1. Foundations of quantum physics

1.1 Unsolved problems in classical physics:

- photoelectric effect
- *Compton effect* (studied subsequent to quantum ideas)
- spectroscopy of atoms and molecules
- thermal (equilibrium) radiation
- heat capacities of solids at low temperatures

1.2 Thermal radiation

Classical results. Thermodynamical equilibrium is not static. Even if the temperature of a body is constant it emits and absorbs energy under the form of em waves. This radiation exchanged by bodies at constant temperature is known as the *thermal radiation.*

Kirchhoff (around 1860) established two laws for the thermal radiation. They are based upon experiments as well as on thermodynamical reasoning.

1st law: thermal radiation is homogeneous, isotropic, non-polarized and does not depend on the specific material bodies are made of.

2nd law: (in a non-rigorous expression): the ratio between energy emitted and absorbed by a body at constant temperature T depends only of T and on the frequency.

Black body. A black body is a body that absorbs all the incident radiation falling upon it. For such a body the energy emitted should have the attribute given by Kirchhoff's 2nd law. This energy emitted is proportional to the *spectral density of energy* of the radiation. The spectral density of energy $u_\omega(T)$ is the existing energy for each unit of volume per unit of frequency:

$$u_\omega(T) = \frac{energy}{unit\ of\ volume \times unit\ of\ \ frequency} = f(\omega, T) \quad (Q1.1)$$

For each frequency the em field can oscillate on several *modes*. The number of such modes per unit of volume and per unit of frequency is the *mode density*

$$g(\omega) = \frac{\omega^2}{\pi^2 c^3} \quad\quad\quad (Q1.2)$$

This is a purely mathematical result, perfectly established. If we multiply this number by the average energy of such a mode we get precisely the spectral density of energy. Very elaborated classical calculations (the so-called *equipartition theorem*) find for the average energy of a mode the relation:

$$\langle \varepsilon \rangle = g \times \frac{k_B T}{2} \qquad (Q1.3)$$

where g is the number of independent polarizations; for em waves $g=2$. Hence:

$$u_\omega(T) = g(\omega) \times \langle \varepsilon \rangle = \frac{\omega^2}{\pi^2 c^3} k_B T \qquad \text{(Rayleigh-Jeans)} \qquad (Q1.4)$$

This is indeed a function which depends only on ω and T but it does not fit experimental data, except at low frequencies, see Fig. 1:
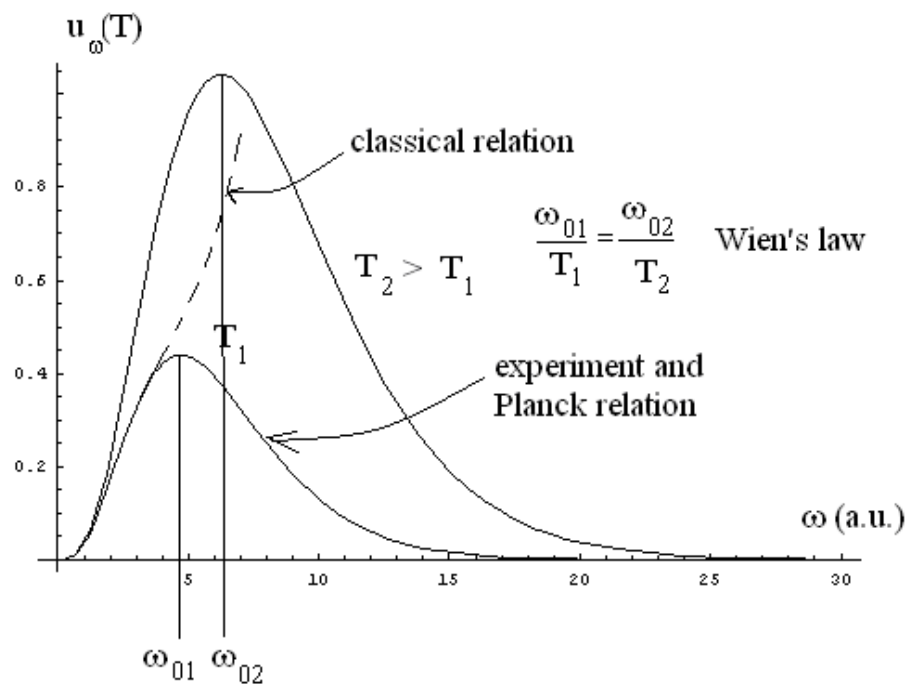

