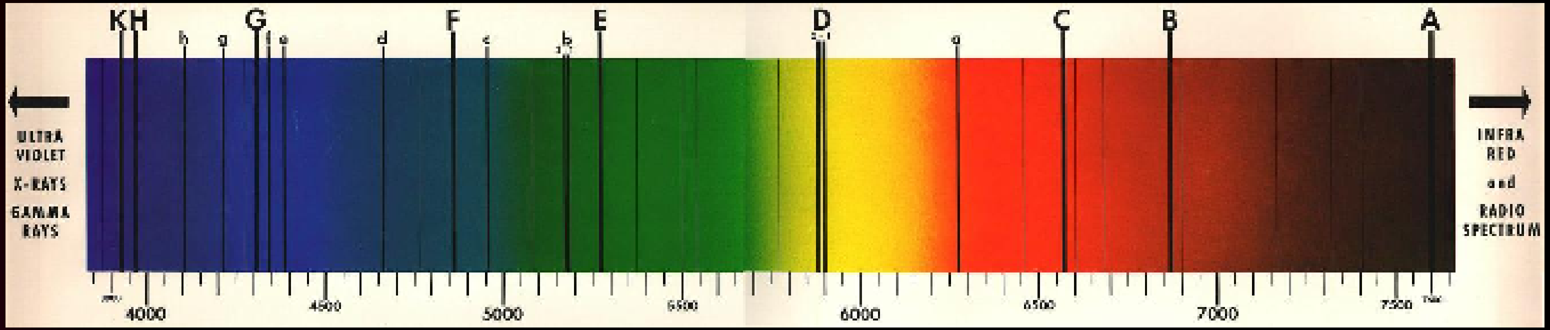
(1821)

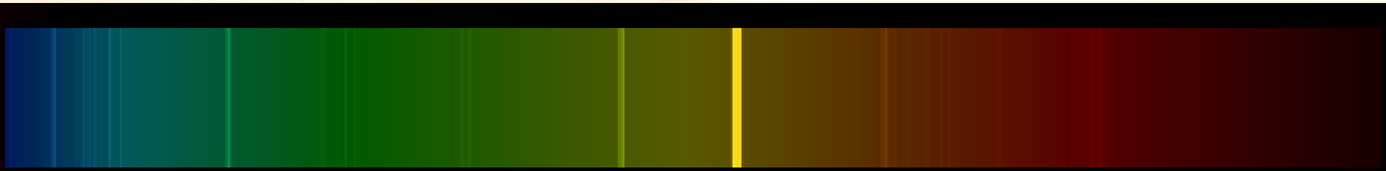
Diffraction Grating



Léon Foucault

(1819-1868)



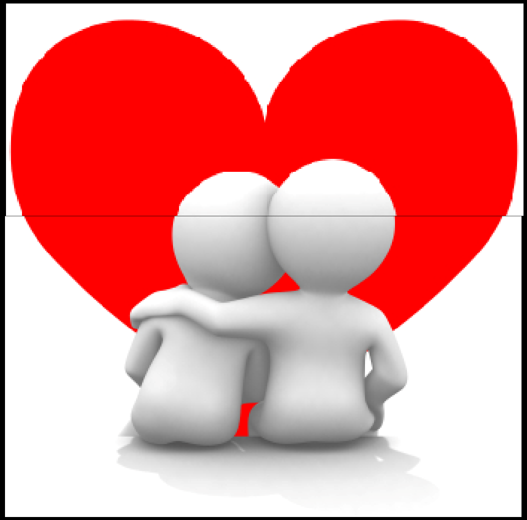


Fraunhofer D lines match Sodium emission spectra. (1849)

Gustav kirchhoff

(1824-1887)

1859 Spectroscopy and Quantum Chemistry start “Dating”



1845 – Circuit Laws

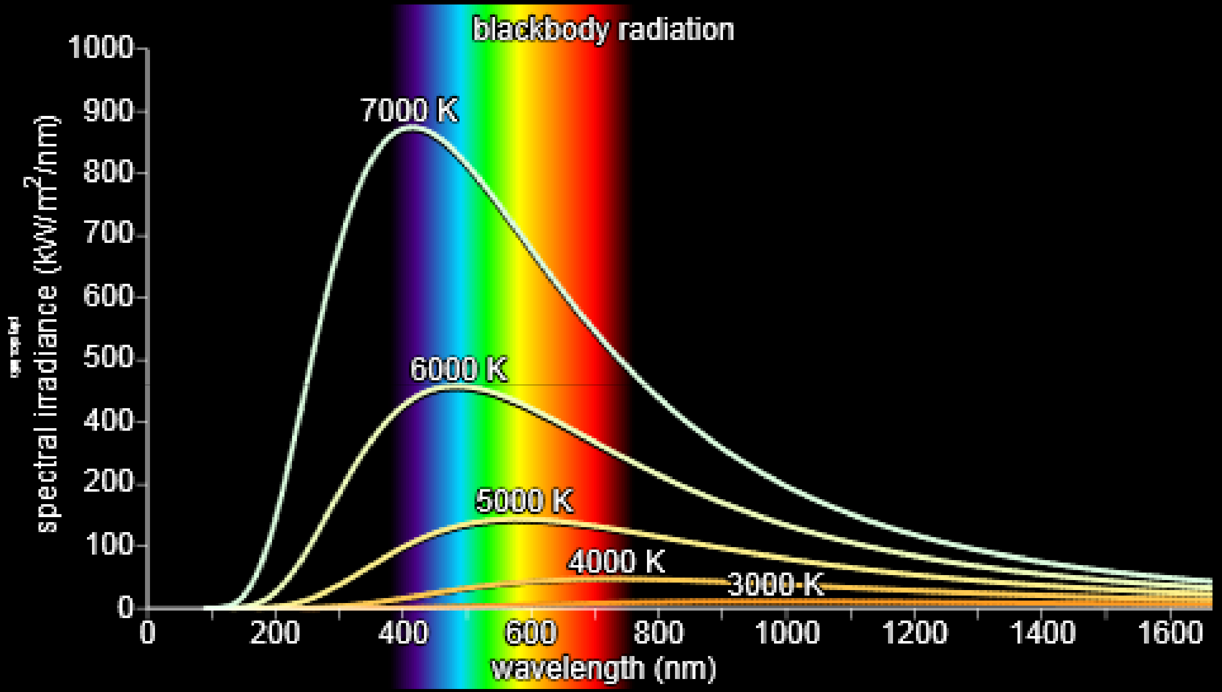
1859 - laws of thermal radiation

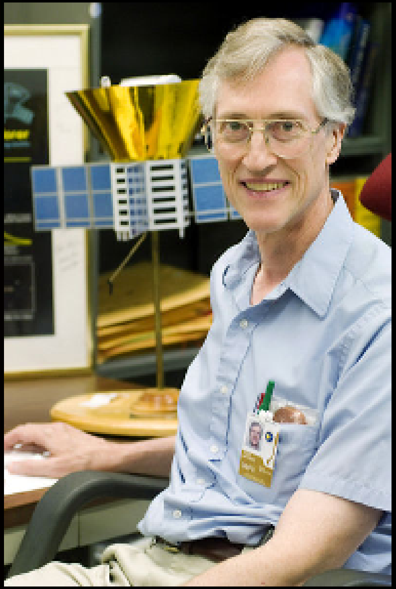
“spectral radiance I was a universal function, one and the same for all black bodies, only of wavelength and temperature”

“For an arbitrary body radiating and emitting thermal radiation, the ratio E / A between the emissive spectral radiance, E, and the dimensionless absorptive ratio, A, is one and the same for all bodies at a given temperature. That ratio E / A is equal to the emissive spectral radiance I of a perfect black body, a universal function only of wavelength and temperature”

Gustav Kirchhoff Challenge

Kirchhoff's challenged his fellow physicists to *devise a full mathematical description of the frequency distribution of heat in the radiation emanating from a perfectly black body*.





