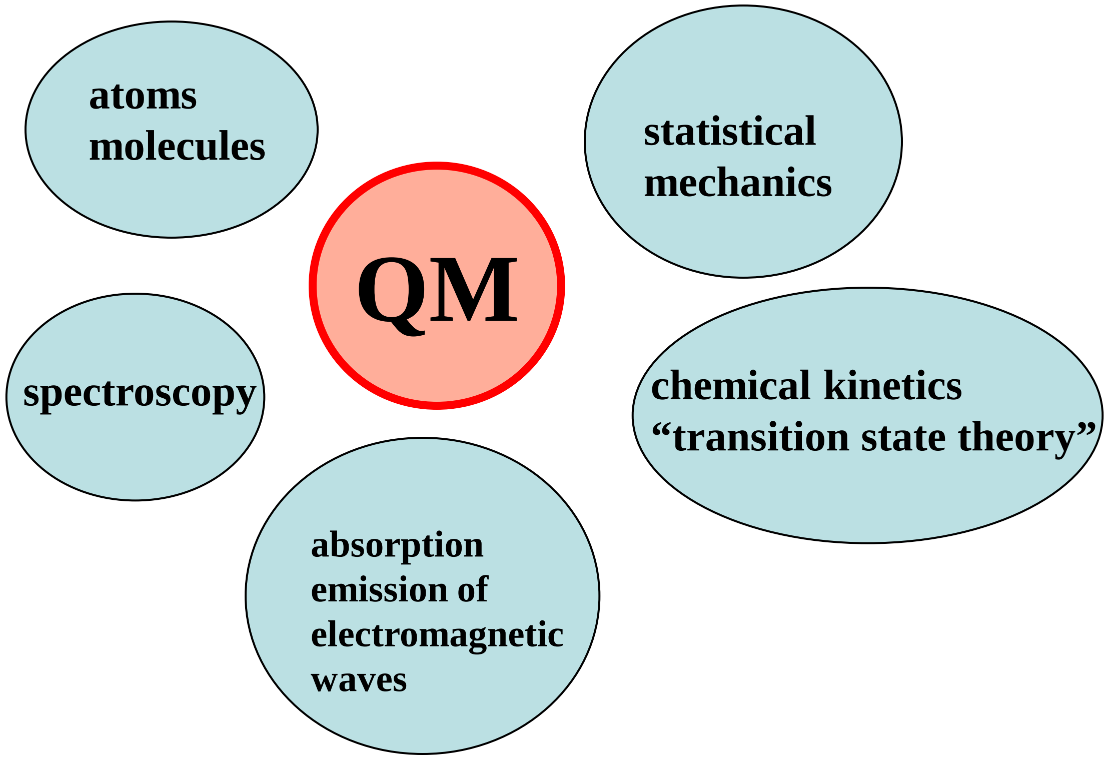
CHEM465-665
Quantum mechanics

Final summary

Basics

All of this is quantum mechanics (QM)



Quantum mechanics deals with phenomena and objects of nanoscopic size. In principle, quantum mechanics provides a mathematical description of close to everything.

Thermodynamics

Relationship between macroscopic properties of a system.

Kinetics

Chemical kinetics, is the study of rates of chemical processes.

Quantum mechanics

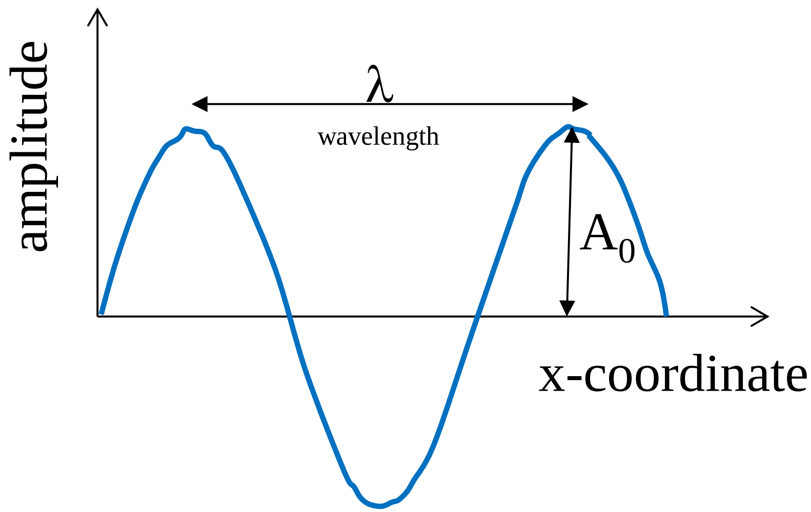
Quantum mechanics deals with phenomena and objects of nanoscopic size. In principle, quantum mechanics provides a mathematical description of close to everything.

Schrödinger's equation is a wave equation

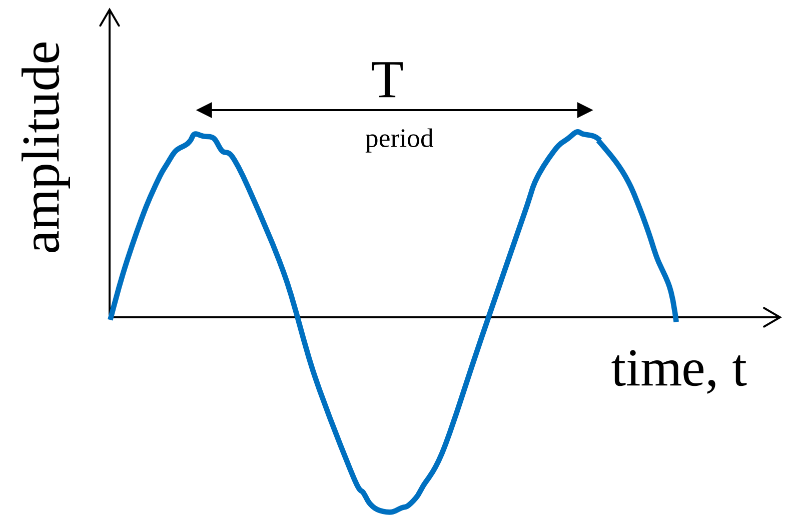
Waves are …

Waves are a disturbance of matter or space that propagates in time and space.

Coordinates



Time



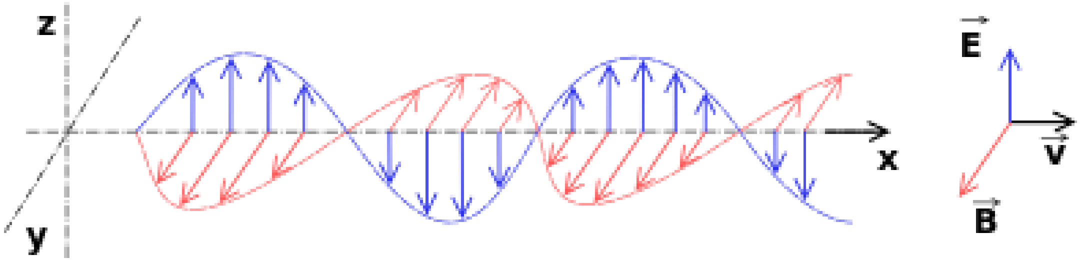
$$\text{Amplitude(coordinates, time)} = A_0\cos(\omega t + kx + \phi)$$

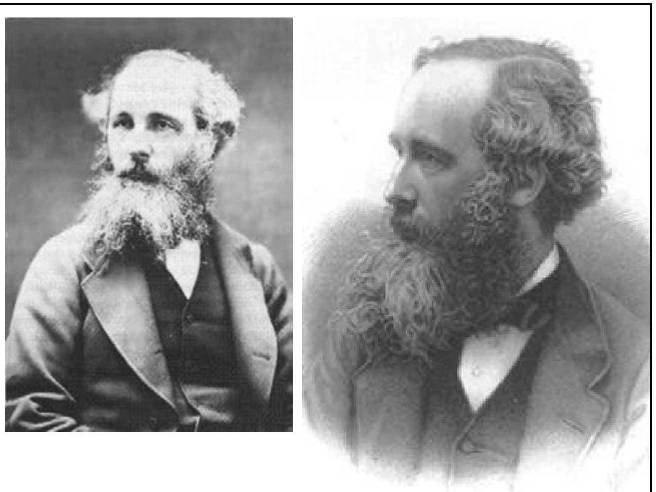
$$\lambda \nu = c$$

A_0	amplitude	ω	angular frequency
x	coordinates	k	wave number
ϕ	phase lag	t	time

Light = electromagnetic wave

1D figure
Snapshot time = t_0





Maxwell

$$\vec{E}(\vec{r},t) = \vec{E}_0 \cos(\vec{k}\vec{r} - \omega t + \phi)$$

$$\vec{B}(\vec{r},t) = \vec{B}_0 \cos(\vec{k}\vec{r} - \omega t + \phi)$$

$\vec{E}$	electric field vector	$\vec{E}_0$	amplitude of electric field vector	$\vec{k}$	wave vector
$\vec{r}$	coordinates	ω	angular frequency	t	time
ϕ	phase lag	$\vec{B}$	magnetic field vector	$\vec{B}_0$	amplitude of magnetic field vector