Fig. 1. Classical and quantum spectral density of energy for thermal radiation emitted by black bodies

Planck's quantum hypothesis. In the classical relation (Q1.4) the first factor is indisputable being a mathematical result. The second is a result of the finest methods of classical statistical physics. Planck suspected this last factor and obtained a result in

accordance with experiment using the **quantum hypothesis**: bodies emit and absorb energy in *quanta*. These discrete or quantified energies are given by

$$\varepsilon_n = n\hbar\omega \qquad (Q1.5)$$

The constant

$$\hbar = h/2\pi \cong 1.05 \times 10^{-34} \ \text{J} \cdot \text{s} = 0.66 \times 10^{-15} \ \text{eV} \cdot \text{s} \qquad (Q1.6)$$

is the reduced Planck constant.

The calculus goes as follows:

Use Boltzmann distribution with $g_i = 1$ (the degeneracy is given by (Q1.2). The probability to have the energy ε_n

$$P_n = \frac{\exp[-\varepsilon_n / k_B T]}{\sum \exp[-\varepsilon_n / k_B T]} = \frac{\exp[-\beta\varepsilon_n]}{\sum \exp[-\beta\varepsilon_n]} \qquad (Q1.7)$$

Hence the average energy is

$$\langle\varepsilon\rangle = \sum \varepsilon_n P_n = \frac{\sum \varepsilon_n \exp[-\beta\varepsilon_n]}{\sum \exp[-\beta\varepsilon_n]} = \frac{-\dfrac{\partial}{\partial\beta} \sum \exp[-\beta\varepsilon_n]}{\sum \exp[-\beta\varepsilon_n]}$$

Assume $\varepsilon_n = n\hbar\omega$ and denote $x = \dfrac{\hbar\omega}{k_B T}$.

$$\sum \exp[-n\beta\hbar\omega] = \sum \exp[-nx] = \frac{1}{1 - e^{-x}} = \frac{1}{1 - \exp[-\beta\hbar\omega]}$$

The derivative becomes:

$$-\frac{\partial}{\partial\beta} \sum \exp[-\beta\varepsilon_n] = -\frac{\partial}{\partial\beta}\left(1 - \exp[-\beta\hbar\omega]\right)^{-1} = \frac{\hbar\omega \exp[-\beta\hbar\omega]}{\left(1 - \exp[-\beta\hbar\omega]\right)^2} \ .$$

$$\langle\varepsilon\rangle = \frac{\hbar\omega \exp[-\beta\hbar\omega]}{\left(1 - \exp[-\beta\hbar\omega]\right)} = \frac{\hbar\omega}{\exp[\beta\hbar\omega] - 1} \qquad (Q1.8)$$

Put it in (Q1.4) instead of $k_B T$ we find the Planck relation:

$$u_\omega(T) = g(\omega)\langle\varepsilon\rangle = \frac{\omega^2}{\pi^2 c^3} \frac{\hbar\omega}{\exp[\beta\hbar\omega] - 1} \qquad (Q1.9)$$

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This expression fits well experimental data and allows to find experimental laws (see exercice below).

Exercice: Show that:

a) The maxima of the curves appear at frequencies ω_{0i} such as

$$\frac{\omega_{01}}{T_1} = \frac{\omega_{02}}{T_2} \qquad \text{(Wien's displacement law)} \qquad \text{(Q1.10)}$$

b) The area under the curves is proportional to T^4 (Stefan-Bolzmann law).