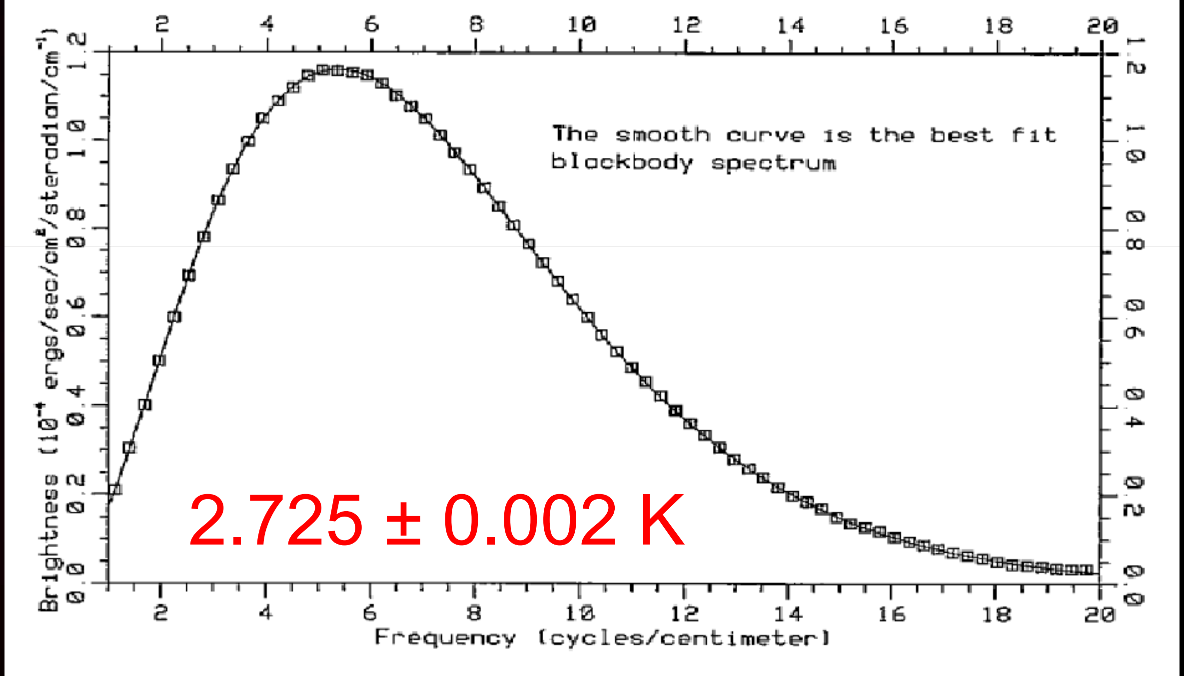
John Mather

Nobel

2006

COBE

George F. Smoot III



2.725 ± 0.002 K

$= aT^4$

Back to 1859


Planck 1859


Planck 1878


Planck 1901

1865 Maxwell

(1831-1879)

Maxwell’s equations

1879 Stefan

(1835-1893)

$$\mathrm{E(T)} = \int_0^\infty f(\lambda, T)\, d\lambda = \mathrm{aT}^4$$

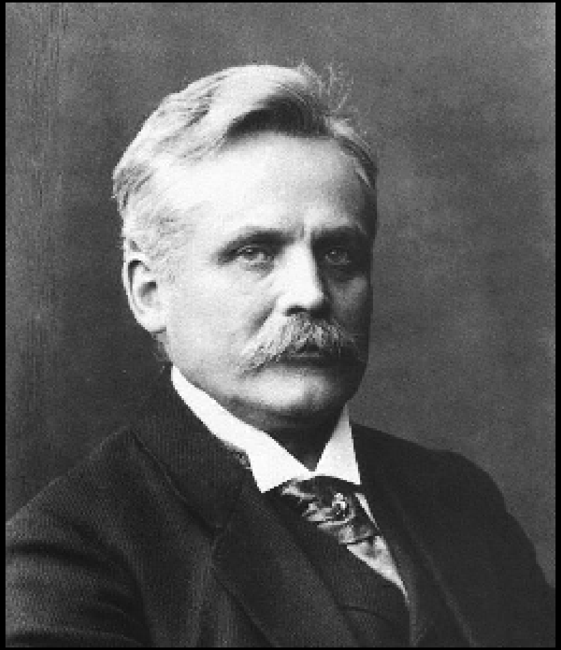
1884 Boltzmann

(1844-1906)

Proved Stefan Law

1893 Wien

(1864-1928)