Electromagnetic spectrum

infrared
light

ultraviolet
light

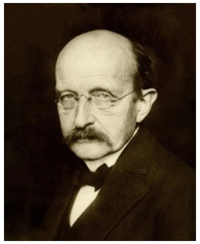
700 nm 400 nm

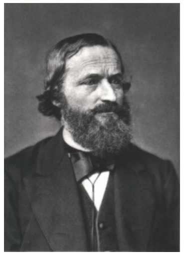
radiofrequency microwaves infrared optical ultraviolet X-rays

rotations vibrations electronic

Historic experiments

Historic experiments


Planck


Kirchhoff

Blackbody radiation

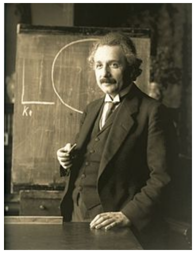

Einstein

Photo effect


Davisson & Germer


de Broglie

Electron scattering

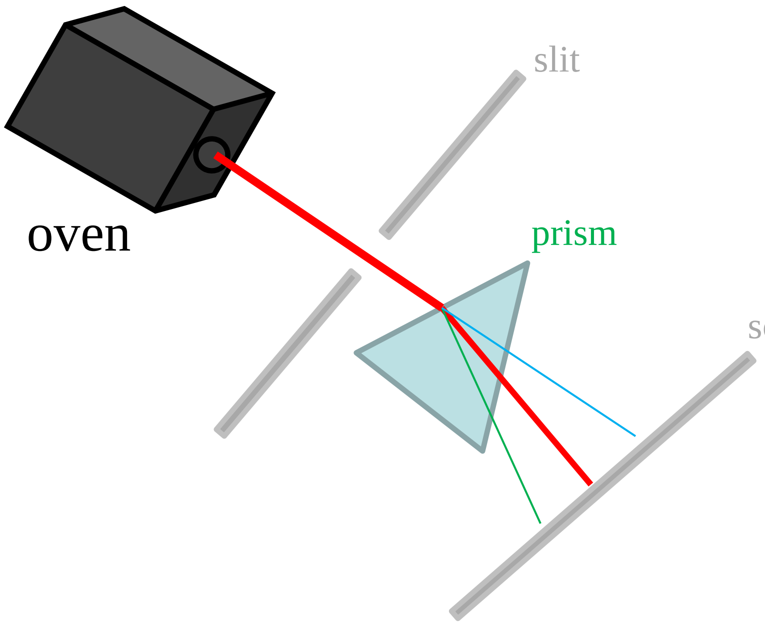

Ångström

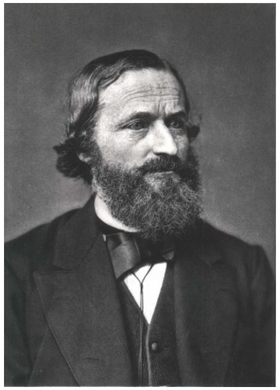

Balmer


Bohr

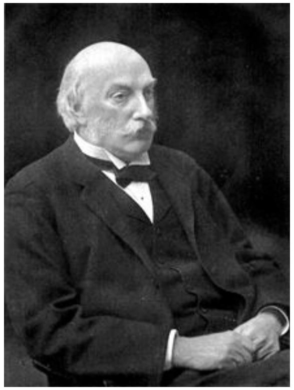
Hydrogen early models & experiments

Historic experiment – Blackbody radiation





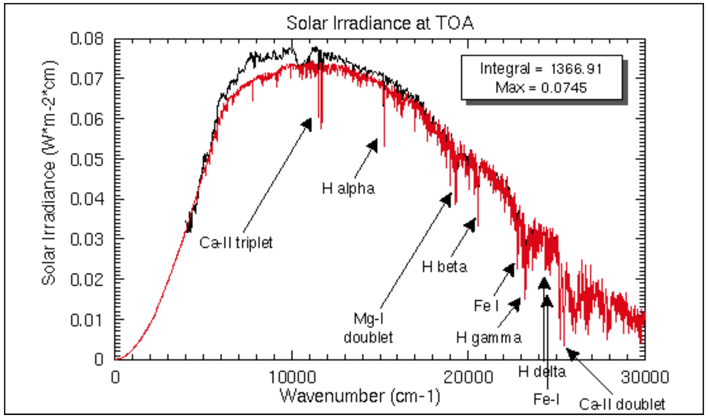
Gustav Kirchhoff



Lord Rayleigh, John William Strutt

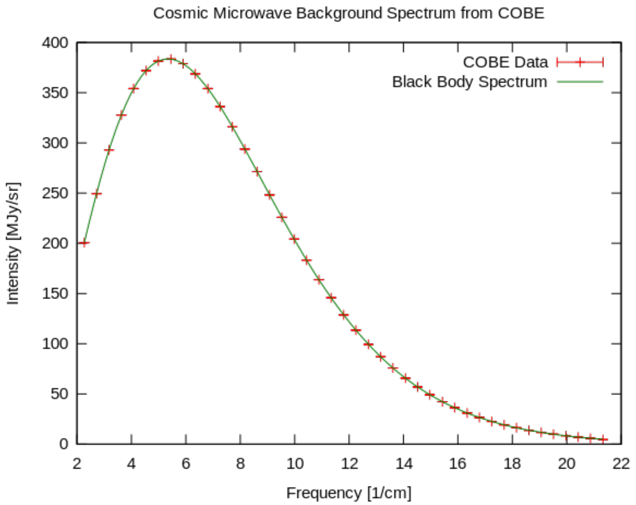
James Hopwood Jeans

Historic experiment – Blackbody radiation experimental result



electromagnetic spectrum of our sun

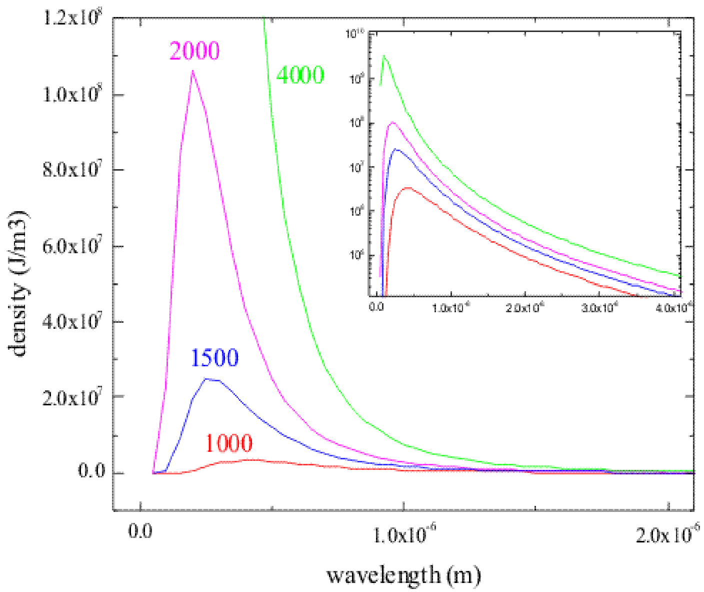
$T = 6000$ K



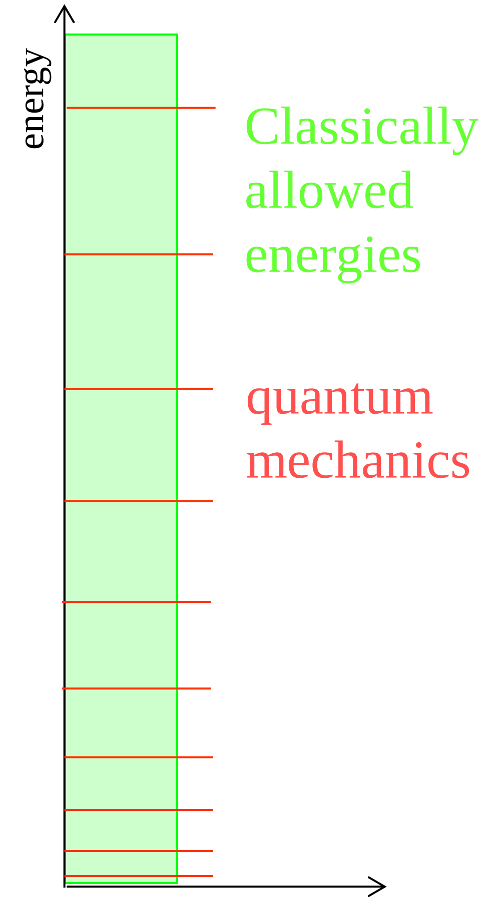
Cosmic background radiation

$T = (2.735 \pm 0.06)$ K

Historic experiment – Blackbody radiation - modeling



$$u(\nu)d\nu = \frac{8\pi h V}{c^3}\left[\frac{\nu^3}{e^{h\nu/kT}-1}\right]d\nu$$



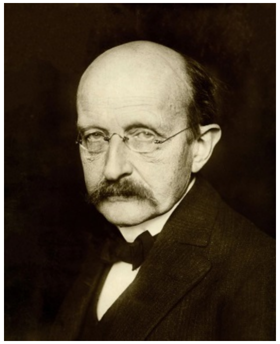
Planck found for a black body:

$$E = nh\nu;\ n = 0,1,2,3,\ldots$$

Take home message:
Quantization of energy.

Why is the blackbody radiation equation from Planck of fundamental importance?

$$u(\nu)d\nu = \frac{8\pi h V}{c^3}\left[\frac{\nu^3}{e^{h\nu/kT}-1}\right]d\nu$$