1.3 Photoelectric effect

Electrons leave a material (usually a metal) illuminated with light. The experiment must be done in vacuum. In the tube from Fig. 2 an electric current appears immediately after the metal is illuminated.
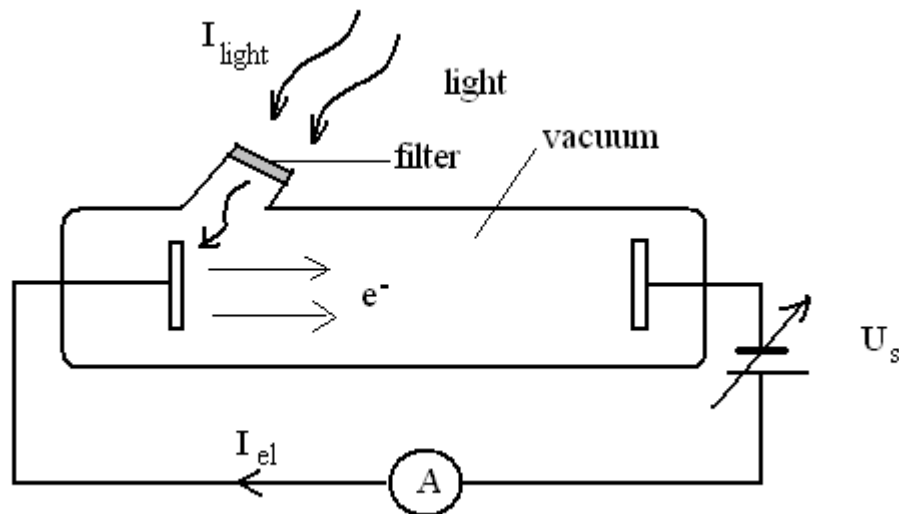

Fig. 2. Photoelectric effect

Experimental laws:

1. The effect appears instantaneously
2. The electric current is proportional to the light intensity
3. The stopping potential U_s depends linearly on the frequency of the light

4. There is a threshold frequency for which $U_s=0$; for smaller frequencies the effect disappears.

All but the second law are impossible to explain in classical physics where light is an electromagnetic wave.

Einstein's explanation: light does not behave as an elmgn wave, but as a flux of particles which today are called *photons*. These photons with frequency ω has an energy given by the Planck quantum hypothesis, namely $E_{ph} = \hbar\omega$. This energy splits in two. A part is used to extract the electron from the material, *the extraction work* W_{extr}. The other part is given to the electron as kinetic energy. The energy conservation is:

$$\hbar\omega = W_{extr} + \frac{mv^2}{2} = \hbar\omega_0 + eU_{st} \qquad \text{(Q1.11)}$$

Exercise: explain the laws using the Einstein relation.

Light used is usually in the UV or visible regions of the spectrum.

1.4 Compton effect

If we use em waves with bigger energy such as *X*-rays or gamma rays another effect emerges – the Compton effect. Wavelength of incoming rays is shifted towards the lengthier part of the spectrum. The incoming wavelength λ has values of the order of 0.1 nm, hence the frequency is roughly 10^{19} Hz. The energy given by Planck's relation is $E_{ph} \cong 10^{-15}$ J $\cong 5$ keV. Electrons may be considered free, because in materials they are linked with energies of roughly 1-10 eV. We must use relativistic equations to write down conservation of energy and momentum (see the lectures for figure and equations). The final relation is:

$$\Delta\lambda = \lambda' - \lambda = 2\Lambda_C \sin^2\frac{\theta}{2} \qquad \text{(Q1.12)}$$

where λ' is the wavelength of the emergent *X*-ray, $\Lambda_C = \dfrac{h}{m_0 c} \cong 2.4$ pm is the Compton wavelength and θ is the deviation angle of the photon.

Exercises: 1). Compare photoelectric and Compton effects. Why equations are different ? Why do we not use momentum conservation for the photoelectric effect ?

2). Light is a wave or is made of particles (this is a VERY difficult question).

1.5 Wave-particle dualism. De Broglie hypothesis

Light has sometimes wavy character and sometimes seems to be made of particles. Louis de Broglie put forth the hypothesis that *each microscopic entity has both wave and particle characteristics*. The wave-particle duality has a universal applicability to all microscopic entities.