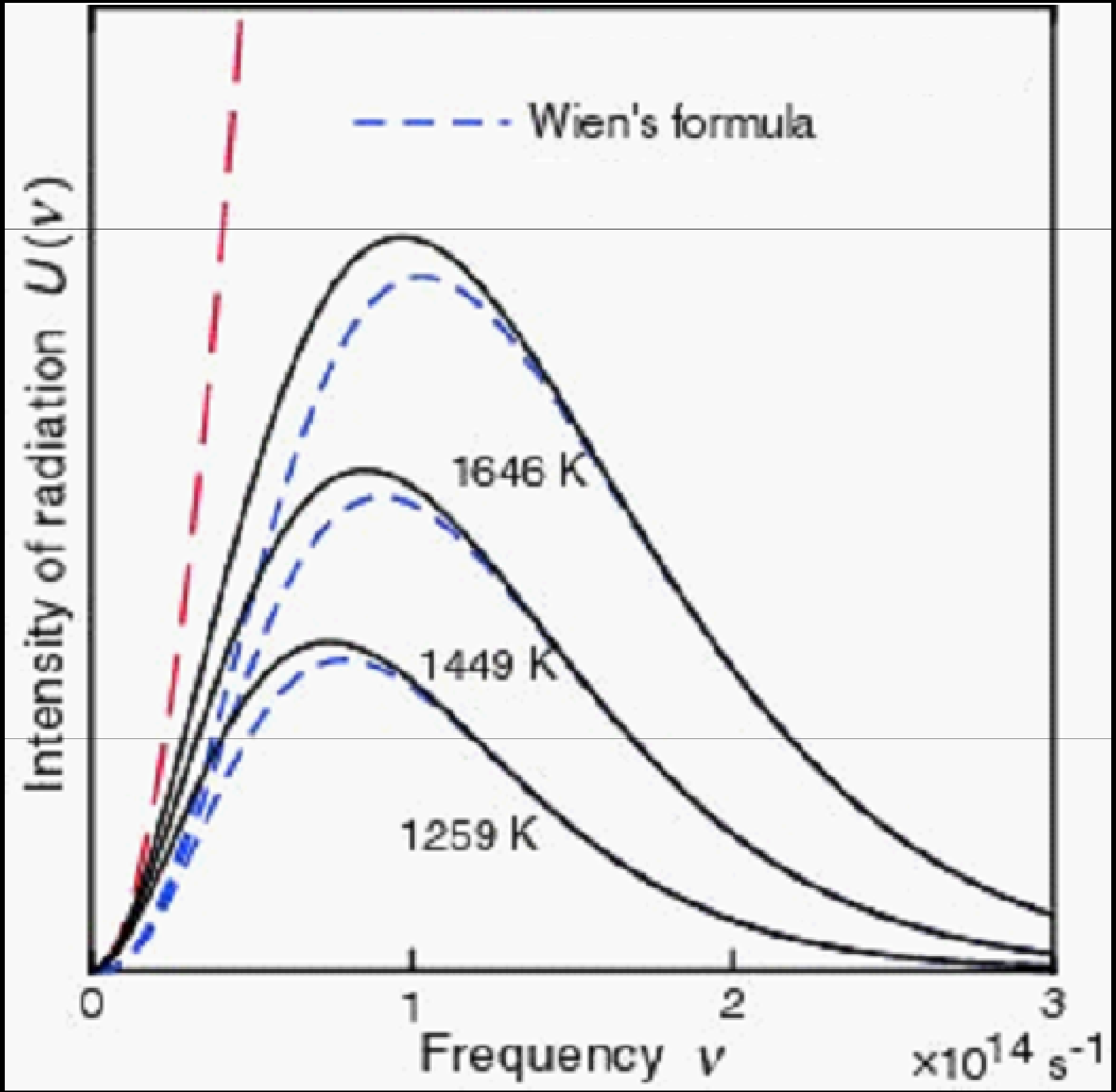
$\lambda_m T$ = constante

Displacement law

(1896)

$$f(\lambda,T) = b\ \nu^3 \exp(-\ a\ \nu/T)$$

Wien’s law fails for low frequency



Planck (1894)

Harmonic oscilator under viscous damping

$$\frac{d^2x}{dt^2} - \frac{2e^2}{3mc^3}\omega^2\frac{dx}{dt} + \omega_o^2\, x = \frac{eE}{m}\cos(\omega t)$$

$$f(\nu,T) = 8\,\pi\,\nu^2/c^3\,U(\nu,T)$$

Comparing Planck and Wien

$$U(\nu,T) = B\,\nu\,\exp(-\,A\,\nu/T)$$

A and B universal constants

The thermodynamic connection

Planck (1899/1900)

2ª Law **$dU = T\,dS$**

$$\frac{1}{T} = \frac{\delta S}{\delta U} \qquad \frac{\delta^2 S}{\delta U^2} = -f(U)$$

$$f(U) = \frac{\alpha}{U} \quad \alpha > 0 \qquad \int \ln(x) = x\ln(x) - x$$

$U(\nu,T) = B\,\nu\,\exp(-A\,\nu/T)$

Lummer, Pringsheim, Rubens and Kurlbaum

Formula fails for high wavelenghts

Rubens: spectral intensity proportional to temperature

Planck (1901)

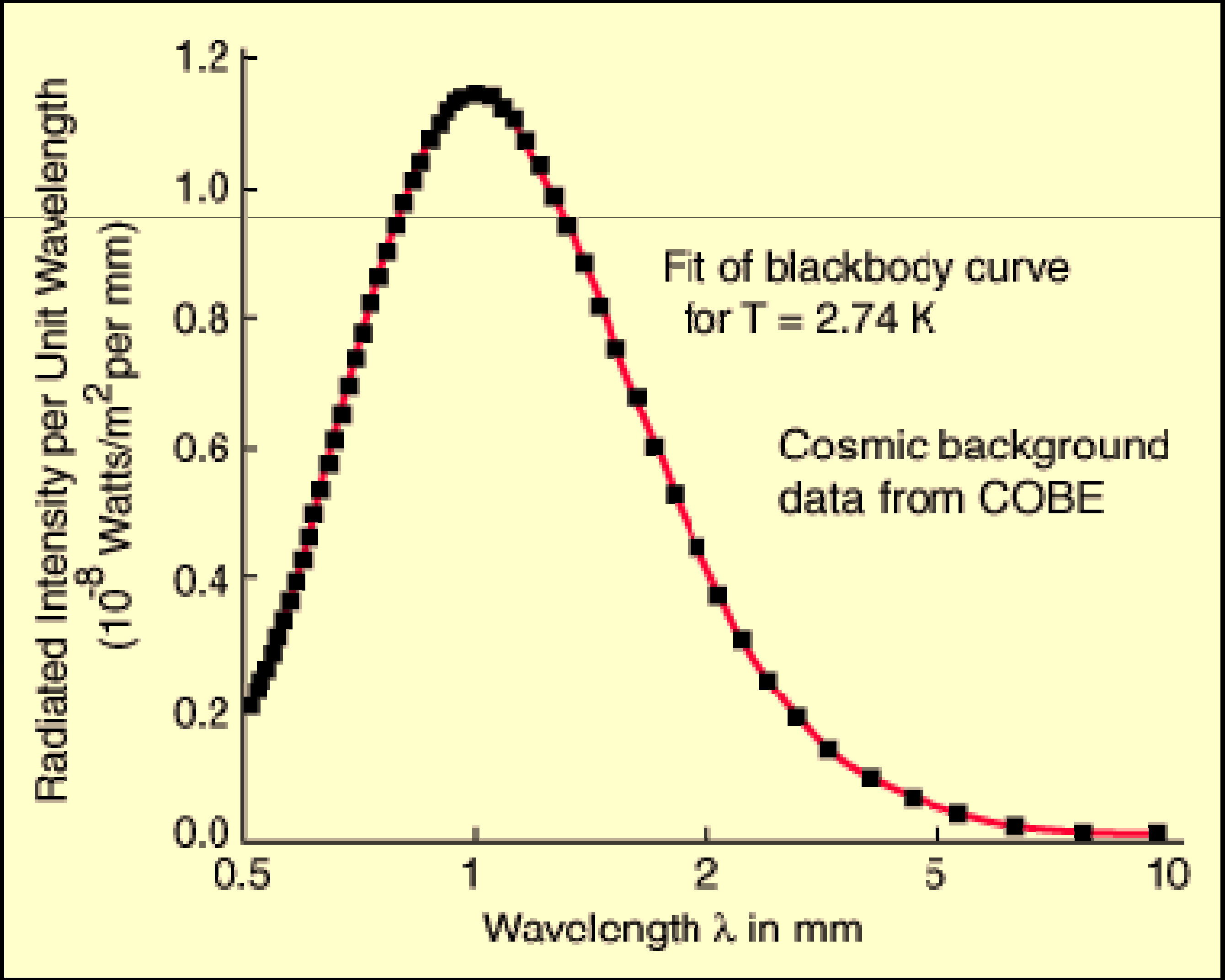
$$\frac{\delta S}{\delta U} = \frac{1}{T} = \frac{\alpha}{U} \qquad f(U) = \frac{\alpha}{U^2}$$

$$f(U) = \frac{\alpha_1}{U(\alpha_2 + U)}$$

$$f(\nu, T) = \frac{8\pi \nu^2}{c^3} \frac{h\nu}{\exp\left(\frac{h\nu}{KT}\right) - 1}$$

h quantum of action

K Boltzmann constant


Radiated Intensity per Unit Wavelength
(10^{-8} Watts/m^2 per mm)
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0.5
1
2
5
10
Wavelength λ in mm
Fit of blackbody curve
for T = 2.74 K
Cosmic background
data from COBE