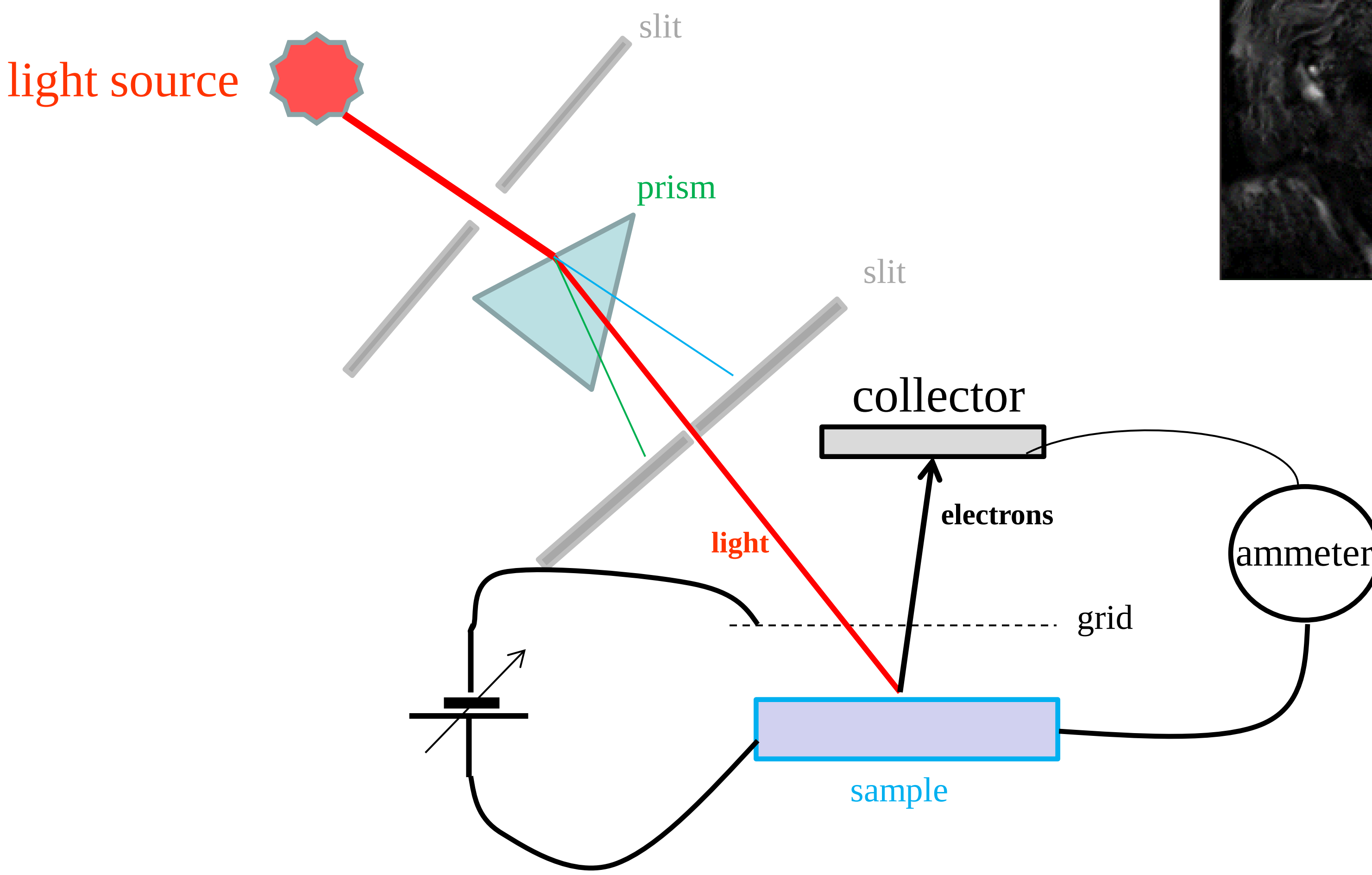


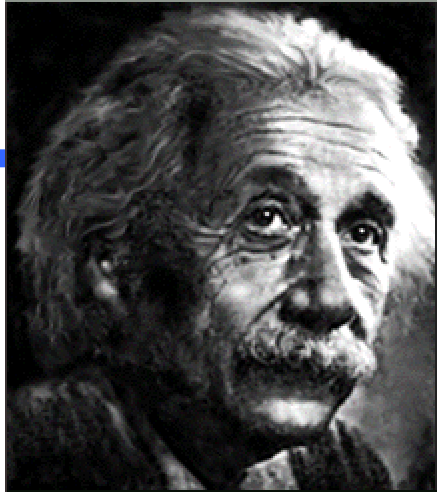
→ It provided a proof of the quantization idea of Planck

→ Very diverse observations can be explained/fitted with the backbody radiation equation such as

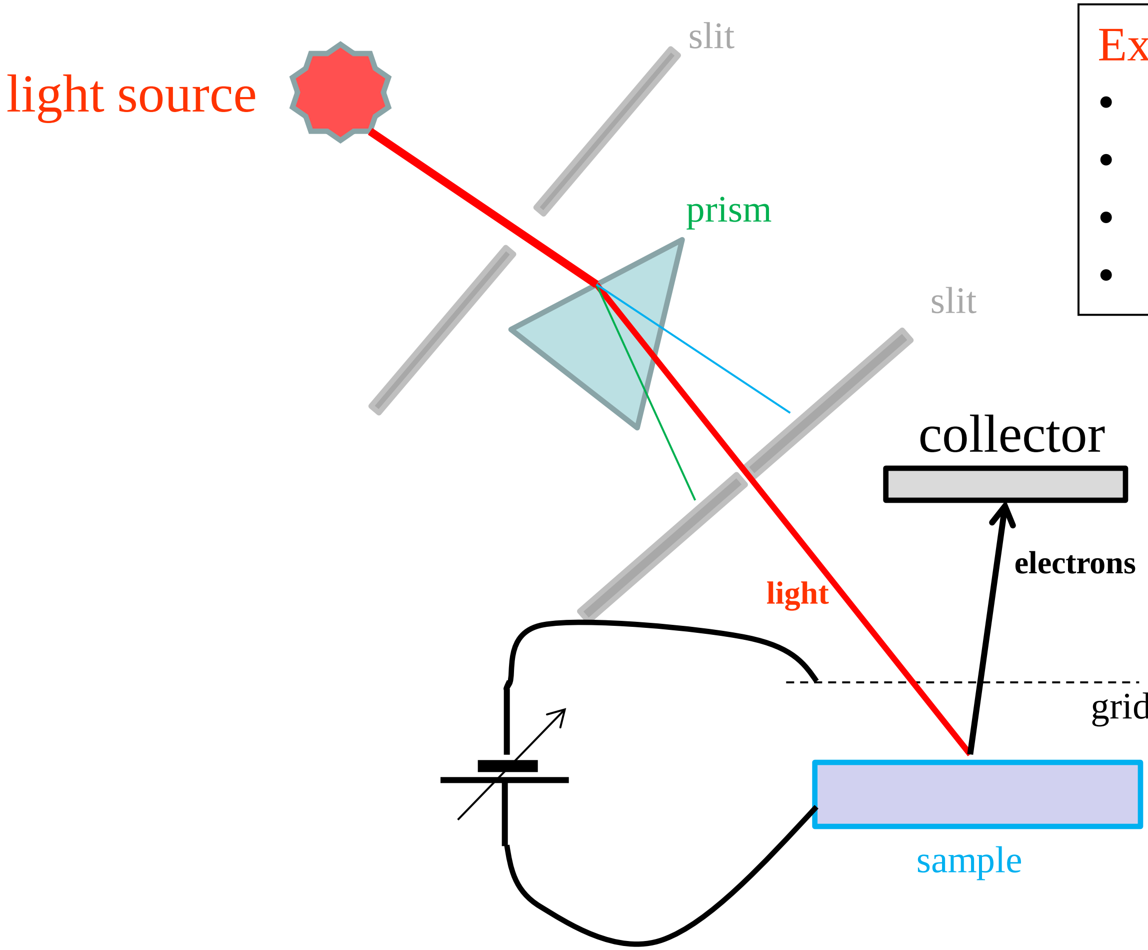
- the emission spectrum of our sun with a surface temperature of 6000 K or so
- the IR emission of earth (300 K)
- the cosmic background radiation (2.7 K) which has implications for cosmological models
- the emission of your department's oven stove
- etc.

Photoeffect experiment





Photoelectric effect -- results



Experimental results:

- threshold frequency ν_0
- ν_0 depends on substance
- light intensity ~ # of photoelectrons
- E_{kin} independent of light intensity