Consider a microparticle moving in vacuum with constant velocity $\vec{v}$. Its particle features are given by its energy and its momentum; from SR:

$$E = \frac{m_0 c^2}{\sqrt{1 - v^2/c^2}} \qquad\qquad \vec{p} = \frac{m_0 \vec{v}}{\sqrt{1 - v^2/c^2}} \qquad (Q1.13)$$

On the other hand, in the wave approach the entity is described by its frequency ω and its wavelength λ, or its wave-vector $\vec{k} = \frac{2\pi}{\lambda} \vec{u}_k$. We already know that for light (in general for em waves) we have $E_{ph} = \hbar\omega$. De Broglie assumed that the same is true for each microparticle: $E = \hbar\omega$. Moreover, a similar relation exists between momentum and wave-vector: $\vec{p} = \hbar\vec{k}$. One may write:

$$E = \hbar\omega \qquad\qquad \vec{p} = \hbar\vec{k} \qquad\qquad \text{or} \qquad \mathcal{P} = \hbar\,\mathcal{K} \qquad\qquad \text{for 4-vectors} \quad (Q1.14)$$

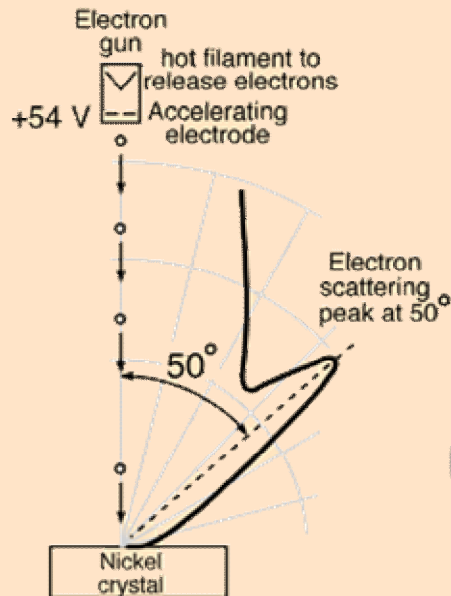The wavelength associated with the particle is *the de Broglie wavelength*:

$$\lambda = 2\pi/k = \frac{h}{p} \qquad\qquad (Q1.15)$$

A hpw (or a plane monochromatic wave) can be written in two ways:

$$\Psi(\vec{r}, t) = A\exp[i(\omega t - \vec{k}\cdot\vec{r})] = A\exp[\frac{i}{\hbar}(Et - \vec{p}\cdot\vec{r})] \qquad\qquad (Q1.16)$$

Experimental evidence: de Broglie made his assumption in 1924. Three years later Davisson and Germer detected electron diffraction by metal surfaces.
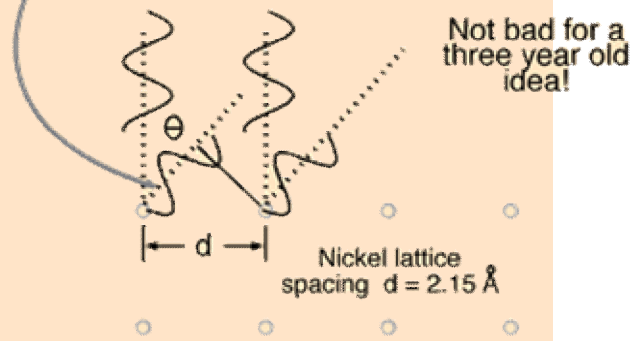
Davisson-Germer Experiment

Electron gun
hot filament to release electrons
+54 V
Accelerating electrode

Electron scattering peak at 50°

50°

Nickel crystal

Theory

$\lambda = \dfrac{h}{mv} = 1.67$ Å for 54 V

Experiment

Pathlength difference

$d \sin \Theta = 2.15 \sin 50° = \lambda = 1.65$ Å

for constructive interference

Not bad for a three year old idea!