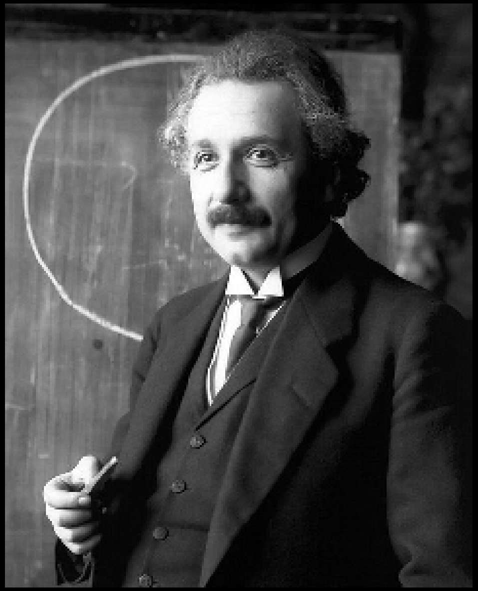
Wien Nobel 1911

Planck Nobel 1918 (given in 1919)

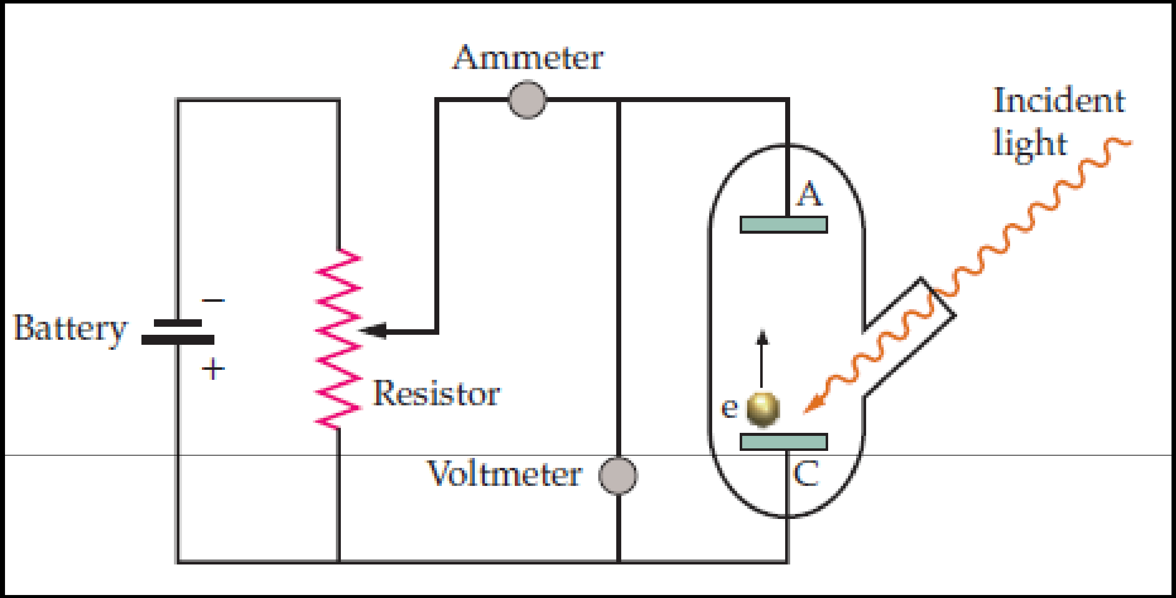
1901 Heisenberg's
Mammy was delivering
a baby.

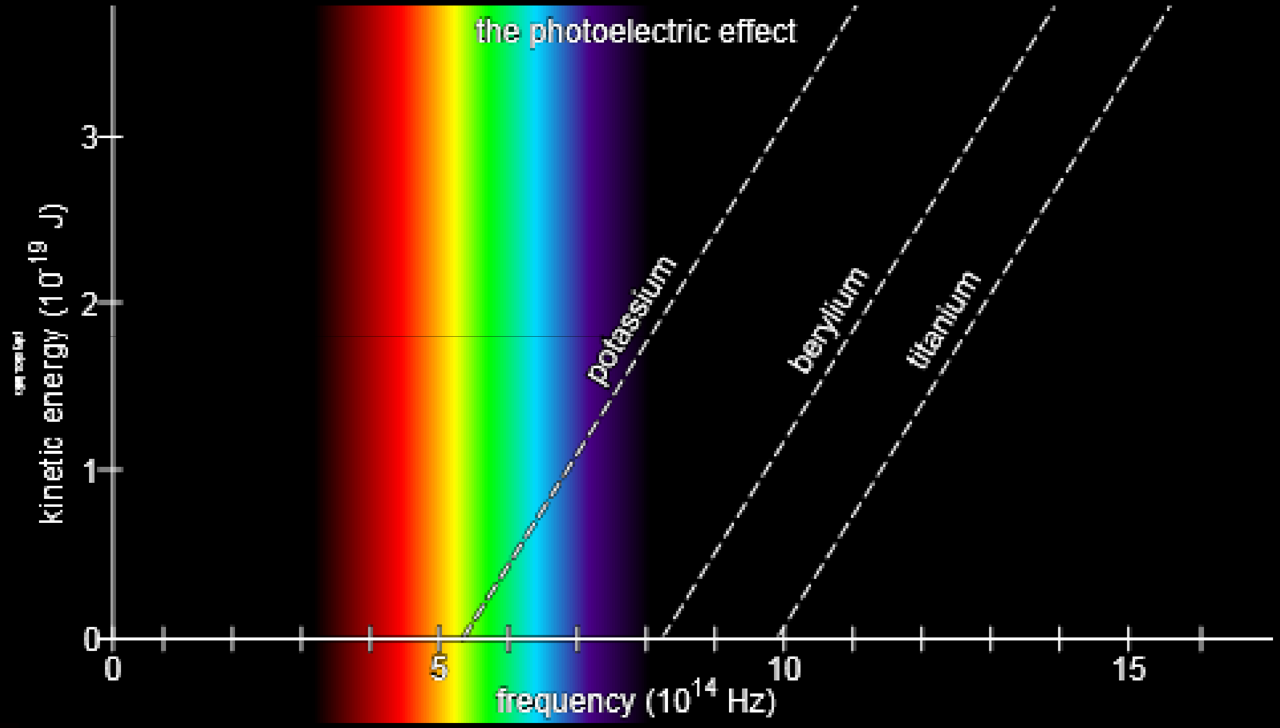
1905 Einstein

(1879-1955)



- Special relativity
- Matter/energy relationship
- Brownian Motion
- Photoelectric effect


Ammeter
Incident light
A
Battery
−
+
Resistor
e
Voltmeter
C


the photoelectric effect
kinetic energy (10^{-19} J)
0
1
2
3
potassium
beryllium
titanium
0
5
10
15
frequency (10^{14} Hz)