Quantization of light

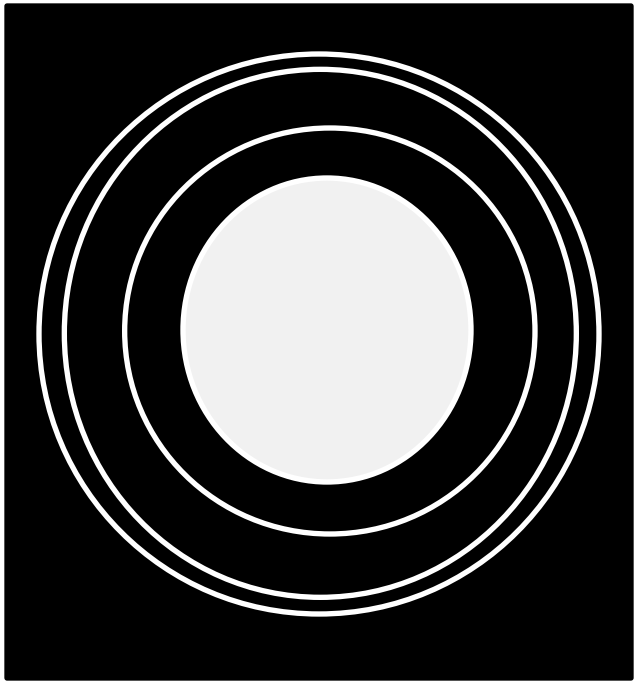
$$E_{photon} = h\nu$$

particle – wave duality

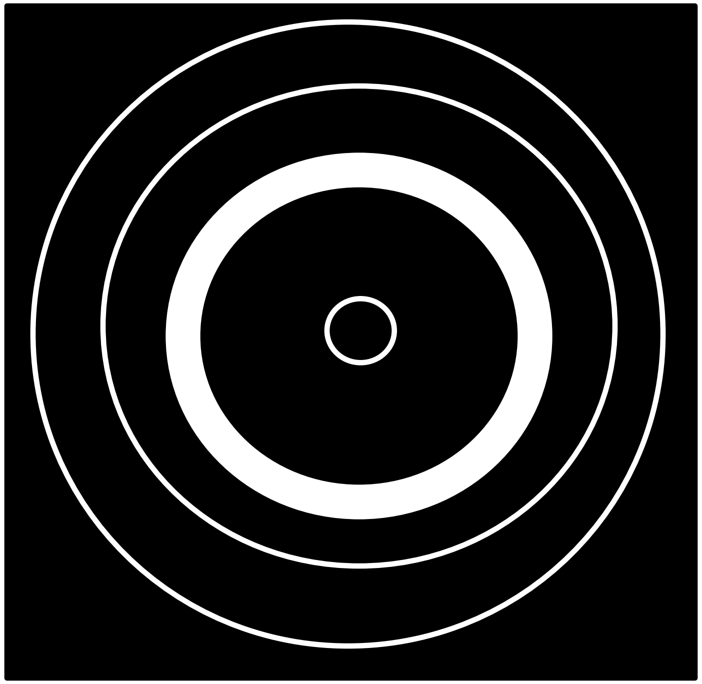
Photoelectric effect

$$E_{kin} = h\nu - \phi$$

Electrons as waves – de Broglie‘s idea



X-ray scattering



electron scattering

De Broglie

$$\lambda_{matter} = \frac{h}{p}$$

Sample: aluminum foil

Schematic representation of the historical experiment

Davisson & Germer

Experimental verification by Davisson and Germer 1927: electron scattering

http://en.wikipedia.org/wiki/Davisson%E2%80%93Germer_experiment

Particle – wave duality

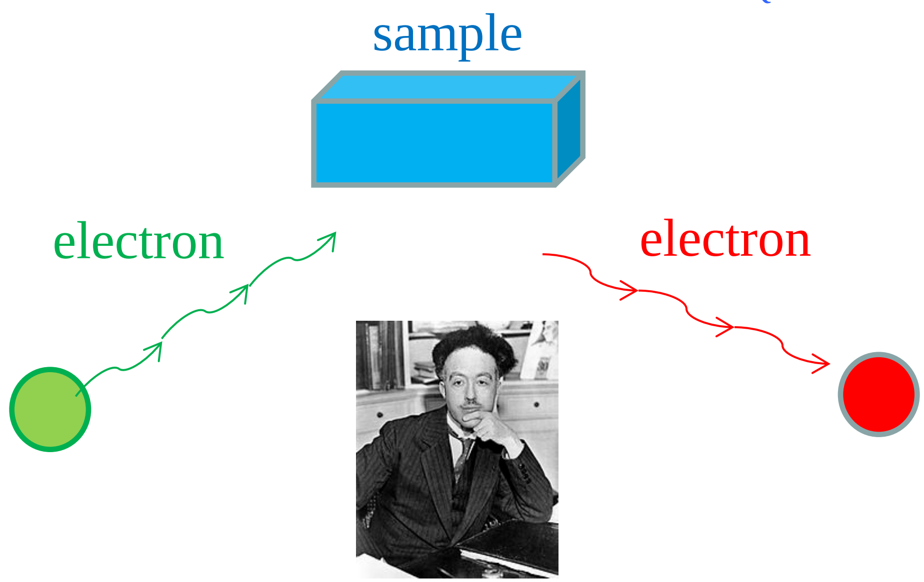
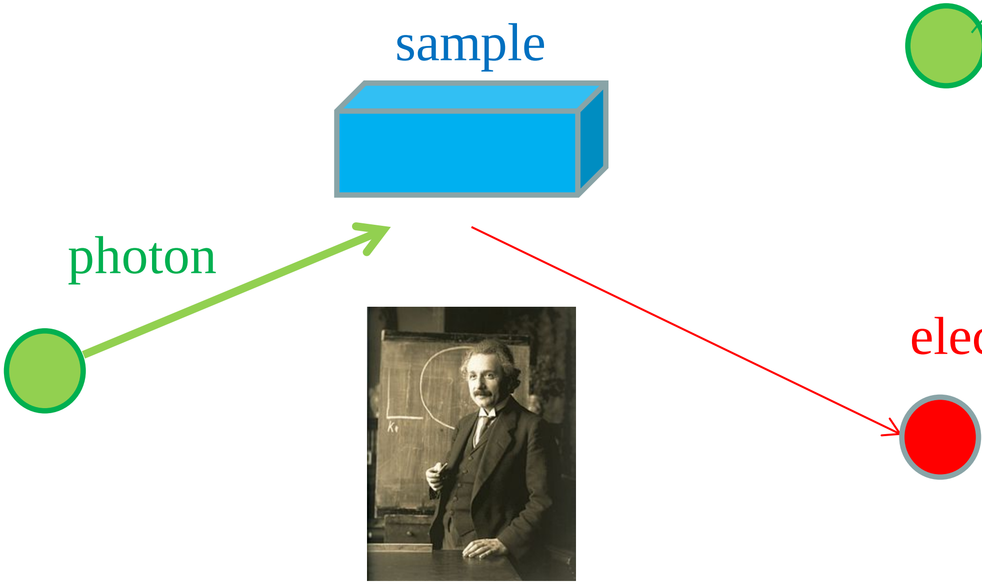


Photo-effect
Einstein, Lenard



Electron scattering
de Broglie
Davisson and Germer

Particle – wave duality

$$E_{photon} = h\nu$$

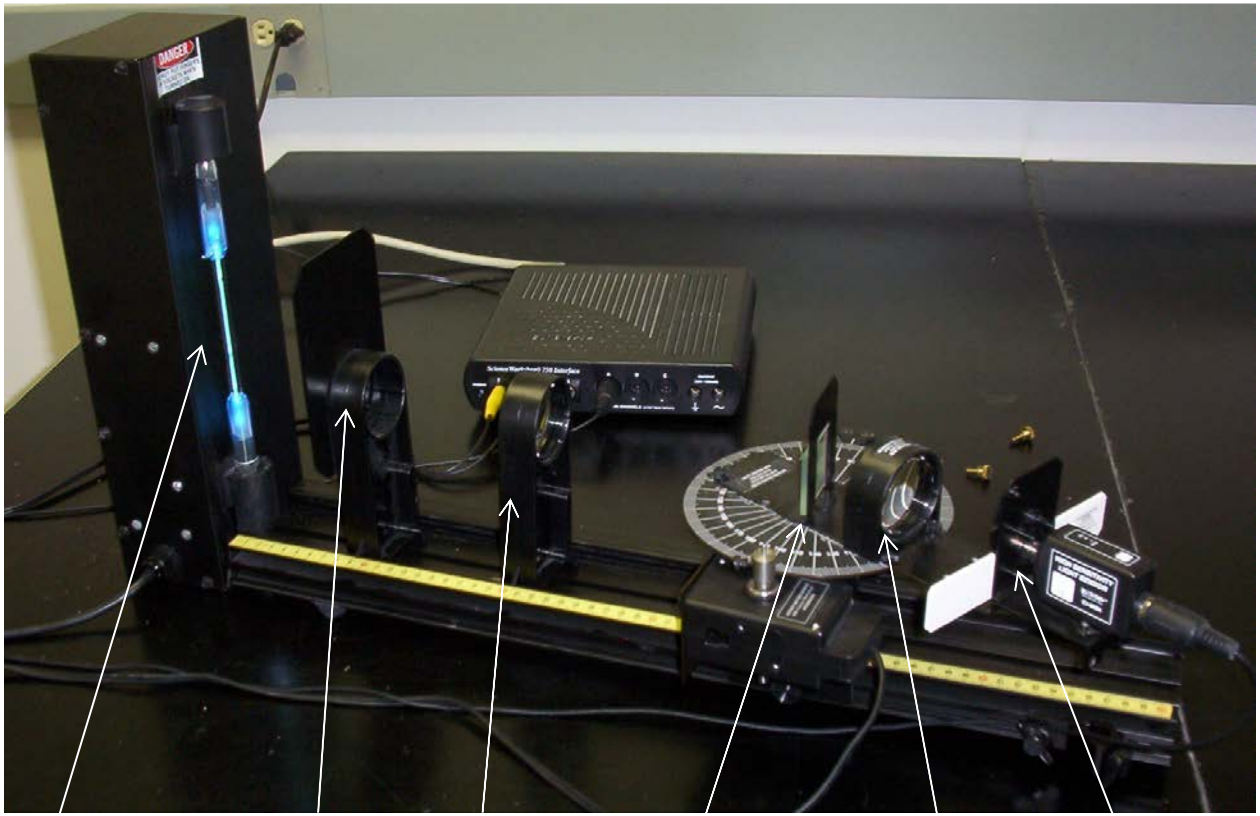
Particle
photoeffect

Wave
diffraction

That does not make sense: an electron is neither a particle nor a wave.

Better statement: an electron is something that cannot be adequately described in terms of simple classical models one can visualize.

Emission (/Absorption) spectroscopy



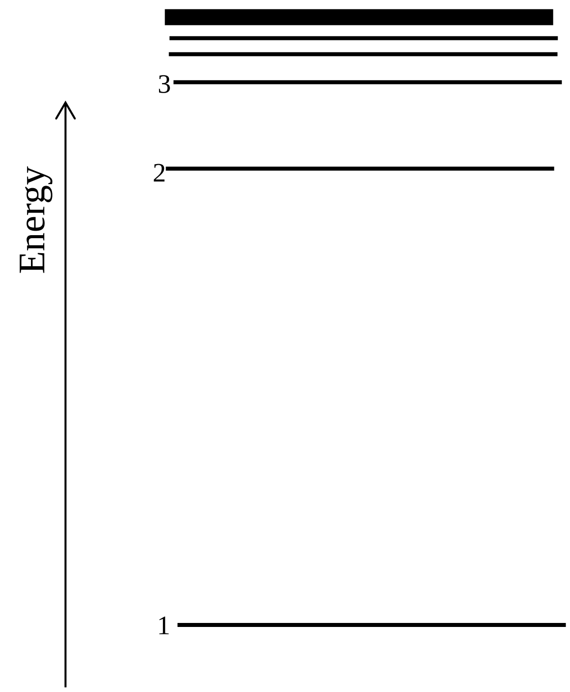
Emission/Absorption spectra

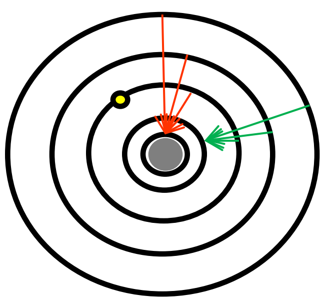
Bohr's postulates

1) **Stationary states, E_1, E_2, E_3, …**
2) **No radiation on stationary states**
3) **$\Delta E = E_n - E_{n+1} = h\nu$ (transitions)**
4) **F(Coulomb) = F(Centrifugal)**
5) **Quantization of angular momentum**
   $l = n\, h/(2Pi)$; $n = 1,2,3,\ldots$

$$\bar{\nu} = 1/\lambda = E_n - E_m$$

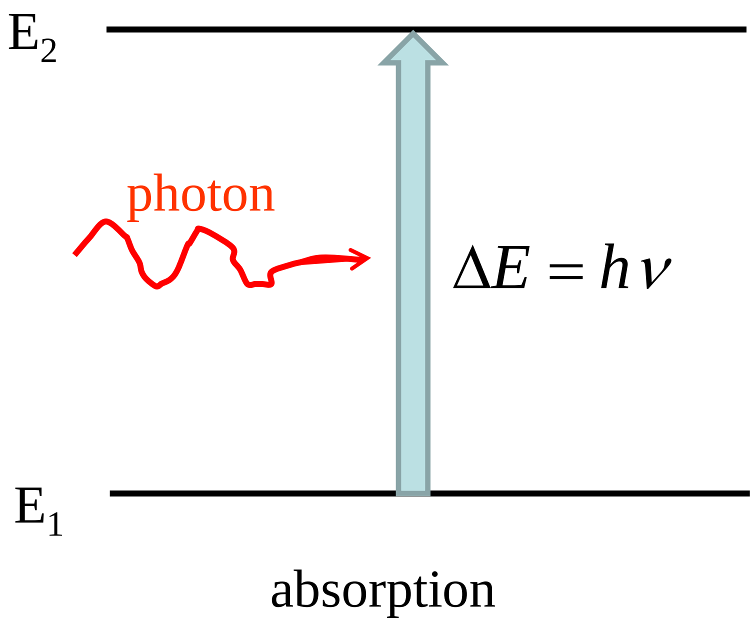
$$= \underbrace{\frac{e^4 m_0 Z^2}{64\pi^3 \varepsilon^2 \hbar^3 c}}_{R_\infty \text{ (Rydberg constant)}} \left(\frac{1}{m^2} - \frac{1}{n^2}\right)$$