Θ

← d →

Nickel lattice spacing d = 2.15 Å

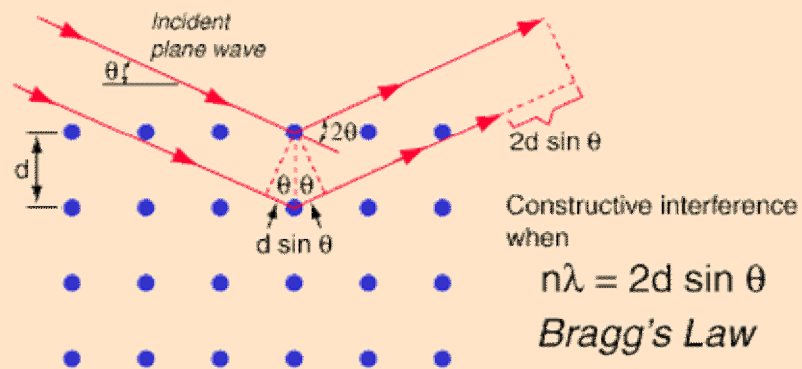| 1924	1927	1929
de Broglie's hypothesis	Davisson-Germer experiment	Nobel Prize for de Broglie

This experiment demonstrated the wave nature of the electron, confirming the earlier hypothesis of deBroglie. Putting wave-particle duality on a firm experimental footing, it represented a major step forward in the development of quantum mechanics. The Bragg law for diffraction had been applied to x-ray diffraction, but this was the first application to particle waves.

From http://hyperphysics.phy-astr.gsu.edu/hbase/quantum/bragg.html#c1

Bragg's Law

When x-rays are scattered from a crystal lattice, peaks of scattered intensity are observed which correspond to the following conditions:

1. The angle of incidence = angle of scattering.
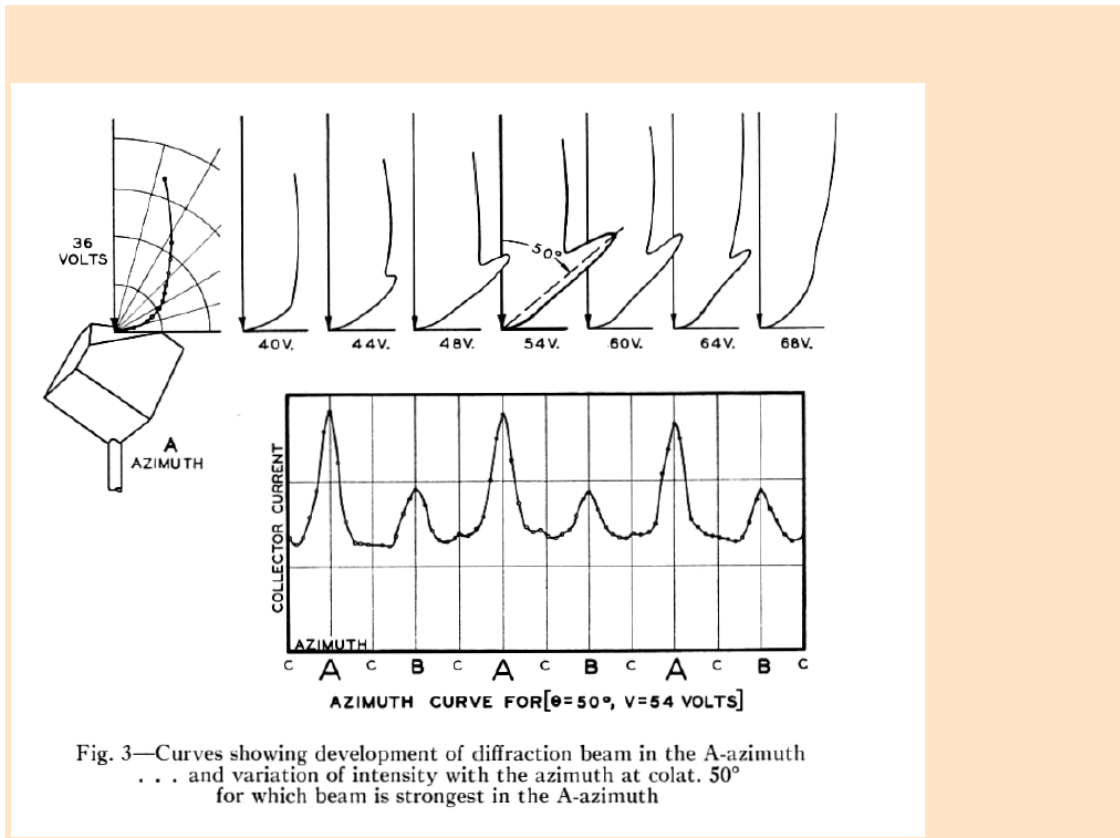2. The pathlength difference is equal to an integer number of wavelengths.