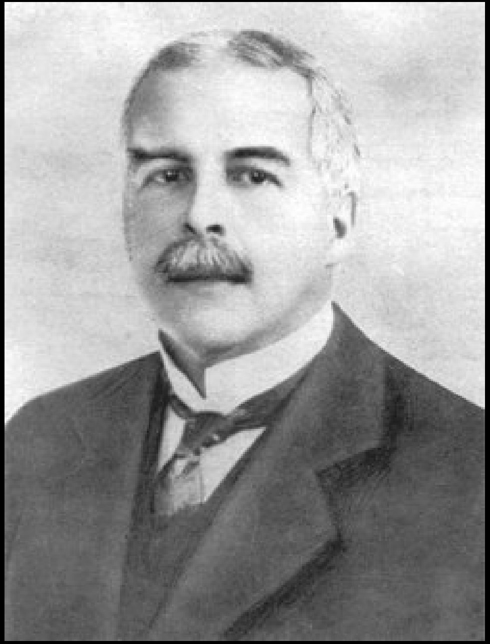
“Quantum of light” $h\nu$

$h\nu = h\nu_o + E_{kinetics}$ ν_o threshold frequency

Einstein Nobel 1921

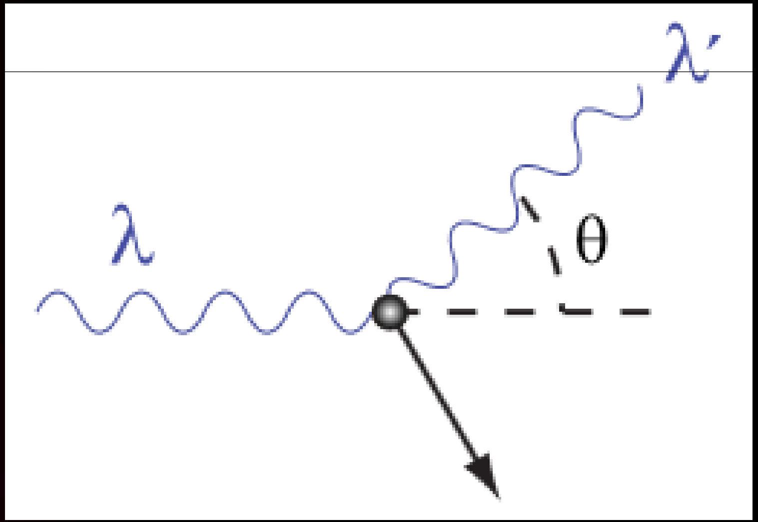
"I therefore take the liberty of proposing for this hypothetical new atom, which is not light but plays an essential part in every process of radiation, the name *photon.*"

-Gilbert N. Lewis, 1926



Einstein 1917 Quantum theory of radiation

$p = h\nu / c$ Photons carry momentum



$$\lambda' - \lambda = \frac{h}{m_e c}(1 - \cos\theta)$$

Compton 1923
(1892-1962)

Compton Nobel 1927

1924 de Broglie

(1892-1987)

Wave Particle duality

Nobel 1929

Einstein 1917

$p = h \nu / c = h / \lambda$	Photons carry momentum
$\lambda = h / p$	Particles have wave properties

1927 Davisson-Germer

Davisson Nobel 1937

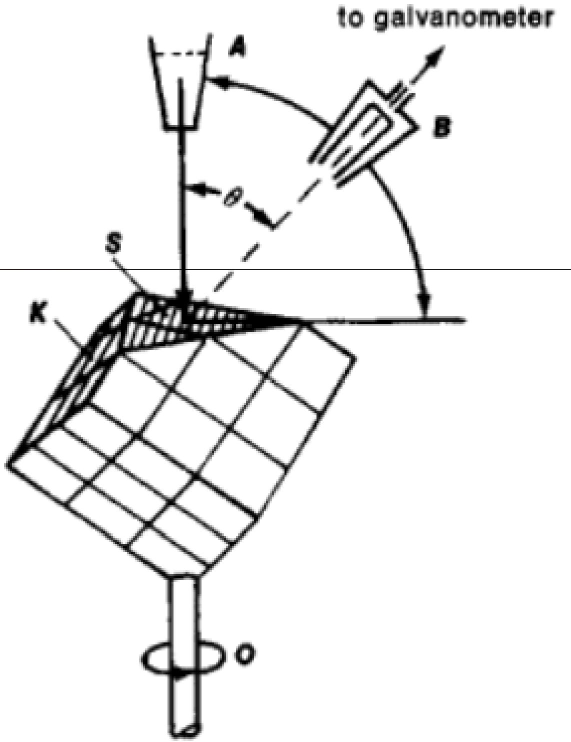


Figure 2. Diagram of the Davisson-Germer experiment. (*K*) monocrystal of nickel, (*A*) electron source, (*B*) electron detector, (*θ*) angle of deflection of the electron beams. The electron beam is perpendicularly incident to the polished crystal plane *S*. When the crystal is rotated around the axis *O*, a galvanometer attached to detector *B* shows periodic maxima.

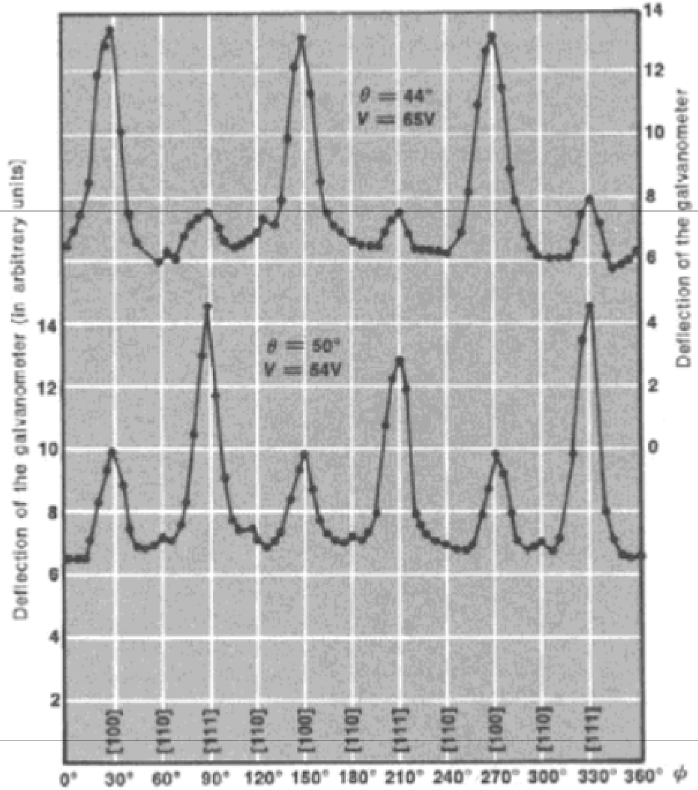


Figure 3. Diffraction maxima in the Davisson-Germer experiment on electron diffraction at various angles of rotation of a crystal, φ, for two values of the angle of deflection of the electrons, *θ*, and two accelerating voltages *V*. The maxima correspond to reflection from the various crystal planes, whose indexes are indicated in brackets.