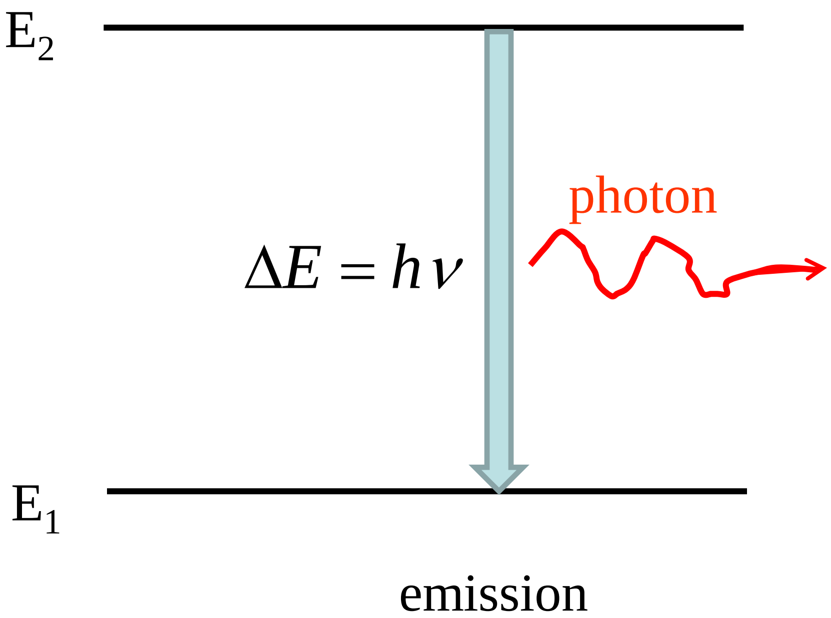


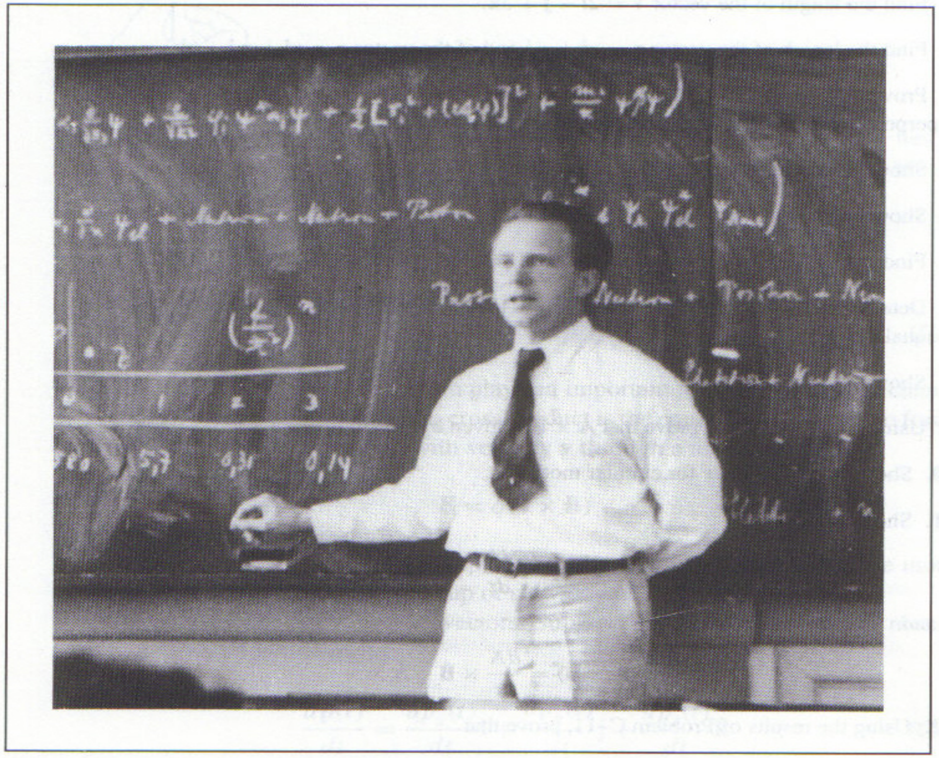


m_0: electron mass for speed = zero
ε: dielectric constant
e: electron charge
c: speed of light
Z: charge number
h: Planck's const.
m, n: quantum #
λ: wavelength
h_bar = $h/2\pi$
$1/\lambda$: wave number

Absorption / Emission of a photon





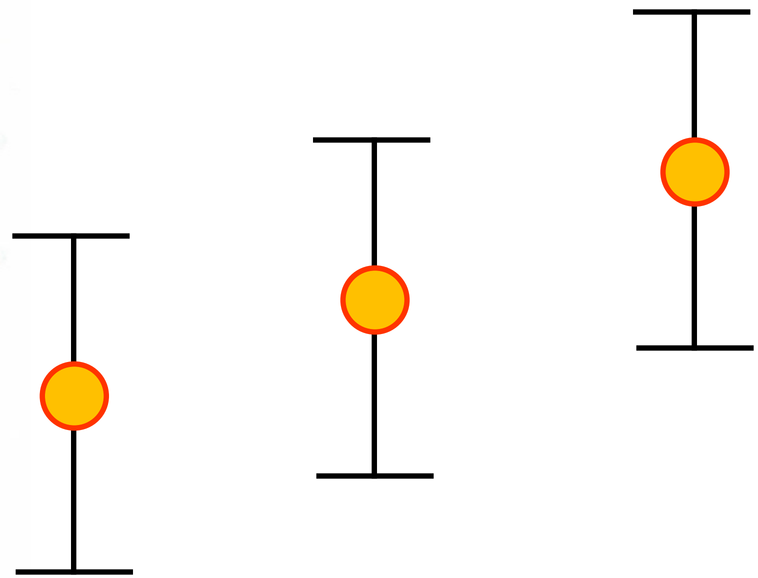


Werner Heisenberg was born on December 5, 1901 in Duisburg, Germany, grew up in Munich, and died in 1976. In 1923, Heisenberg received his Ph.D. in physics from the University of Munich. He then spent a year as an assistant to Max Born at the University of Göttingen and three years with Niels Bohr in Copenhagen. He was chair of theoretical physics at the University of Leipzig from 1927 to 1941, the youngest to have received such an appointment. Because of a deep loyalty to Germany, Heisenberg opted to stay in Germany when the Nazis came to power. During World War II, he was in charge of German research on the atomic bomb. After the war, he was named director of the Max Planck Institute for Physics, where he strove to rebuild German science. Heisenberg developed one of the first formulations of quantum mechanics, but it was based on matrix algebra, which was less easy to use than the wave equation of Schrödinger. The two formulations, however, were later shown to be equivalent. His Uncertainty Principle, which he published in 1927, illuminates a fundamental principle of nature involving the measurement and observation of physical quantities. Heisenberg was awarded the 1932 Nobel Prize for physics in 1933 "for the creation of quantum mechanics." His role in Nazi Germany is somewhat clouded, prompting one author (David Cassidy) to title his biography of Heisenberg *Uncertainty* (W.H. Freeman, 1993).