The condition for maximum intensity contained in Bragg's law above allow us to calculate details about the crystal structure, or if the crystal structure is known, to determine the wavelength of the x-rays incident upon the crystal.

$$n\lambda = 2d\sin\theta \quad \text{\tiny Bragg's Law}$$

From http://hyperphysics.phy-astr.gsu.edu/hbase/quantum/davger2.html

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Fig. 3—Curves showing development of diffraction beam in the A-azimuth
. . . and variation of intensity with the azimuth at colat. 50°
for which beam is strongest in the A-azimuth

The electron beam was directed at the nickel target, which could be rotated to observe angular dependence of the scattered electrons. Their electron detector (called a Faraday box) was mounted on an arc so that it could be rotated to observe electrons at different angles. It was a great surprise to them to find that at certain angles there was a peak in the intensity of the scattered electron beam. This peak indicated wave behavior for the electrons, and could be interpreted by the Bragg law to give values for the lattice spacing in the nickel crystal.

The experimental data above, reproduced above Davisson's article, shows repeated peaks of scattered electron intensity with increasing accelerating voltage. This data was collected at a fixed scattering angle. Using the Bragg law, the deBroglie wavelength expression, and the kinetic energy of the accelerated electrons gives the relationship

$$\frac{1}{\lambda} = \frac{n}{2d\sin\theta} = \frac{p}{h} = \frac{\sqrt{2mE}}{h} = \frac{\sqrt{2meV}}{h}$$

| Electron wavelength | Bragg law | deBroglie relationship | | Acceleration through voltage V |

Quantum world embraces all phenomena for which the quantity *action* has the order of a few $\hbar$'s. the table shows some processes and their associated action.

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From *Chr. Schiller, Motion Mountain, the adventure of physics, 2006*

TABLE 56 Some small systems in motion and the observed action values for their changes

SYSTEM & CHANGE	ACTION	MOTION
Light		
Smallest amount of light absorbed by a coloured surface	$1\,\hbar$	quantum
Smallest hit when light reflects from mirror	$2\,\hbar$	quantum
Smallest visible amount of light	$c.\,5\,\hbar$	quantum
Smallest amount of light absorbed in flower petal	$c.\,1\,\hbar$	quantum
Blackening of photographic film	$c.\,3\,\hbar$	quantum
Photographic flash	$c.\,10^{17}\,\hbar$	classical
Electricity		
Electron ejected from atom	$c.\,1-2\,\hbar$	quantum
Electron added to molecule	$c.\,1-2\,\hbar$	quantum
Electron extracted from metal	$c.\,1-2\,\hbar$	quantum
Electron motion inside microprocessor	$c.\,2-6\,\hbar$	quantum
Signal transport in nerves, from one molecule to the next	$c.\,5\,\hbar$	quantum
Current flow in lighting bolt	$c.\,10^{38}\,\hbar$	classical
Materials science		
Tearing apart two neighbouring iron atoms	$c.\,1-2\,\hbar$	quantum
Breaking a steel bar	$c.\,10^{35}\,\hbar$	classical
Basic process in superconductivity	$1\,\hbar$	quantum
Basic process in transistors	$1\,\hbar$	quantum
Basic process in magnetic effects	$1\,\hbar$	quantum
Chemistry		
Atom collisions in liquids at room temperature	$c.\,1\,\hbar$	quantum
Shape oscillation of water molecule	$c.\,1-5\,\hbar$	quantum
Shape change of molecule, e.g. in chemical reaction	$c.\,1-5\,\hbar$	quantum
Single chemical reaction curling a hair	$c.\,2-6\,\hbar$	quantum
Tearing apart two mozzarella molecules	$c.\,300\,\hbar$	quantum
Smelling one molecule	$c.\,10\,\hbar$	quantum
Burning fuel in a cylinder in an average car engine explosion	$c.\,10^{37}\,\hbar$	classical
Life		
Air molecule hitting ear drum	$c.\,2\,\hbar$	quantum
Smallest sound signal detectable by the ear	Challenge 1170 ny	
DNA duplication step in cell division	$c.\,100\,\hbar$	quantum
Ovule fecundation	$c.\,10^{14}\,\hbar$	classical
Smallest step in molecular motor	$c.\,5\,\hbar$	quantum
Sperm motion by one cell length	$c.\,10^{15}\,\hbar$	classical
Cell division	$c.\,10^{19}\,\hbar$	classical
Fruit fly's wing beat	$c.\,10^{24}\,\hbar$	classical
Person walking one body length	$c.\,2\cdot10^{36}\,\hbar$	classical
Nuclei and stars		
Nuclear fusion reaction in star	$c.\,1-5\,\hbar$	quantum
Particle collision in accelerator	$c.\,1\,\hbar$	quantum
Explosion of gamma ray burster	$c.\,10^{80}\,\hbar$	classical