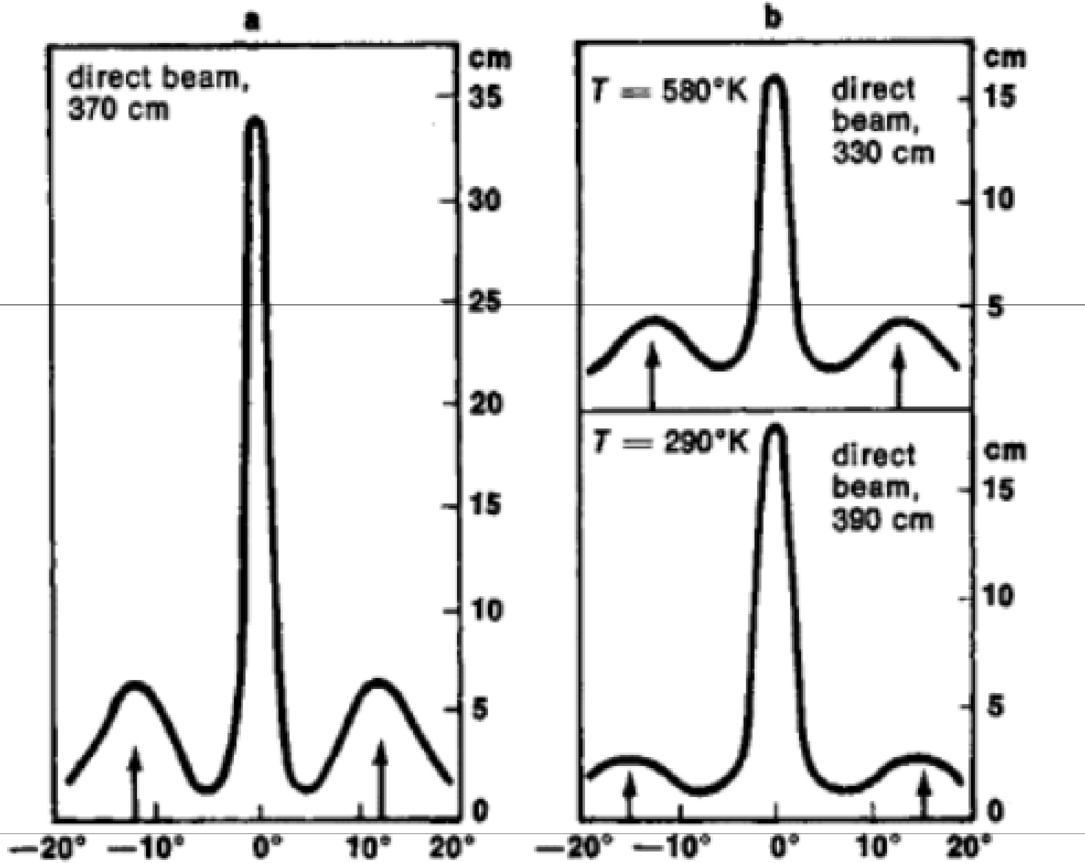


Figure 5. Lithium fluoride crystal diffraction of helium atoms (a) and hydrogen molecules, at two values of absolute temperature, *T* (b). The angle of diffraction θ is plotted along the abscissa; the intensity of the diffracted beams (in cm of deflection of the needle of the measuring instrument), along the ordinate. In addition to a peak at $\theta = 0°$ (from the mirror reflection of the initial beam), two side peaks can be observed. At $T = 580°K$ the side peaks are somewhat closer to the central peak than at $T = 290°K$. This corresponds to the decline in wavelength λ as the temperature rises; see formula (7).

1925 Heisenberg

(1901 - 1976)

Matrix Mechanics

Nobel 1932

1926 Schrödinger

(1887- 1961)