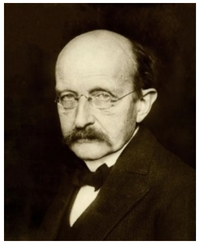
Heisenberg's uncertainty principle

$$\Delta p_x \Delta x > h$$

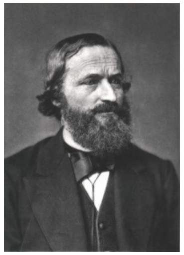
$$\Delta E \Delta t > h$$



Historic experiments



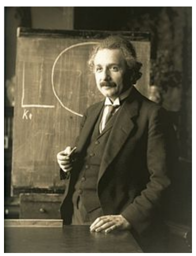
Planck



Kirchhoff

Blackbody radiation

quantization



Einstein

Photo effect

Photons

Particle-wave-duality

Davisson & Germer

de Broglie

Particle-wave duality

Ångström

Balmer

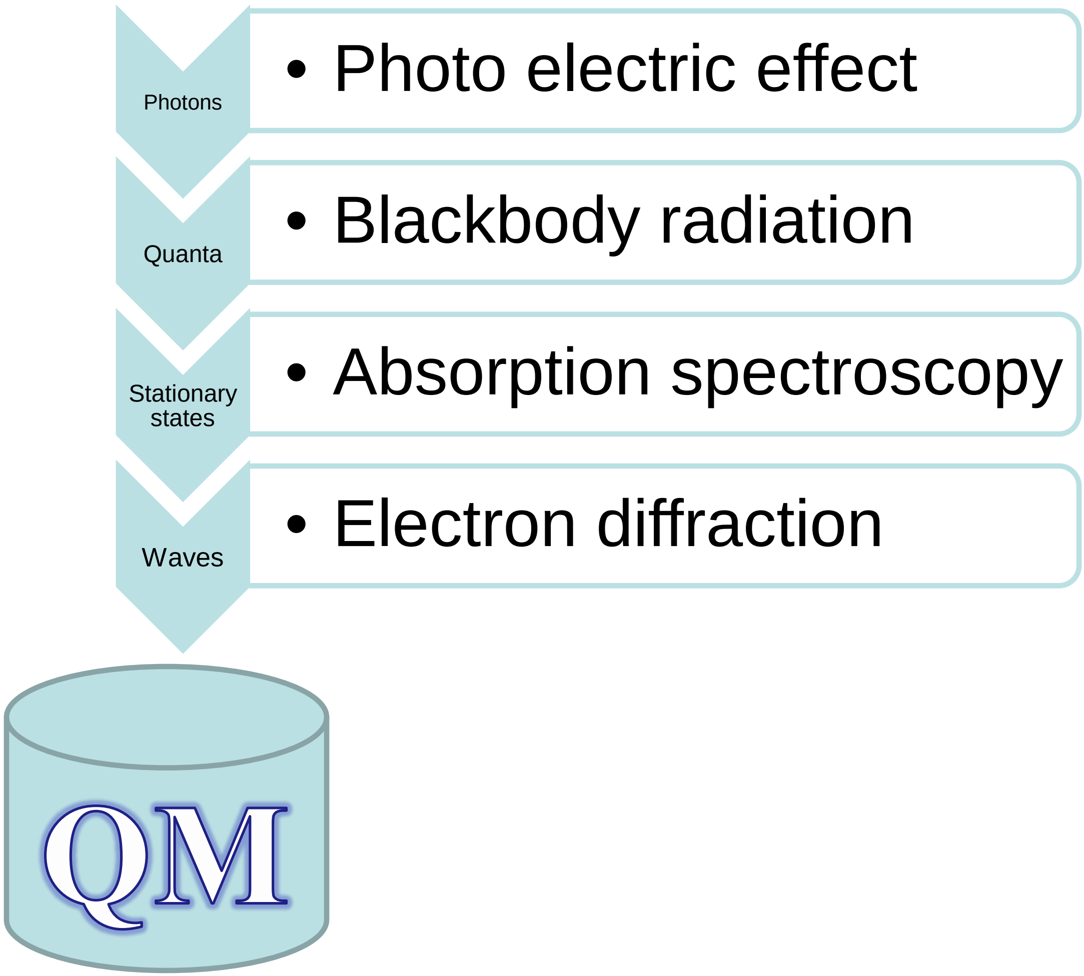
Bohr

Hydrogen early models & experiments

quantization

stationary states

Historic experiments



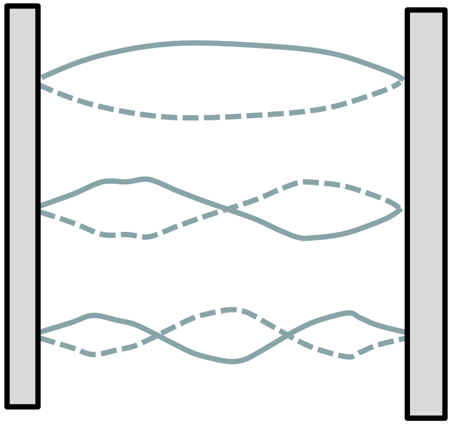
Schrödinger equation

$$\frac{\partial^2\psi}{\partial x^2}+\frac{8\pi^2 m}{h^2}(E-V)\psi=0$$

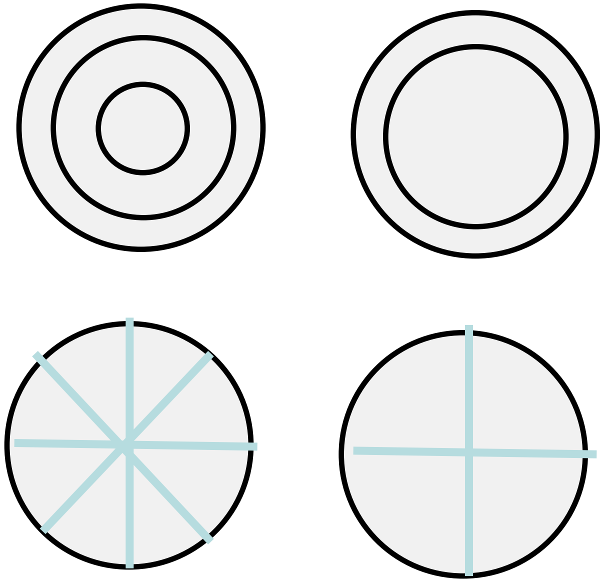
Stationary states

The solution to the time-independent Schroedinger equation are the time-independent wave functions they define the stationary states.

Classical analog – standing waves

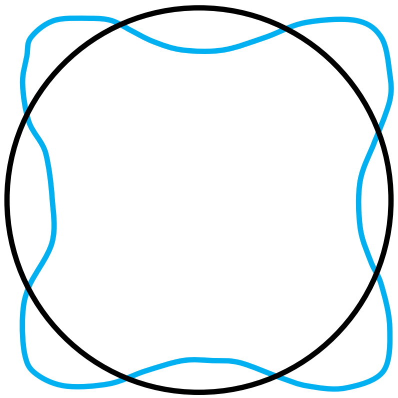


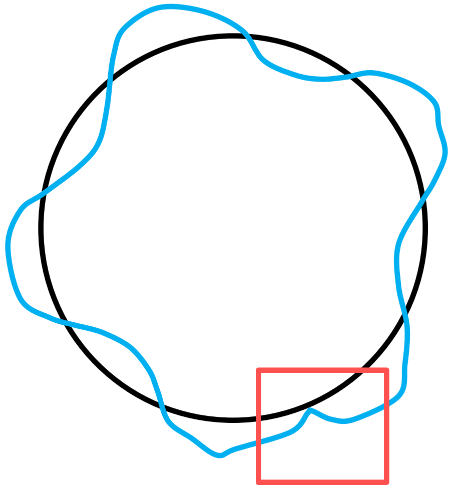
String fixed at wall



Glass plate with powder

Standing waves & stationary states in quantum mechanics





5th postulate

5) Quantization of angular momentum

l = n h/(2Pi); n = 1,2,3,…

wave fits in orbit

allowed

wave does NOT fits in orbit

forbidden

http://www.youtube.com/watch?v=EILGg3HZIK0

What is $\psi = ???$

Quantum mechanics

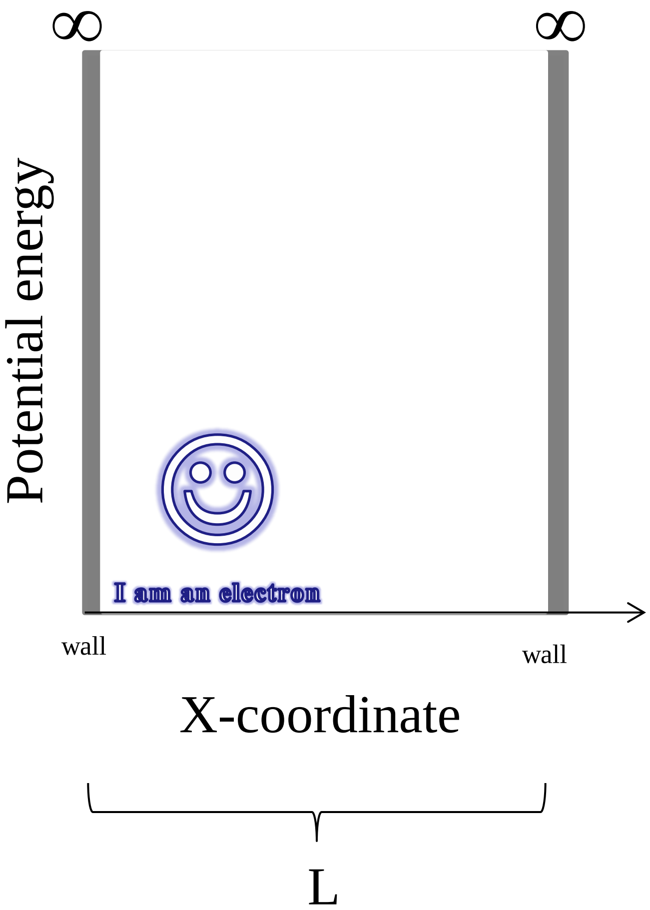
Born's interpretation of the wave function:

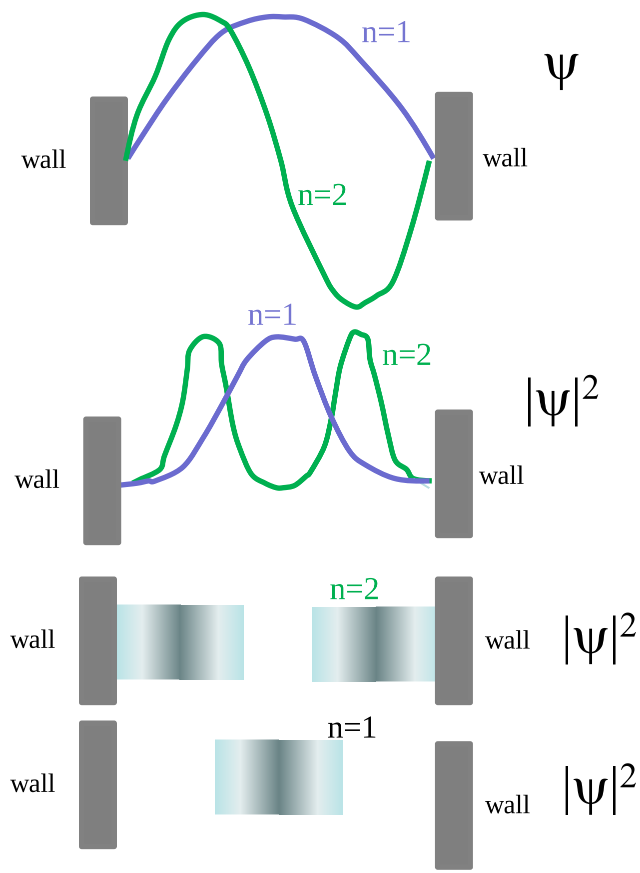
$$|\psi(x)|^2$$ Probability density for finding particles at a given location

$$P = |\psi(x)|^2 \, dx$$ Probability for finding the particle at a given location

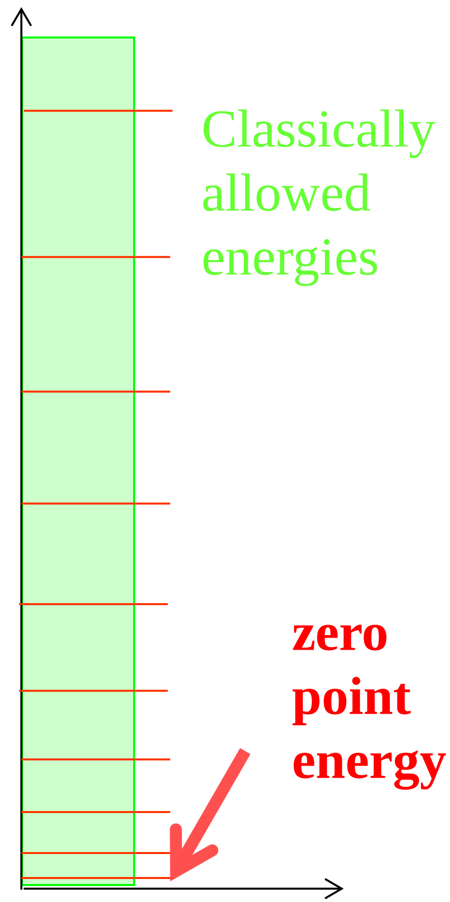
Max Born (1882-1970)