1.6 Spectral series. The naïve Bohr's theory

Atomic spectra from gases show remarkable regularities. Spectral lines arrange themselves in *series*. A spectral series is a family of lines emitted by an atom whose frequencies may be deduced from a simple law, by the change of just one parameter. The first spectral series was observed by Balmer in 1855, in the visible spectrum of atomic hydrogen. The inverse of the wavelength – (the wavenumber $\tilde{\nu}$ – is given by:

$$\tilde{\nu} = R_H \left(\frac{1}{2^2} - \frac{1}{n^2} \right), \qquad n=3,4,\dots \qquad (Q1.17)$$

Here $R_H \cong 1.097 \cdot 10^7$ m^{-1} is the Rydberg constant. Other series of atomic hydrogen are obtained from

$$\tilde{\nu} = R_H \left(\frac{1}{m^2} - \frac{1}{n^2} \right) \qquad n>m \qquad (Q1.18)$$

Similar relations, although more complex, exist for all elements. The *combination principle* (Rydberg-Ritz, 1908) follows: *the wavenumber $\tilde{\nu}_{mn}$ of a spectral line is always given by the difference of two terms, known as spectral terms*:

$$\tilde{\nu}_{mn} = T(m) - T(n) \qquad (Q1.18')$$

Classical explanations fail to explain such a simple relation.

In 1913 Niels Bohr put forward a new theory based on two postulates and a quantified condition.

1st postulate. Each atom (in general each microsystem) is characterized by a family of stationary states with discrete energies E_1, E_2, E_3,… E_n. When in these states the system does not emit or absorb energy.

2nd postulate. The energy of a microsystem may vary only by discrete values by transitions from a stationary state of energy E_m to a stationary state of energy E_n. The transition is associated to an emission or an absorption of a photon with frequency given by

$$\hbar \omega_{mn} = E_m - E_n \qquad (Q1.19)$$

If $\omega_{mn} > 0$ the photon is emitted if $\omega_{mn} < 0$ the photon is absorbed.

The Bohr condition (Q1.19) represents the energy conservation for each process of exchange of energy with emission or absorption of photons. It explains the combination principle (Q1.18').

The quantum condition specifies that the angular momentum of an electron in an atom is quantified:

$$l_n = m_0 vr = n\hbar \qquad\qquad n=1, 2, 3,\ldots \qquad\qquad (Q1.20)$$

This condition could be understood using a model where the electron moves on a circular orbit around the nucleus as in Fig. 3.
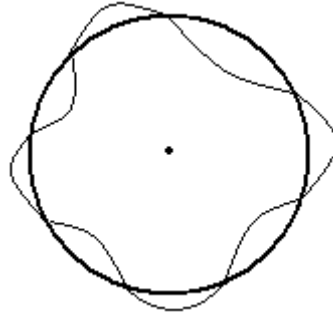

Fig. 3. The orbit of an electron and the de Broglie associated wave.