Wave Mechanics

Nobel 1933

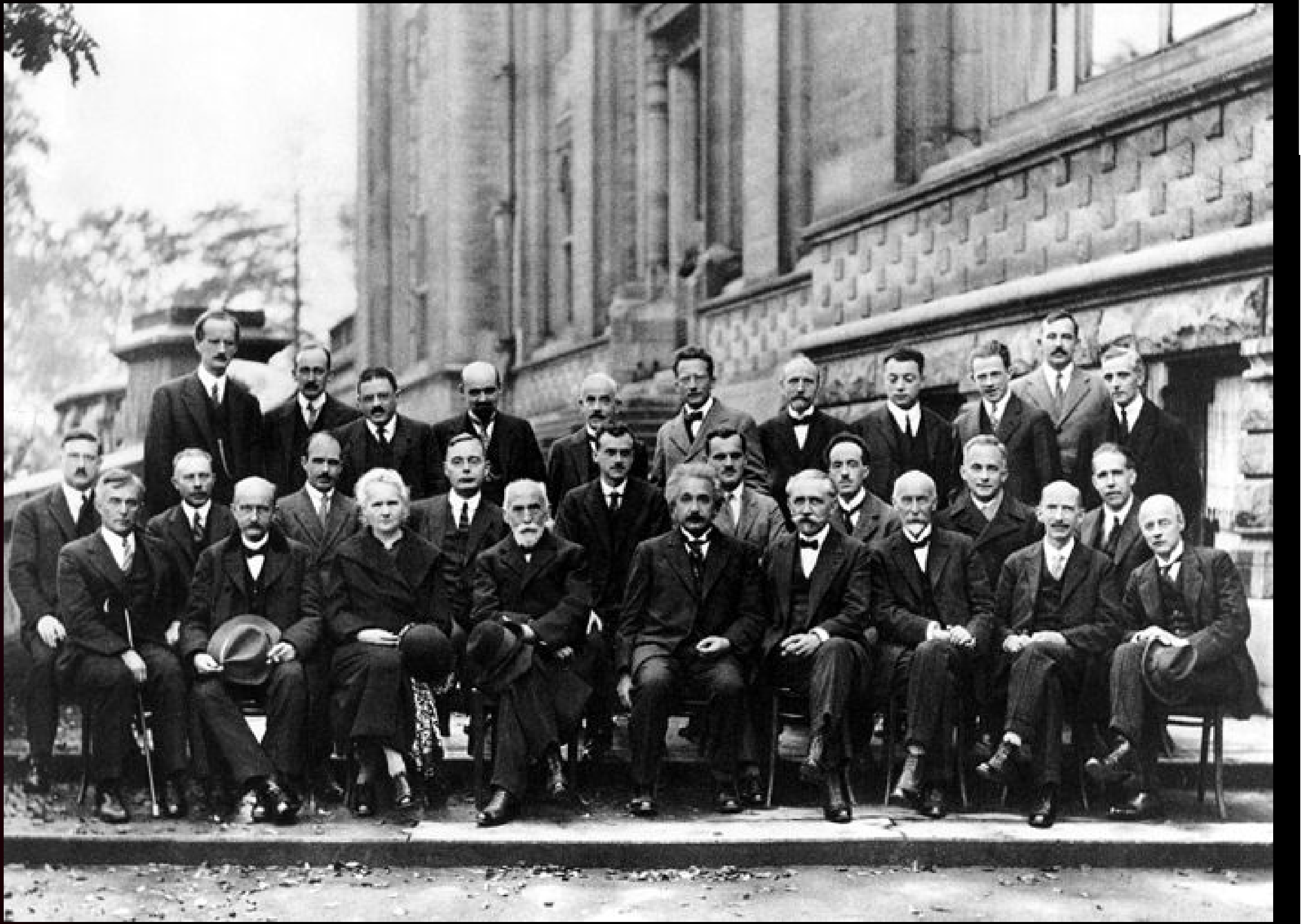
1932 Von Neumann

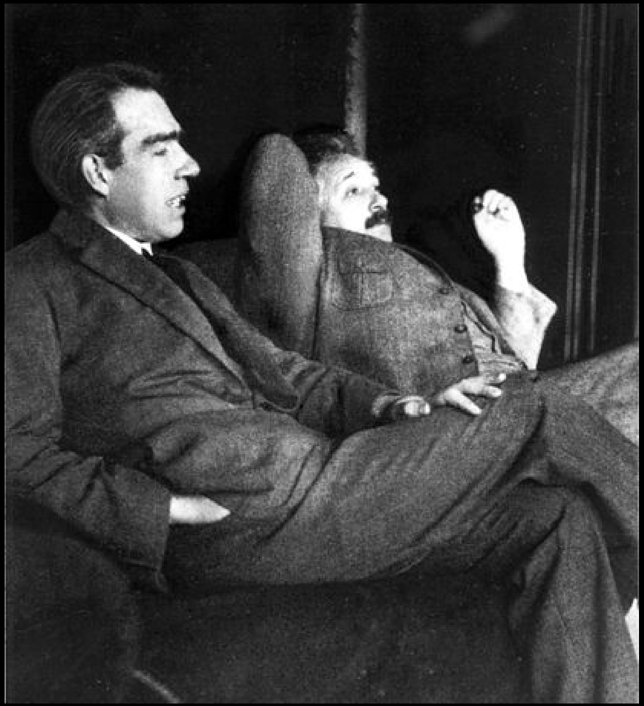
(1903- 1957)

Operators Algebra

1927 Fifth Solvay Conference

Electrons and Photons





Niels Bohr with Albert Einstein at Paul Ehrenfest's home in Leiden (December 1925)

“God does not play dice with the universe.”
Einstein

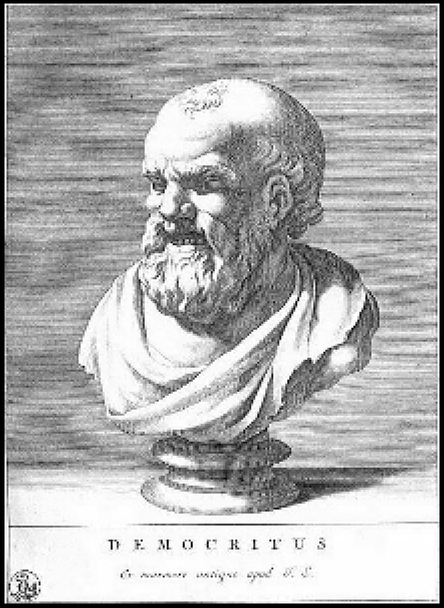
“Who are you to tell God what to do?”
Bohr

“God not only plays dice, but sometimes throws them where they cannot be seen.”
Modern answer by Hawking

Meanwhile in atomic theory

450 BC –

Democritus



All matter is made up of atoms. Atoms are eternal and invisible and so small that they can’t be divided, and they entirely fill up the space they’re in.

1808 Dalton

New System of Chemical Philosophy

Elements are made of extremely small particles called atoms.

Atoms of a given element are identical in size, mass, and other properties; atoms of different elements differ in size, mass, and other properties.

Atoms cannot be subdivided, created, or destroyed.
Atoms of different elements combine in simple whole-number ratios to form chemical compounds.

In chemical reactions, atoms are combined, separated, or rearranged

1897 Thomson

Electron

(Nobel 1906)

1913 Moseley

Proton

1932 Chadwick

Neutron

(Nobel 1935)

1904 plum pudding model

By Thomson

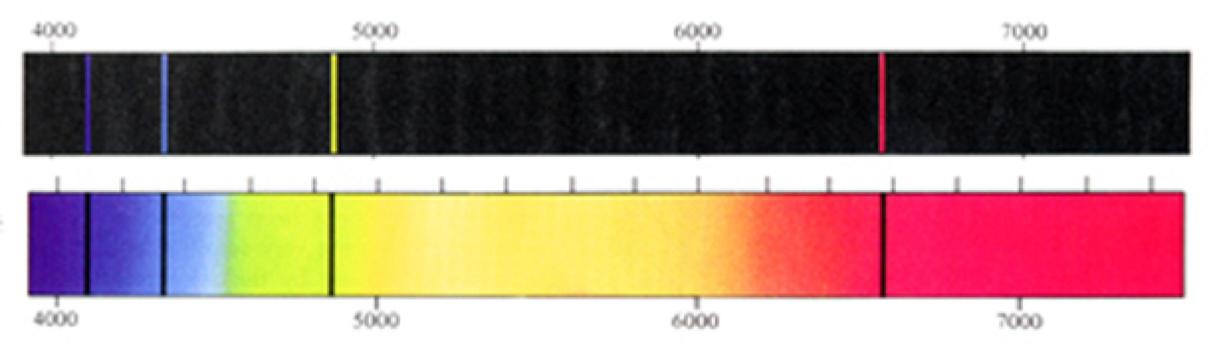
1904 Saturnian (gravitational)

By Nagaoka

1911 Rutherford (electrostatic)

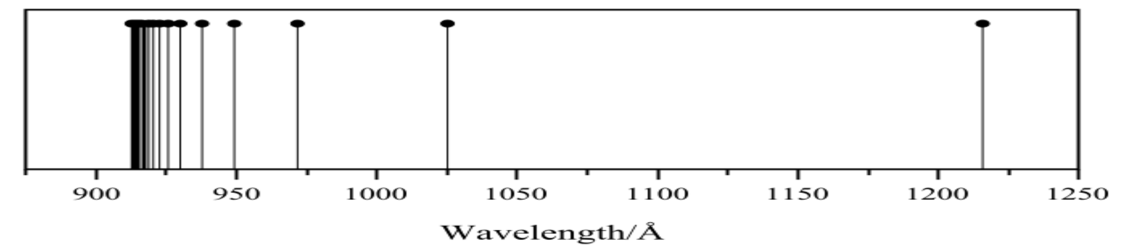
(Nobel 1908 - Chemistry)

rotating around the nucleus the electron should radiate electromagnetic waves ending up falling on it.