1D box – results





$$|\psi|^2 = \tfrac{2}{L}\sin^2\left(\frac{n\pi}{L}x\right)$$

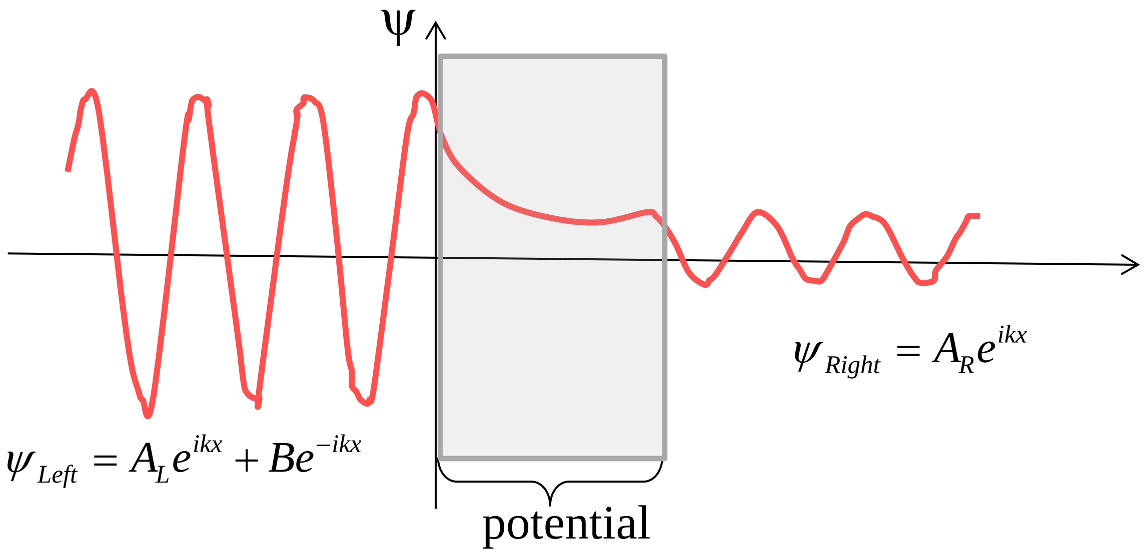


$$E = \frac{h^2}{8mL^2}n^2 \approx n^2$$

$$E_0 = E(n=1)$$

Scattering problems in Q.M.

wave functions



$$\psi_{Right} = A_R e^{ikx}$$

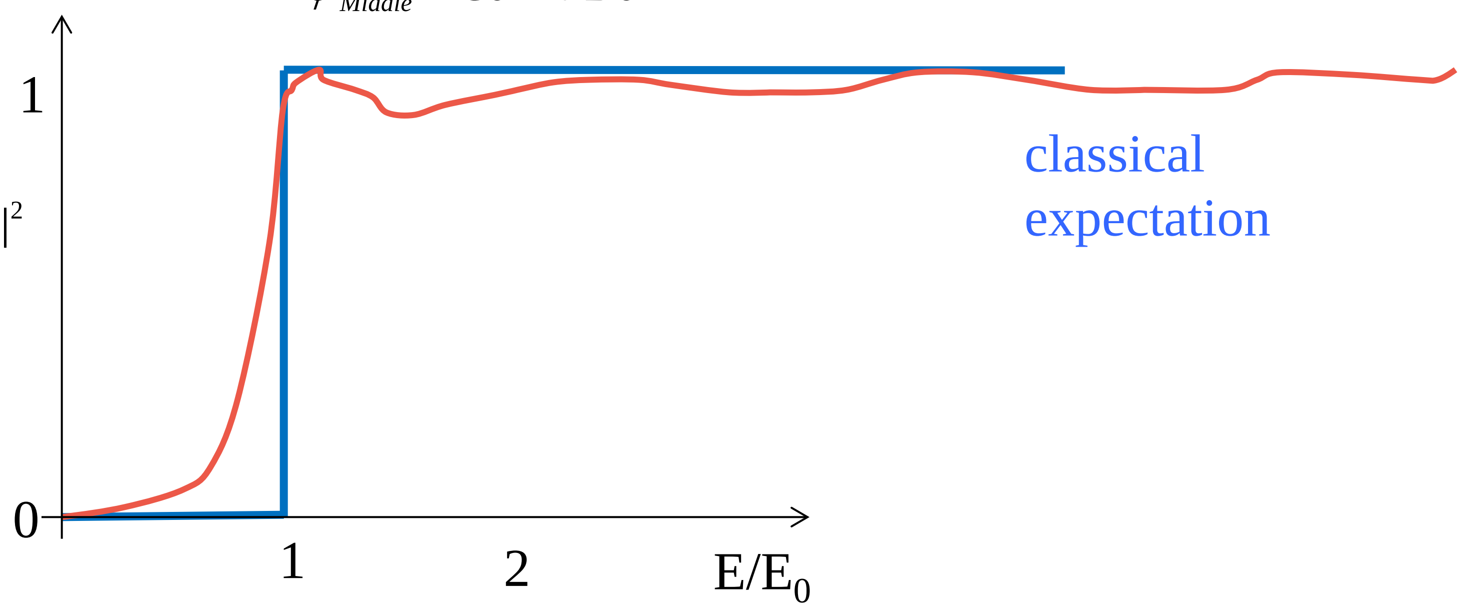
Ansatz / Starting equations

$$\psi_{Left} = A_L e^{ikx} + B e^{-ikx}$$

$$\psi_{Middle} = C e^{i\breve{k}x} + D e^{-i\breve{k}x}$$

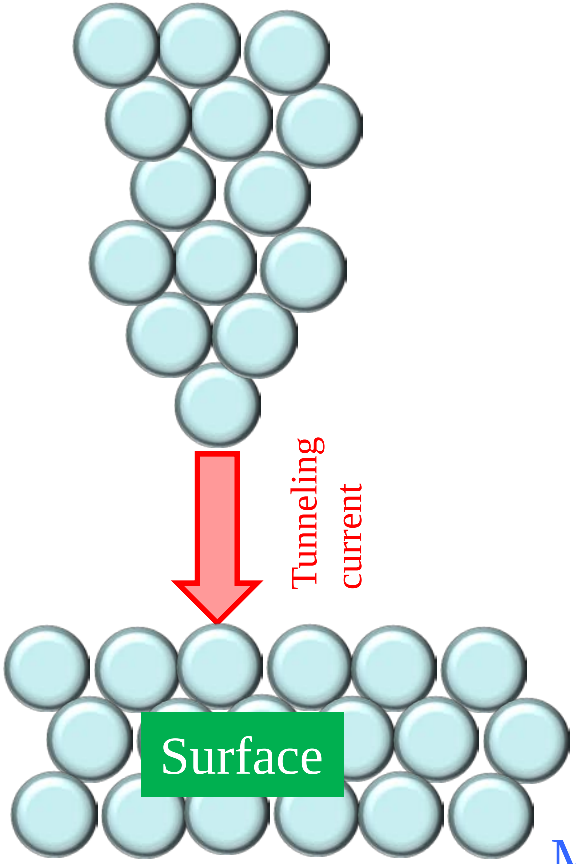
Result

Transmission coefficient $|\frac{A_R}{A_L}|^2$

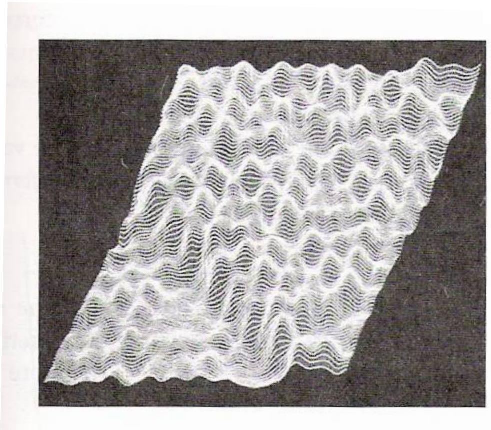


Tunnelling effect – STM – Scanning Tunnelling Microscope

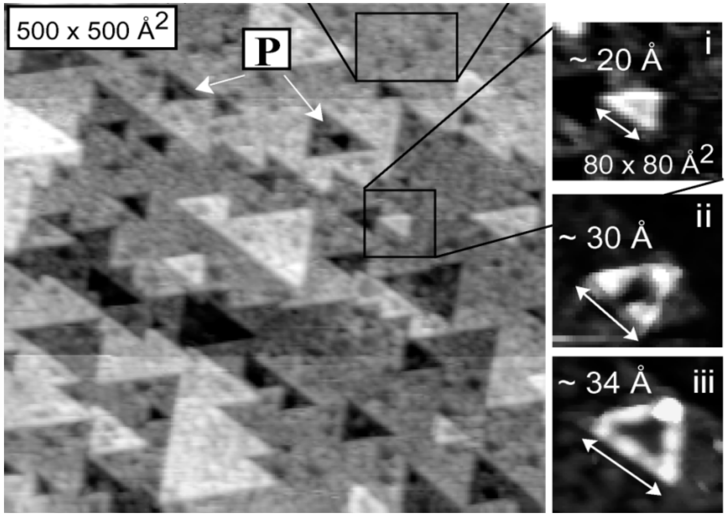
Principle of operation



Examples



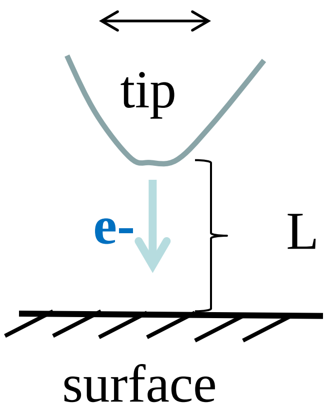
Silicon surface

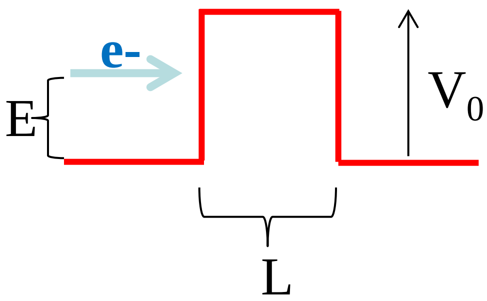


Zinc oxide

Modes:
Constant current
Constant distance

How to model an STM
STM as electron scattering devise





$$\text{tunneling probability}: P \approx e^{-\sqrt{m}} \approx e^{-\sqrt{L}}$$

$$\text{tunneling probability}: P \approx e^{-2L\sqrt{2m(V_0-E)}/\hbar}$$

Classical limit

- Large mass
- Large system size
- Large quantum numbers
- Smaller Planck constant → Mr. Q. http://www.youtube.com/watch?v=5xdbPhnfFEI

H atom summary

H atom – mathematical structure of the solution

$$\hat{H} = -\frac{\hbar}{2\mu}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) - \frac{Ze^2}{4\pi\varepsilon_0 r};\ \hat{H}\psi = E\psi$$

Idea: use spherical coordinates, separate variables → 3-separte differential equations

$$-\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin\Theta}\frac{\partial}{\partial\Theta}\left(\sin\Theta\frac{\partial\psi}{\partial\Theta}\right) + \frac{1}{r^2\sin\Theta}\left(\frac{\partial^2\psi}{\partial\phi^2}\right)\right) - \frac{e^2}{4\pi\varepsilon_0 r}\psi = E\psi$$

$$\boxed{\psi_{n,l,m} = R_{n,l}(r)\Theta_{l,m}(\theta)\Phi_m(\phi)}$$

Quantum numbers for one electron system (H atom)