The electron has an associated wave and as its movement ought to be stable the orbit must contain an integer number of wavelengths: $2\pi r = n\lambda = n\dfrac{h}{p}$. Hence $pr = l = n\hbar$.

Assume a hydrogen atom with the nucleus made of one proton. This proton is more than 1800 times heavier than the electron and we shall consider it at rest. Write the equality of Coulomb and centrifugal forces: $\dfrac{m_0 v^2}{r} = \dfrac{e^2}{4\pi\varepsilon_0 r^2} = \dfrac{e_0^2}{r^2}$. Using (Q1.20) one finds:

$$v_n = \frac{e_0^2}{n\hbar} = \frac{v_1}{n} \qquad\qquad r_n = n^2\frac{\hbar^2}{m_0 e_0^2} = n^2 r_1 \qquad\qquad n=1, 2, 3,\ldots \quad (Q1.21)$$

$r_1 \cong 5.29\cdot10^{-11}$ m is the first Bohr radius. Velocities and radii are quantified.

The energy of the electron on the n-th orbit is quantified too and given by:

$$E_n = \frac{m_0 v_n^2}{2} - \frac{e_0^2}{r_n} = -\frac{e_0^2}{2r_n} = -\frac{e_0^2}{2r_1}\frac{1}{n^2} = -\frac{1}{n^2}\frac{m_0 e_0^4}{2\hbar^2} = -\frac{13.6}{n^2} \text{ eV} \qquad \text{(Q1.22)}$$

Exercise: Compute the Rydberg constant as:

$$R_H = \frac{e_0^2}{4\pi c \hbar r_1} = \frac{m_0 e_0^4}{4\pi c \hbar^3} \qquad \text{(Q1.23)}$$

The existence of stationary states was demonstrated by the Franck-Hertz experiment (http://en.wikipedia.org/wiki/Franck%E2%80%93Hertz_experiment).

1.7. Measurements on microscopic systems. The uncertainty principle

Heisenberg has shown that measurements disturb in an uncontrollable way the microscopic systems.

Example 1. Assume we want to measure the position of an electron in a Hydrogen atom. Dimensions of the atom are of the order of $r_1 \cong 5 \cdot 10^{-11}$ m. The momentum of the electron is roughly $p_e = m_0 v_1 = m_0 \frac{e_0^2}{\hbar}$. We need a γ-ray microscope with a wavelength smaller than r_1, let's say $\lambda_{meas} \approx \frac{r_1}{5} = 10^{-11}$ m. Such a photon has a momentum given by (Q1.15): $p_\gamma = \frac{5h}{r_1} = 10\pi \cdot m_0 \frac{e_0^2}{\hbar} \cong 30 p_e$. Measuring the position of the electron means to change without control its momentum.

Example 2. Assume a particle with momentum p moves in the Oy direction and goes through a slit of width Δx. Due to diffraction, behind the screen the particle moves no more in the Oy direction and acquires a momentum along Ox, namely Δp_x. This momentum is given by $\Delta p_x \approx p \sin \alpha$, where α is the diffraction angle. From the theory of the diffraction through a slit $\Delta x \sin \alpha \approx \lambda = h/p$. Therefore

$$\Delta x \Delta p_x \approx h \qquad \text{(Q 1.24)}$$

Therefore h is a limit for the product of uncertainties in measuring the position and the corresponding momentum. Relations of type (Q1.24) are known as

uncertainty relations. One can show that the following relations, named the Heisenberg uncertainty relations, are true in the area of quantum mechanics:

$$\Delta x \Delta p_x \geq \frac{\hbar}{2}, \qquad \Delta y \Delta p_y \geq \frac{\hbar}{2}, \qquad \Delta z \Delta p_z \geq \frac{\hbar}{2}, \qquad \Delta E \Delta t \geq \frac{\hbar}{2} \qquad (Q1.24)$$

Here ΔE is the error in measuring energy E and Δt the time interval during which one measures this energy. These relations are true even if we don't interact with the system: *a quantum system has no simultaneous precise values for conjugated physical quantities*. Examples of conjugated quantities: each position and the corresponding momentum, energy and time.