1885 Balmer Series (visible)

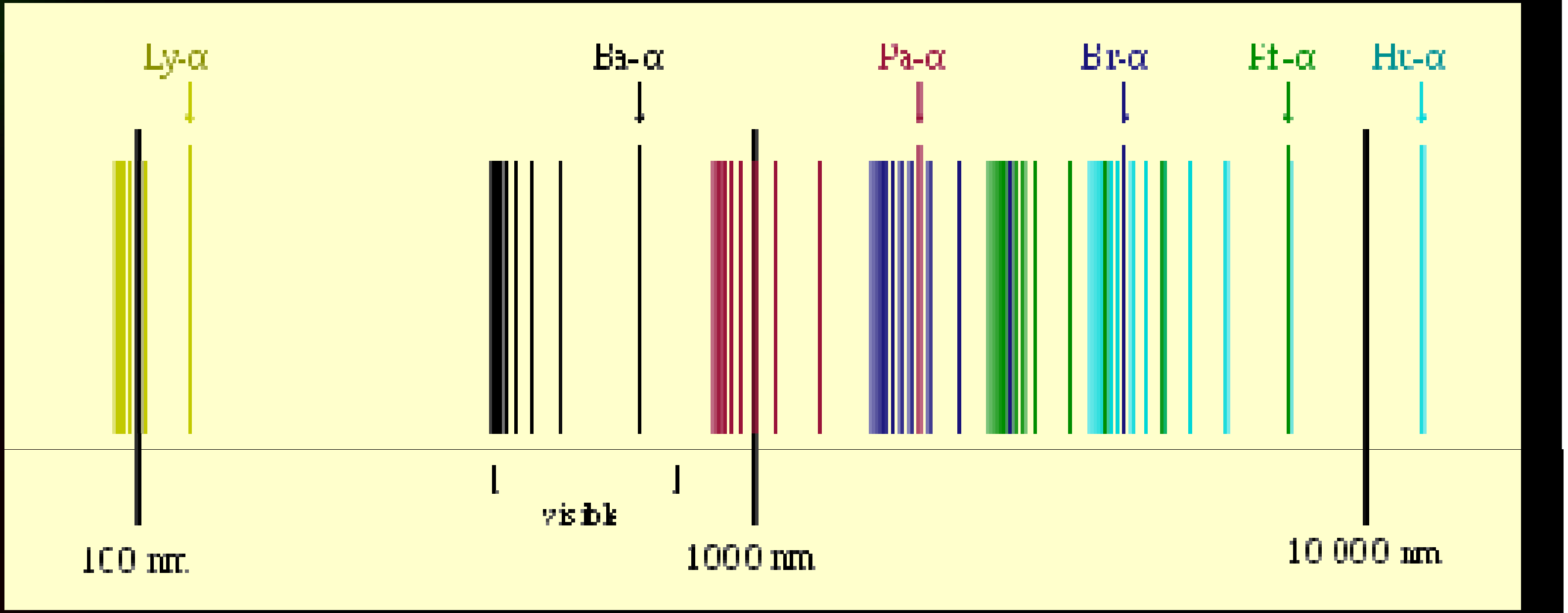
1906-1914 Lyman (UV)



1908 Paschen (IV)

1922 Brackett (IV)

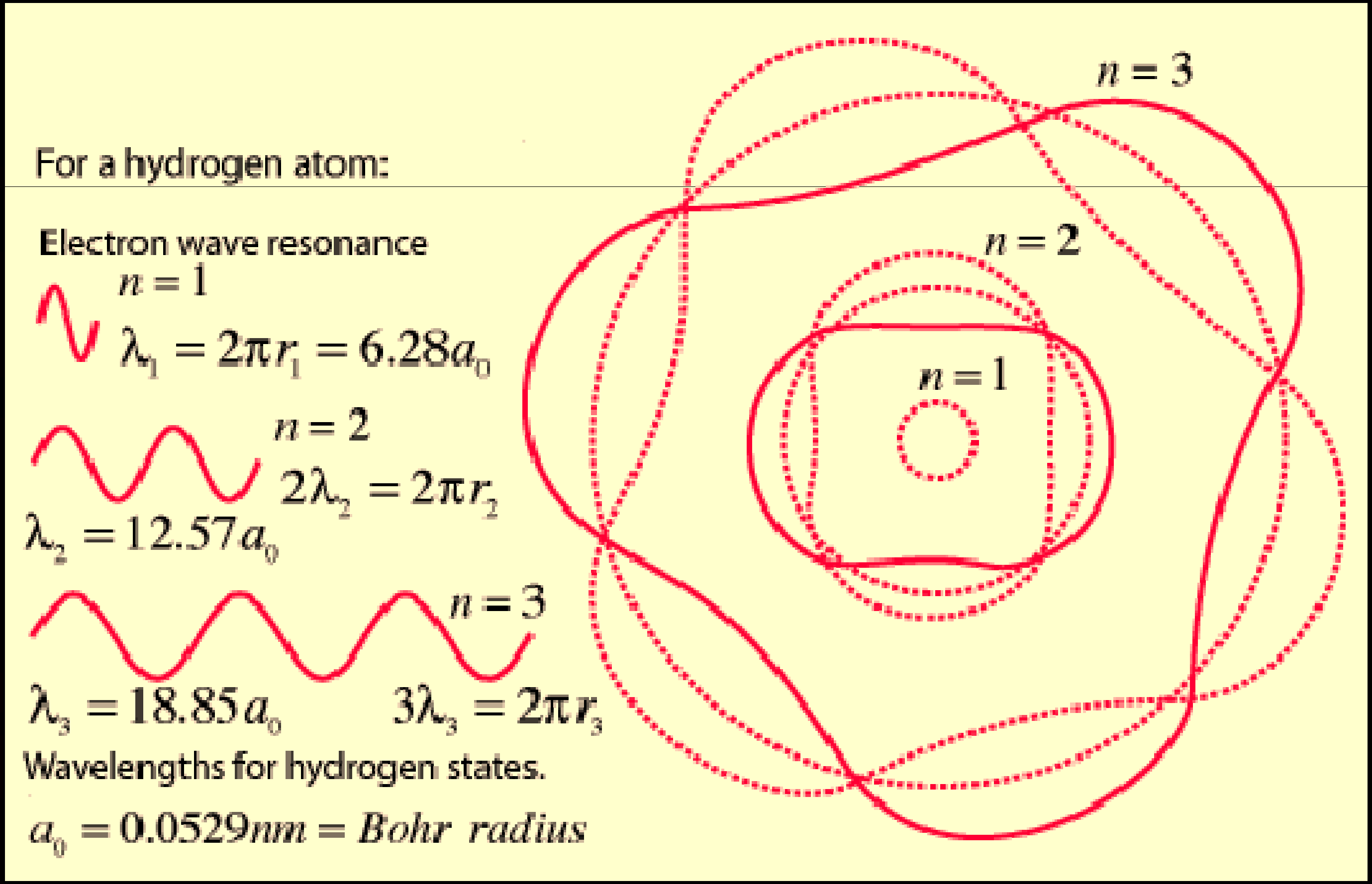
1924 Pfund (IV)



1913 Bohr (Nobel 1922)

Rutherford model limited to orbits where angular momentum (*mvr*) is a multiple of $h/2\pi$

An electron gains or loses energy by jumping between orbits absorbing or emiting light according to $\Delta E = h v$



For a hydrogen atom:

Electron wave resonance

$n = 1$

$\lambda_1 = 2\pi r_1 = 6.28 a_0$

$n = 2$

$2\lambda_2 = 2\pi r_2$

$\lambda_2 = 12.57 a_0$

$n = 3$

$\lambda_3 = 18.85 a_0$

$3\lambda_3 = 2\pi r_3$

Wavelengths for hydrogen states.

$a_0 = 0.0529 nm = Bohr\ \ radius$