$n = 1, 2, 3, \ldots$ principal quantum number

$l = 0, 1, 2, 3, \ldots, n\text{-}1$ angular momentum quantum number

$m_l = 0, \pm 1, \pm 2, \pm 3, \ldots, \pm l$ magnetic quantum number

Table 11.2
Hydrogen Atom Wave Functions for $n = 1, 2,$ and 3

n	l	m_l	$R(r)^a$	$\Theta(\theta)$	$\Phi(\phi)^b$
1	0	0	$\frac{2}{\sqrt{a_0^3}}e^{-\rho}$	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2\pi}}$
2	0	0	$\frac{1}{\sqrt{2a_0^3}}\left(1-\frac{\rho}{2}\right)e^{-\rho/2}$	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2\pi}}$
2	1	0	$\frac{1}{\sqrt{24a_0^3}}\rho e^{-\rho/2}$	$\sqrt{\frac{3}{2}}\cos\theta$	$\frac{1}{\sqrt{2\pi}}$
2	1	±1	$\frac{1}{\sqrt{24a_0^3}}\rho e^{-\rho/2}$	$\sqrt{\frac{3}{4}}\sin\theta$	$\frac{1}{\sqrt{2\pi}}e^{\pm i\phi}$
3	0	0	$\frac{2}{\sqrt{27a_0^3}}\left(1-\frac{2}{3}\rho+\frac{2}{27}\rho^2\right)e^{-\rho/3}$	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2\pi}}$
3	1	0	$\frac{8}{27\sqrt{6a_0^3}}\rho\left(1-\frac{\rho}{6}\right)e^{-\rho/3}$	$\sqrt{\frac{3}{2}}\cos\theta$	$\frac{1}{\sqrt{2\pi}}$
3	1	±1	$\frac{8}{27\sqrt{6a_0^3}}\rho\left(1-\frac{\rho}{6}\right)e^{-\rho/3}$	$\sqrt{\frac{3}{4}}\sin\theta$	$\frac{1}{\sqrt{2\pi}}e^{\pm i\phi}$
3	2	0	$\frac{4}{81\sqrt{30a_0^3}}\rho^2 e^{-\rho/3}$	$\sqrt{\frac{5}{8}}(3\cos^2\theta-1)$	$\frac{1}{\sqrt{2\pi}}$
3	2	±1	$\frac{4}{81\sqrt{30a_0^3}}\rho^2 e^{-\rho/3}$	$\frac{\sqrt{15}}{2}\sin\theta\cos\theta$	$\frac{1}{\sqrt{2\pi}}e^{\pm i\phi}$
3	2	±2	$\frac{4}{81\sqrt{30a_0^3}}\rho^2 e^{-\rho/3}$	$\frac{\sqrt{15}}{4}\sin^2\theta$	$\frac{1}{\sqrt{2\pi}}e^{\pm 2i\phi}$

[a] The variable $\rho = r/a_0$, where a_0 is the Bohr radius.
[b] The symbol i denotes the complex number, $\sqrt{-1}$.

In your book, see page 429

$$\psi_{n,l,m} = R_{n,l}(r)\Theta_{l,m}(\theta)\Phi_m(\phi)$$

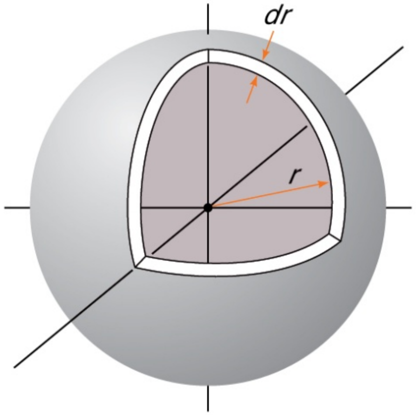
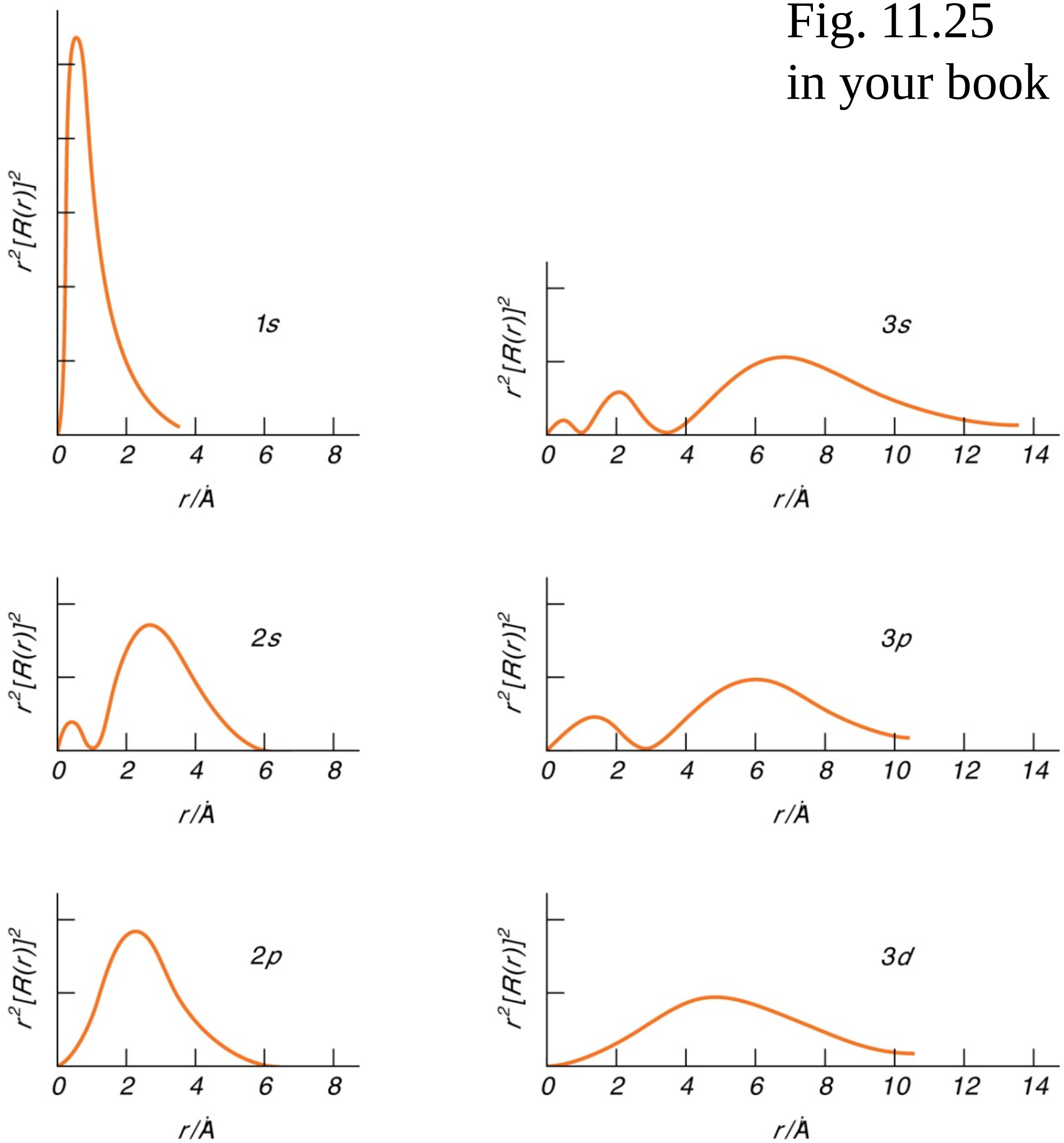


Fig. 11.24
in your book

Fig. 11.25
in your book



$$\psi_{n,l,m} = R_{n,l}(r)\boxed{\Theta_{l,m}(\theta)\Phi_m(\phi)}$$

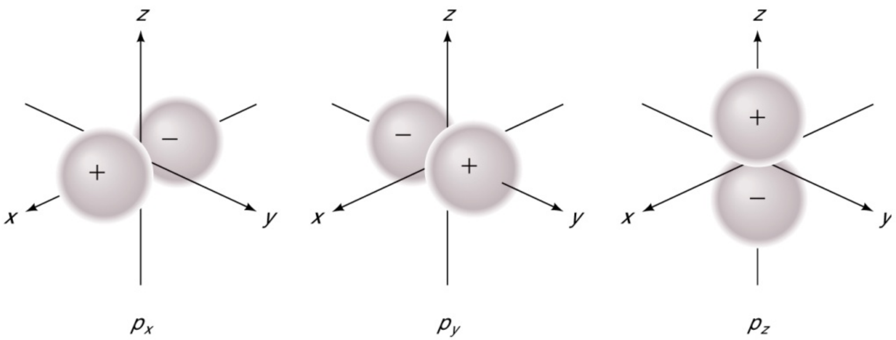


Fig. 11.26 in your book

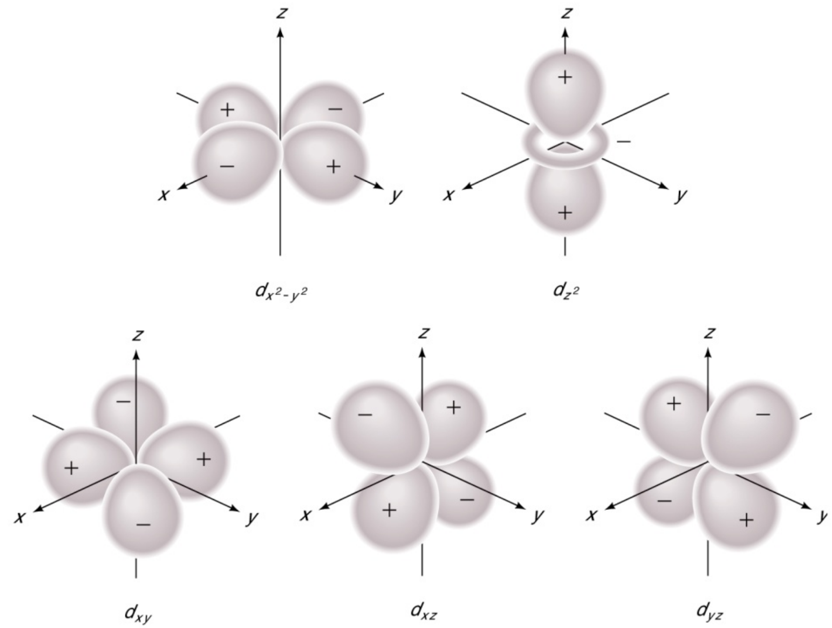


Fig. 11.27 in your book

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